

DESCRIPTION

METHOD FOR TREATING DILUTE GASEOUS HYDROCARBONS CONTAINED IN
WASTE GASES AND DEVICE FOR PERFORMING THE METHOD

5

TECHNICAL FIELD

The present invention relates to a method for treating dilute gaseous hydrocarbons contained in waste gases and a device for performing the method, and particularly to a method and device for efficiently separating hydrocarbons from waste gases containing noxious gaseous hydrocarbons which cause air pollution, thereby rendering the waste gases innoxious.

More specifically, the present invention relates to a method and device for treating waste gases containing gaseous hydrocarbons such as benzene, toluene, methyl ethyl ketone, trichloroethylene, fluoro carbons, and the like which are carcinogenic and cause air pollution, and reducing the content of the hydrocarbons in the waste gasses to 100 ppm or less (preferably 10 ppm or less) before discharging to the atmosphere.

BACKGROUND ART

Gaseous hydrocarbons such as benzene, toluene, methyl ethyl ketone, trichloroethylene, and fluoro carbons are substances causing air pollution. Emission of these hydrocarbons into atmosphere is stringently controlled by regulation in developed countries such as the U.S.A, European



countries, and Japan. The level of control differs according to the situation in the respective country. Emission of benzene, for example, is controlled to 5 ppm or less in developed countries except for Japan. In Japan, the emission has been
5 controlled to 30 ppm or less according to the Announcement No. 5 of the Environment Agency dated February 6, 1997.

A particularly problematic source of emission of these gaseous hydrocarbons is a large amount of dilute waste gases containing about 5,000 ppm or less of hydrocarbons discharged
10 from printing factories, cleaning factories, coating factories, and the like. Such waste gases are discharged not only from the factories, but also from storage tanks when materials are loaded or unloaded.

15 PRIOR ART TECHNOLOGIES FOR TREATING WASTE GASES

The methods for treating such waste gases containing gaseous hydrocarbons to produce innocuous gases which have been widely accepted in the past are (1) combination of a membrane gas separation method and an adsorption method, (2) an
20 adsorption method using activated carbon, zeolite, hydrophobic silica gel, etc., and the like.

Of the above two methods, the method (1) is a mainstream technology adopted in European countries. This method comprises a membrane gas separation technique (pressure
25 membrane method), followed by an adsorption technique as a polishing step. Technologies relating to this field have been published also in Japan, as can be seen in Japanese Patent

Publication No. 23568/1992 and Japanese Patent Application Laid-open No. 284623/1995, for example.

On the other hand, the most widely used method in the U.S. is the above-mentioned adsorption method, particularly an
5 adsorption method using activated carbon. This method has been disclosed in Japanese Patent Applications Laid-open No. 14687/1982, No. 42319/1982, Japanese Patent Publications Laid-open No. 50715/1984, No. 50716/1984, and No. 46630/1990.

The adsorption method using activated carbon is the
10 currently available most excellent method for treating a large amount of waste gases containing dilute gaseous hydrocarbons and reducing the content of gaseous hydrocarbons remaining in the clean gas to be discharged to atmosphere to 1000 ppm or less. A catalyst combustion method is also a simple and effective
15 method. However, because this method may involve a risk of explosion according to the gaseous hydrocarbon concentration in the waste gases, the method encounters a strong rejection from inhabitants residing near the treating facility.

Steam is commonly used as a purge gas for desorption in
20 the above-mentioned adsorption method using activated carbon. The amount of steam required for desorption is very large, approximately three times the amount of adsorbent used. In addition, when condensed into water, steam condenses hydrocarbons, resulting in water contaminated with
25 hydrocarbons. Such contaminated water requires a waste water treating facility such as an active sludge process to remove hydrocarbons in order to meet stringent water quality



standards.

To overcome this problem, a method of using high temperature nitrogen instead of steam as a purge gas for desorption and circulating the nitrogen gas has been proposed.

5 However, the circulating nitrogen gas must be cooled to 0°C or less to remove dilute gaseous hydrocarbons accumulated therein. This requires a large refrigerator and is thus uneconomical.

As a means for solving this problem, Japanese Patent No. 2823835 discloses a method of condensing dilute gaseous
10 hydrocarbons in purge exhaust gas via a cascade-type concentration adsorption column (adapter) prior to recovery of gaseous hydrocarbons from the purge exhaust gas, and removing the condensed hydrocarbons from the concentration adsorption column (adapter).

15 Another method of solving the above problem is to apply a prior replacing purge means to a desorption column when sucking the desorption column by a vacuum pump after switching the column from an adsorption column to a desorption column, whereby the purge exhaust gas containing concentrated gaseous
20 hydrocarbons is discharged and cooled to liquefy for separation.

Although liquefaction of gaseous hydrocarbons in the purge exhaust gas can be achieved by only cooling the purge exhaust gas, either of the above methods requires a means for
25 concentrating gaseous hydrocarbons in the purge exhaust gas and this concentration means is itself complicated.

Because hydrocarbons with a low boiling point cannot be

easily cooled, either of the above methods requires a strong refrigerating means. Thus, these methods are complicated as a means for concentrating dilute gaseous hydrocarbons.

Therefore, to overcome the above problems when processing
5 a large amount of gas, e.g. in an amount as much as several hundred cubic meters, the activated carbon adsorption method, which has been widely used heretofore, has mainly employed fibrous activated carbon and an adsorption device with a number of cylinders or boxes arranged therein, in which adsorbent
10 layers consisting of fibrous activated carbon are thinly encircled by a thickness of several to several tens of centimeters. Such an adsorption device is typified by K-filter (trademark, manufactured by NITTO BOSEKI Co., Ltd.) and Pilomex (trademark, manufactured by Toho Layon Co., Ltd.).

15 This method does not include a step of concentrating dilute hydrocarbons as employed in the present invention, which will be later discussed in detail, but comprises an adsorption step carried out over a long period of time, e.g. from several tens of minutes to several hours, followed by a desorption step using
20 steam.

Although a feature of this method is in providing an adsorption apparatus with adsorption layers to allow the device to process a large quantity of gas, it is difficult to decrease the concentration of hydrocarbons discharged to atmosphere to
25 as low as 100 ppm or less.

PRIOR ART TECHNOLOGIES FOR SWITCHING ADSORPTION-DESORPTION



In the method of treating waste gases containing gaseous hydrocarbons using the above adsorption method, switching of adsorption-desorption operations is performed by time control through electromagnetic valves. However, when time control is adopted for switching, the time required for the adsorption column to reach break-through must be previously known by experiment or experience.

Although switching by time control is simple and easy, an excessive amount of adsorbent must be used and operation must be switched earlier than necessary when the amount and concentration of gaseous hydrocarbons at the adsorption column entrance consistently varies to a significant degree. This entails inefficient use of the adsorbent.

To overcome this problem, a method is used for detecting "break-through" of the adsorption column using various measuring instruments and switching the operation from adsorption to desorption when the concentration becomes high enough to detect the break-through.

However, according to the present stringent air pollution regulations the concentration when the adsorption reaches break-through is very small, e.g. in the order of several tens of ppm. The concentration that must be detected prior to this timing is in the order of 1-2 ppm or less, which requires a significantly accurate measuring apparatus.

In addition, there have been a number methods proposed in the past relating to the above detection. For example, Japanese Patent Application Laid-open No. 55-35996 discloses



a method of automatically controlling the
adsorption-desorption switch timing in a moisture-removing
method using an adsorption-desorption two-column PSA purifier,
wherein wet gas is adsorbed without using a vacuum pump when
5 the adsorption column is pressurized to 5-10 kg/cm² while
removing dry gas from the column top, and regenerating the
column by returning the column pressure to atmospheric pressure
and discharging the adsorbed gas. According to the proposed
method, operation data, changing every moment, such as the gas
10 flow rate through the column, temperatures and pressures at the
column entrance and exit, regeneration pressure of the column,
and the like, are stored in a microcomputer, which
instantaneously calculates the mass balance and heat balance.
Adsorption-desorption operations are switched according to
15 desorption time controlled based on the results of the
calculated mass balance and heat balance.

The method disclosed by the Japanese Patent Application
Laid-open No. 55-35996 is epoch-making in that the
adsorption-desorption operations are switched not by time
20 control, but according to instructions from a microcomputer in
which operating conditions of the device are stored. However,
a simulation technique was not adopted because there was no
adsorption model as excellent as that available today at that
point in time. Specifically, no idea of predicting the
25 break-through concentration by simulation of an adsorption
model was created at that time.

Thereafter, a method of detecting the concentrations of



adsorbed components in gas as soon as possible before break-through is reached using a measuring port embedded in the absorbance layers, and automatically switching the electromagnetic valve when the concentration becomes a certain level has been proposed.

However, when the adsorbent is a material having an adsorption pore size distribution ranging from 5Å to 100Å, such as particulate activated carbon or silica gel, both the concentration and temperature locally change. Therefore, there is no guarantee that the adsorption band layer will uniformly ascend toward the exit in the same width without clustering on either side along the gas stream. So it is difficult to decide the position in which measuring port is embedded. The method is not necessarily superior to the time control method if the measurement port must be inserted very far from the top. Therefore, a more simple and easy time control method is a current mainstream technology for adsorption-desorption switching.

The present invention has been completed in view of the problems and drawbacks described in the above sections relating to prior art technologies for treating waste gases and prior art technologies for switching adsorption-desorption, and is based on further improvement over such prior art technologies.

A technological problem to be solved by the present invention is to significantly reduce an economical burden encountered when removing dilute gaseous hydrocarbons contained in a large amount of waste gases as a very small amount



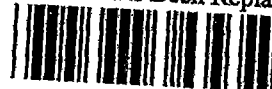
of concentrated gas, and disposing of this concentrated gas by means of burning, waste treatment, or liquefaction.

An object of the present invention is therefore to provide a method for treating a large amount of waste gases containing dilute gaseous hydrocarbons to make the gas innocuous, and a device for performing the method, wherein noxious hydrocarbons are safely, easily, and efficiently separated by using a solid adsorbent such as hydrophobic silica gel, activated carbon, or synthetic zeolite, whereby the content of gaseous hydrocarbons remaining in the waste gases to be discharged to atmosphere is reduced to 100 ppm or less.

Another object of the present invention is to provide a method and device enabling such a device to be movably mounted on a skid by integrating the system.

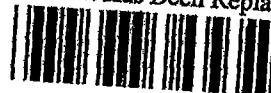
DISCLOSURE OF THE INVENTION

(1) In the method of the present invention, i.e. the method of treating dilute gaseous hydrocarbons contained in waste gases, a pair of adsorption devices having an adsorbent layer for alternately performing adsorption and desorption [particularly adsorption devices in which multiple adsorbent layers are arranged when a large quantity of waste gases, e.g. several hundred cubic meters per minute (see (9)-(12) below)] is employed,) waste gases containing gaseous hydrocarbons are caused to pass through one of the adsorption devices to cause the gaseous hydrocarbons to be adsorbed in the adsorbent layers in the adsorption device so that waste gases substantially free



from gaseous hydrocarbons are discharged to atmosphere, while the other adsorption device is switched to desorption operation by which gaseous hydrocarbons adsorbed in the adsorbent layers in the adsorption device are removed by a vacuum pump and transferred to a purge exhaust gas, wherein all or a major portion of the purge exhaust gas is returned to the untreated waste gases, thereby increasing the concentration of gaseous hydrocarbons in the adsorbent layers, and switching the operation from adsorption to desorption prior to the time when the adsorption device reaches break-through conditions. One feature of the present invention is the return of all or a major portion of the purge exhaust gas to the untreated waste gases, thereby increasing the concentration of hydrocarbons in the adsorbent layers. Another feature is the switching of the operation from adsorption to desorption prior to the time when the adsorption device reaches break-through conditions. These features ensure safe, easy, and efficient treatment of a large amount of waste gases containing dilute gaseous hydrocarbons and reduction of the content of gaseous hydrocarbons remaining in the waste gases to be discharged to atmosphere to 100 ppm or less, particularly preferably to 20 ppm or less.

(2) The method of the present invention is characterized in that the liquefied-hydrocarbons in purge exhaust gas are burned when part of the hydrocarbons is liquefied or otherwise made innocuous as an industry waste. This feature eliminates complicated procedures otherwise required for the recovery of gaseous hydrocarbons.



(3) The adsorbent layers used in the method of the present invention are layers of activated carbon and/or hydrophobic silica gel, over which a synthetic zeolite layer is placed. Such a combination of adsorbents can rapidly bring the
5 temperature in the adsorbent layers close to atmospheric temperature and constantly maintain that temperature. This ensures that the adsorbent to fully exhibits its performance without loss.

(4) According to the method of the present invention,
10 adsorbents filled in or to be filled in the adsorbent layers are precoated by gaseous hydrocarbons. Precoating of adsorbents with gaseous hydrocarbons prevents adsorption of nitrogen gas, oxygen gas, and water in the waste gases, which are otherwise adsorbed preferentially, and ensures efficient
15 adsorption of gaseous hydrocarbons in the waste gases, thereby attaining most efficient use of the adsorbent layers.

(5) The method of the present invention is characterized by the use of air or liquid water heated to above the boiling point of adsorbed hydrocarbons for removing the gaseous
20 hydrocarbons adsorbed in the adsorbent layers in the adsorption device.

Use of heated air, however, should be avoided when activated carbon is used as the adsorbent. When an adsorbent other than activated carbon such as non-combustible hydrophobic
25 silica gel is used, high temperature purge gas up to the maximum temperature of 250°C can be used.

The use of liquid water in the method of the present

invention brings about a remarkable effect. Specifically, water not only can exhibit the same effect as purge gas if gasified within the desorption column by a vacuum pump, but also can exhibit the same purge effect as steam in an amount as small
5 as one several tenths ($1/50$ to $1/60$) the amount required for steam.

(6) As a means for switching the operation from adsorption to desorption prior to the time when the adsorption device reaches break-through conditions, which is a second feature of
10 the present invention, a temperature detecting port is located on top of the absorbance layers to switch the electromagnetic valve when the temperature from the temperature detecting port no more increases.

(7) In the seventh place, according to the method of the
15 present invention, the gas flow rate at the entrance, the hydrocarbon concentration in the gas at the entrance, and a desirable hydrocarbon concentration (a hypothetical value) in the gas at the exit of the absorber during the adsorption operation are input into a chip as numerical data, and the
20 switching time is previously set using a control simulation model installed in the chip.

These method enable the absorber to automatically detect the break-through timing of the adsorbent layers, whereby the adsorption and desorption operations can be automatically
25 switched.

(8) The method of the present invention can reduce the hydrocarbon concentration to be discharged from the adsorption

device to 100 ppm or less.

(9) The present invention provides a device for carrying out any one of the methods described in (1) to (8) above. In the device of the present invention, the adsorption device
5 having adsorbent layers is a component holding the adsorbent layers, and this component is a container which can be enclosed but not sealed. Specifically, the container containing the adsorbent filled therein does not allow the adsorbent to leak out irrespective of its shape. In addition, the container is
10 provided with a number of minute pores through which the gas may enter or exit the container.

(10) The adsorption device having adsorbent layers is a device containing a multiple of cylinders which encircle the adsorbent layers and through which waste gases can pass in the
15 circumferential direction.

(11) The enclosure for the adsorbent layers is a box-type component or honeycomb-type component, and the adsorption device contains multiple layers of the component.

(12) The above adsorbent layer is filled with an adsorbent
20 of fine particles with a diameter of 0.1-1 mm. This enables the adsorption device to process a large quantity of waste gases in the order of about several hundred cubic meters per minute.

BRIEF DESCRIPTION OF THE DRAWINGS

25 Figure 1 is a flow sheet for illustrating an embodiment of the method for treating dilute gaseous hydrocarbon in waste gases of the present invention.

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Figure 2 is a drawing showing an embodiment of a control board for monitoring and controlling operating conditions of the method shown in the flow sheet of Figure 1.

Figure 3 is a longitudinal sectional view showing the adsorption column used in Example 1 of the present invention.

Figure 4 is a longitudinal sectional view of the adsorption column used in Example 2 of the present invention.

Figure 5 is a drawing further illustrating the adsorption column of Figure 4, wherein Figure 5(A) is a cross-section along the line A-A and Figure 5(B) is an enlarged detailed illustration of part of Figure 4.

Figure 6 is a chart showing a water adsorption isotherm for activated carbon.

In the Figures, 1a and 1b indicate adsorption columns, 2a and 2b are outer cylinders, 3a and 3b are adsorbent layers, 3-1a and 3-1b indicate activated carbon, 3-2a and 3-2b are Y-type synthetic zeolite, 4a and 4b are inner cylinders, 5 indicates cooling water, 10 is a waste gas generation source, 11 is a waste gas discharge pipe, 12 is an emission pipe, 13 is a water feed pipe, 14 is a water-sealed vacuum pump, 15 is a purge exhaust gas pipe, 16 is a gas/liquid separator, 17 is an industrial waste treating device, 18 is a return gas pipe, 20 is a control board, 21 is a memory, 22 is a CPU (calculation), 23 is a memory (adsorption model), 41a (41b) is an adsorption column, 42a (42b), 42a' (42b') are outer cylinders, 43a (43b) is an adsorbent layer, 43-1a (43-1b) is pulverized activated carbon, and 43-2a (43-2b) is Y-type synthetic zeolite.

BEST MODE FOR CARRYING OUT THE INVENTION

The method and device of the present invention (hereinafter referred to simply as "the present invention") will be described in more detail by way of embodiments.

As mentioned above, the first feature of the present invention is the return of all or a major portion of the purge exhaust gas to untreated waste gases, thereby increasing the concentration of hydrocarbons in the adsorbent layers and the second feature is the switching of the operation from adsorption to desorption prior to the time when the adsorption device reaches break-through conditions. These features ensure safe, easy, and efficient treatment of a large amount of waste gases containing dilute gaseous hydrocarbons and reduce the content of gaseous hydrocarbons remaining in the waste gases to be discharged to atmosphere to 100 ppm or less, and particularly to 20 ppm or less.

Explaining the above first feature of the present invention, in one embodiment of the present invention all purge exhaust gas is returned to the untreated waste gases. However, when the concentration of hydrocarbons in the purge exhaust gas is extremely high, the adsorbent layers reach break-through conditions in a very short period of time. This adversely affects the waste gases treatment operation. Therefore, as another embodiment of the present invention, it is desirable to remove a portion of the purge exhaust gas to make such a portion innocuous by burning, for example, and to return the

other portion (a major portion) of the purge exhaust gas to the untreated waste gases.

In addition, when a part of the gaseous hydrocarbons in the purge exhaust gas is liquefied, it is possible to remove
5 the liquefied hydrocarbons, and burn or otherwise convert such hydrocarbons into an innocuous industrial waste.

Next, turning the discussion to the second feature of the present invention, i.e. the feature of switching the operation from adsorption to desorption prior to the time when
10 the adsorption device reaches break-through conditions, the means for the detection of break-through conditions in the present invention basically employs a circuit chip embedded in the device. Owing to availability of super-miniature chips which have achieved a remarkable advance in recent years, the
15 use of a large micro-processor for calculation described in the above-mentioned prior art (the technology disclosed in the Japanese Patent Application Laid-open No. 55-35996) is not necessary.

In addition, according to a preferable embodiment of the
20 present invention, not only the data obtained during operations is used for calculating mass balance and heat balance, but also an adsorption model is input into a ROM to store data changing every minute during operation as logger signals in a personal computer. The break-through concentration can be predicted by
25 simulation of such data, preferably within several seconds, thereby controlling the adsorption system. This is a feature distinctly differentiating the present invention from prior art



technology. Specifically, the idea of predicting the break-through concentration by simulation of an adsorption model is quite different from the prior art technologies.

Various adsorption models have been proposed. Among them, a famous model is the Frozen Model in which calculation is performed using the values obtained by fixing (freezing) properties of the adsorbent such as an adsorption isotherm curve, adsorption pressure inside the adsorption column, the degree of vacuum in a vacuum pump, the gas flow rate in the column, the height of the adsorbent layer, and the purge coefficient, as frozen values, and the gas flow rate and concentration at the entrance that change every minute as variables, and inputting the switching time or the exit concentration (break-through concentration) of the adsorbent layer into a chip as a hypothetical value.

Another model known in the art is an equilibrium model which requires more time for calculation but excels in accuracy. The adsorption models used in the present invention are not limited to these.

The second feature of the present invention, i.e. switching of the operation from adsorption to desorption prior to the time when the adsorption device reaches break-through conditions, is closely related to the first feature of returning all or a major portion of the purge exhaust gas to the untreated waste gas, thereby increasing the concentration of hydrocarbons in the adsorbent layers.

Specifically, in the case where it is difficult to predict



the time required for the break-through due to the ever-changing amount of waste gases and concentration of gaseous hydrocarbons contained therein, both the concentration of hydrocarbons in the gases at the entrance of the adsorption device and the concentration of hydrocarbons in the adsorbent layer of the adsorption device change even more if uncondensed purge exhaust gas is added to the waste gases by the application of the first feature. For this reason, predicting the time required for the break-through becomes more difficult. Therefore, the above second feature is introduced as an essential constituent to solve this problem.

However, the present invention does not exclude the conventional switching means by time control. This is because when the concentration of gaseous hydrocarbons in the gas (waste gases + the above-mentioned uncondensed purge exhaust gases) at the entrance of the adsorption column is almost constant over time, one convenient way of switching the operation is to previously determine the time required for the adsorption column to reach break-through conditions from start of operation and to use this determined time in the next adsorption operation. In addition, adopting the switching means by time control based on the predicted time required for the desorption operation to be completed is one of the choices in the adsorption device developed by the present inventors. Specifically, the time control means can also be adopted as the switching means from the desorption column to the adsorption column as well as the above-mentioned switching from the adsorption column to the

desorption column. In more detail, this method consists of setting the time when purge gas is introduced into the desorption column after shifting the operation to desorption by operating the vacuum pump and detecting the time at which
5 the prescribed degree of vacuum is attained, and automatically switching the operation to adsorption when the previously set time has elapsed.

When the flow rate and concentration of the gases at the entrance change every minute as mentioned above, the
10 concentration of the gaseous hydrocarbons adsorbed by the adsorbent layers can be automatically concentrated to a concentration as high as the column operation reaches near the break-through.

After removing the gases as a small amount of purge
15 exhaust gas, a portion of the purge exhaust gas may be removed and burned. Alternatively, gaseous hydrocarbons in the purge exhaust gases may be removed as liquid hydrocarbons, and burned or otherwise treated to make them innocuous as an industrial waste material.

20 In spite of these advantages, the method has a drawback in that a long period of time (e.g. several days) is required for the adsorption to reach break-through when there is a significant difference between the time required for adsorption and that required for desorption. On the other hand, the
25 situation where desorption is completed in several hours is not necessarily desirable for the personnel in charge of operation management.



Therefore, when an appropriate adsorbent is filled in an appropriate amount, the amount of gaseous hydrocarbons to be adsorbed is extremely small around the top of the adsorbent layers and, therefore, the amount of adsorption heat is extremely small. In addition, heat in excess of that amount may be consumed by cooling water or may escape from the adsorption column wall. As a result, signals (temperature) from the measuring port inserted into the column near the top to import the data into chips stop, then gradually decrease. The above drawbacks can be overcome if a valve (an electromagnetic valve) for automatically switching adsorption-desorption operations is used in combination at this point in time. This feature is also included in the present invention.

The term "appropriate adsorbent" in this invention means an adsorbent which has the adsorption pore size controlled in a certain range and does not create locally uneven adsorption nor adsorb water while treating waste gases with an RH of about 50% or higher. For example, an adsorbent such as synthetic zeolite is most suitable.

Therefore, in one preferred embodiment of the present invention, a synthetic zeolite layer is provided at the top of the adsorbent layers and a temperature detecting port is inserted in the adsorbent layers of synthetic zeolite. The electromagnetic valve is automatically switched when the temperature from the temperature detecting port does not increase any more. Precoated activated carbon or precoated hydrophobic silica gel is suitable as the adsorbent placed below



the adsorbent layers of synthetic zeolite.

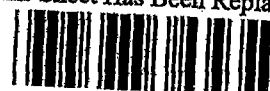
The technological significance of precoating, which is a preferred embodiment of the present invention will now be described.

5 The degree to which the gaseous hydrocarbons are concentrated in the adsorbent layers is theoretically 760/25 when only hydrocarbons are adsorbed at 25 mmHg, which means that the hydrocarbons are concentrated to 25 times the original concentration. Usually, the waste gases contain a large amount
10 of air of which the major components are nitrogen gas and oxygen gas having a molecular diameter smaller than hydrocarbons. Therefore, nitrogen gas and oxygen gas are adsorbed more preferentially than gaseous hydrocarbons. As a result, gaseous hydrocarbons are known by experience to be concentrated
15 only to four times the concentration at the entrance.

The solid adsorbents used in the present invention such as activated carbon, synthetic zeolite, and hydrophobic silica gel are not necessarily adsorbents which do not adsorb water at all, but their water absorption rate significantly varies
20 according to the relative concentration of moisture in the adsorbed gas as shown in Figure 6.

Although these adsorbents adsorb almost no water at an RH of 40% or less when the adsorbed gas is wet air, they rapidly adsorb water when the RH exceeds 50% (see Figure 6). Figure 6
25 is a chart showing a water adsorption isotherm of activated carbon. The same tendency applies to other hydrophobic adsorbents.

This Sheet Has Been Replaced



Therefore, it is desirable to apply a precoat to the adsorbent layers to obstruct adsorption of nitrogen gas, oxygen gas, and moisture in the waste gases which are inherently adsorbed preferentially. As a means of precoating, dripping of liquid hydrocarbons into the waste gases to be processed can be applied. More specifically, an adsorbent layer can be precoated by spraying gaseous hydrocarbons to pipes through which the waste gases to be processed flow. In addition to the liquid hydrocarbons, a substance having affinity with water and having a boiling point higher than water, such as a hydrocarbon, for example, can be used as a precoating material.

As mentioned above, in developing the method for treating a large amount of waste gases containing dilute gaseous hydrocarbons, the present inventor has skillfully incorporated "a logger signal" which is an essential hardware technique to import data. In addition, an adsorption model simulation in the form of an ROM incorporated in the control system was adopted as a novel software means. These means ensure easy monitoring of the break-through concentration within a short time in spite of the hydrocarbon concentration at the entrance changing every minute. In addition, appropriate selection of adsorbent enables the temperature in the adsorption layer to become constant rapidly and easily at around the normal temperature.

As a result, the switch timing from adsorption to desorption can be set not only by a time cycle but also by the decision of a personal computer in which an adsorption model (software) is incorporated, thereby causing the adsorbent to





fully exhibit its performance without loss. For this reason, it is possible to concentrate the dilute hydrocarbons in the purge gases to close to a break-through concentration and to remove an extremely small amount of purge exhaust gases

5 containing hydrocarbons at a very high concentration.

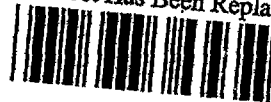
(Adsorbent)

Any material can be arbitrarily used as the adsorbent in the present invention irrespective of its combustibility or noncombustibility, inasmuch as the adsorbent is a solid having
10 affinity with gaseous hydrocarbons in the waste gases.

However, when the concentration of hydrocarbons in the waste gases is small (e.g. about 5000 ppm), hydrophobic silica gel which is easily available at low cost is preferable. The reason is that the hydrophobic silica gel allows a purge gas
15 temperature as high as 250°C.

When noncombustible silica gel is used, silica gel adsorbents treated with a silane coupling agent such as trimethylchlorosilane or the like to provide hydrophobic properties, treated for a long time at a high temperature to
20 provide hydrophobic and lipophilic properties, or precoated with ethylene glycol or a high boiling point hydrocarbon such as heptane are preferable. An ideal adsorbent is a solid adsorbent which does not adsorb water in an amount no more than several percent at an RH of 50% or more.

25 Solid adsorbents used as the adsorbent in the present invention such as activated carbon, synthetic zeolite, silica gel, and activated alumina exhibit strong affinity with gaseous



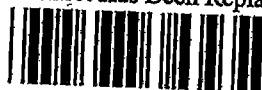
hydrocarbons and are used as an insulation material. In addition, with the exception of synthetic zeolite, these adsorbents do not have uniform adsorption sites due to the broad adsorption pore size distribution and, therefore, tend to cause local
5 heating.

Generally speaking, it is difficult for a layer of hydrophobic silica gel or particulate activated carbon with a thickness of about four inches or more to transfer the heat of adsorption to the cooling water layer within a short period of
10 time, even though this depends on the particle size and the rate of temperature increase.

Therefore, if the thickness is more than four inches, heat transfer in the direction of the perimeter can no longer be expected and, therefore, heat transfer by gases flowing in
15 the longitudinal direction must be relied upon. Therefore, it is important that the adsorption layers with a certain width can be uniformly moved toward the exit of the adsorption column by the influence of the temperature distribution in the adsorption column. Specifically, although there is no problem
20 in the detection of the break-through concentration at the exit of the adsorption column, a problem occurs when detecting such a concentration in the detection port embedded in the adsorbent.

A means recommended for avoiding this problem is to locate the synthetic zeolite on the uppermost adsorbent layer, i.e.
25 the layer nearest to the exit. Examples are Y-type zeolite 360HUD (manufactured by Tosoh Corp.) and the like.

Unlike hydrophobic silica gel and particulate activated



carbon, synthetic zeolite has a strictly controlled pore size distribution. Some synthetic zeolite products cover almost all molecular diameters of gaseous hydrocarbons. In addition, in spite of 15-20% by weight of gaseous hydrocarbons absorbed, the amount of water adsorbed is less than 10% even if the RH of the gas is 50% or more. Because of this, no inclination is created in the adsorption band having a certain width to move this layer.

The detection port for detecting the concentration and temperature and storing the detected data as data logger signals must be located at the center of the synthetic zeolite layer. In this manner, the time when the temperature due to heat of adsorption at the center no longer increases can be utilized as the approximate timing for switching, together with the above means for detecting the time of break-through. The synthetic zeolite preferably has an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 20 or more and a pore size of about $8\text{\AA}$.

(Adsorption device)

Next, embodiments of the adsorption device having adsorbent layers (first and second embodiments) of the present invention will be explained.

(First embodiment of the absorber)

As a means to promptly transfer the heat of adsorption generated in the above adsorbent layers in the lateral direction, thereby removing that heat, to locally homogenize the temperature and concentration of the adsorbent layer, the first embodiment of the adsorption device having adsorbent layers

used in the present invention preferably has a multiple layer cylindrical column, which comprises contiguously arranged adsorbent layers to adsorb gaseous hydrocarbons and cooling water layers to cool the adsorbent layers. Taking into
5 consideration the tendency whereby static electricity generated in the adsorbent layer moves to the center of the layer, the use of an adsorption column with a structure having a metallic cylinder in the center is desirable to cool the adsorption column and cause the static electricity to escape.

10 Describing a specific adsorption column of the first embodiment of the present invention with reference to Figure 3, this adsorption column 1a (1b) consists of an outer cylinder 2a (2b), adsorbent layer 3a (3b), and inner cylinder 4a (4b) in which cooling water 5 flows.

15 This adsorption column 1a (1b) is the column used in later-described Example 1. In the Figure, 3-1a (3-1b) indicates activated carbon and 3-2a (3-2b) indicates Y-type synthetic zeolite.

One feature to be noted with respect to the adsorption
20 column 1a (1b) of the present invention is that, it is extremely desirable to operate the adsorption column 1a (1b) under an internal pressure within the allowable gauge pressure (1 kg/cm² or less) under the High Pressure Regulation. This is because it is natural from the theory of the PSA method that an increase
25 in the internal pressure of the adsorption column accompanies a dramatic increase in the effective adsorption amount of hydrocarbons adsorbed by the adsorbent.



(Second embodiment of the absorber)

Although a conventional column-type adsorption device with adsorbents densely filled therein can be used in the present invention, this type of adsorption device may have
5 problem when processing a large amount of waste gases.

Specifically, when the amount of waste gases to be processed in one hour is 36,000 m³, for example, the column diameter required for a conventional adsorption device will be 10 m.

10 The reason is as follows: the flow rate of waste gases passing through the adsorbent layer (i.e. the time during which waste gases maintain contact with the adsorbent (SV value)) is limited due to the adsorption efficiency. In general, this flow rate is limited to the rate below which the adsorbent particles
15 do not flow, usually in the range of 10-20 cm/sec. The column diameter calculated from the average flow rate of the waste gases, 15 cm/sec (0.15 m/sec), is 10 m as shown by the following formula.

$$\pi R^2 \times 0.15 = 36,000/3,600 = 10$$

20 Using an adsorption column having such a large column diameter in the present invention is not realistic.

On the other hand, the adsorption efficiency is closely related to the size of the adsorbent particles. For example, comparing the case in which an adsorbent with a large particle
25 size makes up an adsorbent layer and the case in which an adsorbent with a small particle size makes up an adsorbent layer of the same volume, the latter case is more efficient as a matter



of course. However, too small a diameter results in a problem because a particle with a small diameter is more fluid. For this reason, a conventionally-used adsorbent having a diameter of 2-3 mm is appropriate, although the specific diameter varies according to the type and configuration of the adsorbent.

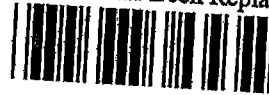
As an adsorption device designed to preclude flowing of an adsorbent thickly filled therein, an adsorption device with a structure in which waste gases flow in the direction crossing a cloth made of fibrous activated carbon arranged therein can be used. Specific examples are the above-mentioned by K-filter (trademark, manufactured by TOYO BOSEKI Co., Ltd.) and Pilomex (trademark, manufactured by Toho Lyon Co., Ltd.).

This structure has an advantage of availability of a larger area for gas flow, but a disadvantage of difficulty in collecting dilute hydrocarbons in waste gases due to a thin adsorbent layer which limits the contact time.

In addition, no way other than using steam is conceivable as a means for desorption. The combined use of a vacuum pump is impossible.

In terms of adsorption theory, the adsorption efficiency is indicated by the K_{fav} , i.e. general mass transfer capacitance coefficient, (1/sec). Based on the analysis of the results of experiments undertaken by the present inventor and the actual results obtained using industrial apparatus constructed by the present inventor, the value of K_{fav} is in the range of 3-6 when the particle size is 2-3 mm, although the specific value varies according to the properties of the gaseous hydrocarbons.





In contrast, when fibrous activated carbon is used, the Kfav is in the range of 15-25, indicating that the fibrous activated carbon exhibits an adsorption performance several times superior to particles. Specifically, the fibrous
5 activated carbon requires a contact time with the gases of only about 1/5 the time that required for particles.

Paying an attention to this point, the inventor of the present invention has developed a second embodiment of the adsorption device having an adsorbent layer which is novel and
10 economical, which can be used for processing a large amount of waste gases.

This novel and economical adsorption device of the present invention (the adsorption device of the second embodiment) is characterized in that the adsorption device
15 having adsorbent layers consists of a component holding the adsorbent layers, and this component is a container which can be sealed but not closed. Specifically, the container containing the adsorbent filled therein does not allow the adsorbent to leak out, irrespective of its shape. In addition,
20 the container is provided with a number of minute pores through which the gases may enter or exit the container. More specifically, the adsorption device having adsorbent layers is a device containing a plurality of cylinders which encircle the adsorbent layers and through which waste gases can pass in the
25 circumferential direction. In addition, the enclosure for the adsorbent layers is a box-type component or honeycomb-type component, and the adsorption device contains multiple layers

of the component.

As the adsorbent to be filled, fine particles with a diameter of 0.1-1 mm (preferably 0.2-0.5 mm) are used because small diameter particles can reduce the contact time with the gases. In addition, to expand the area through which the gases pass, multiple layers of the adsorbent are used.

In this manner, an excellent effect of reducing the contact time to about $1/5$ the time required for the conventional technique can be obtained by using fine particles with a diameter of 0.1-1 mm as an adsorbent. Reduction of the contact time to about $1/5$ enables reduction of the thickness of the adsorbent layers to about $1/5$.

Conventional commercial plants employ a one-column system having adsorbent layers with a thickness of 1-2 m. The reduction of the thickness of the adsorbent layers to about $1/5$ can reduce the thickness of the adsorbent layers to 20-40 cm, which brings about a great advantage of principally making it unnecessary to cool the adsorbent layers.

This is because the concentration of hydrocarbon gases contained in a large quantity of the waste gases passing through the adsorbent layers is very small and, therefore, most of the gases is air, and the heat of adsorption in excess of the heat removed by air will not remain in the adsorbent layers.

In addition, because one pass of the waste gases through the adsorbent layers has been normal for the above-mentioned conventional adsorption device using fibrous activated carbon to complete the processing of the waste gases, the concentration

of the adsorbed hydrocarbons is very small. Therefore, no gaseous hydrocarbon desorption means other than the means using steam was considered. However, because it is possible to increase the hydrocarbon concentration in the adsorbent layers
5 by returning all or a major portion of purge exhaust gases to the waste gases, combined use of a vacuum pump, not conceivable in the conventional adsorption device, is possible in the adsorption device of the present invention.

Furthermore, the combined use of a vacuum pump allows
10 the use of water as a purge medium for desorption. (Refer to later discussions for "combined use of a vacuum pump" and "use of water as a purge medium")

A specific example of the novel and economical adsorption device of the second embodiment of the adsorption device having
15 an adsorbent layer exhibiting the above-mentioned outstanding effect will now be explained referring to Figure 4, Figure 5(A), and Figure 5(B). The adsorption column 41a (41b) comprises a double layer cylinder 42a (42b) and 42a' (42b') in which an adsorbent layer 43a (43b) is filled. The waste gases pass
20 through the adsorbent layer 43a (43b) as shown by an arrow in Figure 5 (B). The passage area of the gases is expanded in this manner.

This adsorption column 41a (41b) is the column used in later-described Example 2. In the Figure, 43-1a (43-1b)
25 indicates pulverized activated carbon and 43-2a (43-2b) indicates Y-type synthetic zeolite.

(System integration)

The present inventor has further devoted his efforts to the investigation of integrating the device proposed in the present invention as a portable system placed on a skid.

Specifically, the inventor proposed a simple and economical method in which a recovery means was omitted. The method is not an adapter method or substitution purge method disclosed by Japanese Patent No. 2840563, No. 2766793, or 2823835, and does not use a method of recovery of gaseous hydrocarbons in purge gases by washing the purge gases with analogous liquid hydrocarbons, nor use a method of recovering gaseous hydrocarbons as a liquid by condensing the concentration of hydrocarbons in an adsorption column by recycling desorbed gases and cooling the condensed gaseous hydrocarbons by a complicated refrigeration means.

(Desorption means)

As a means of removing gaseous hydrocarbons adsorbed in adsorbent layers, air or water heated to a temperature above the boiling point of the adsorbed hydrocarbons is used. The use of water is more preferable (see later discussion). As the source of air, part of the clean gas exhausted from the adsorbent layers to the atmosphere can be used.

Conventionally, the adsorption method has been mainly used for the process of making dilute hydrocarbons contained in a large quantity of waste gases innocuous, which is one field of application of the present invention. With some exceptions, particulate activated carbon or fibrous activated carbon is used as the adsorbent.

Although these activated carbons have an outstanding superior adsorption capability as compared with other adsorbents, they exhibit difficulty in desorbing the materials once adsorbed. For this reason, the amount of steam required for desorption is very large, approximately three times the amount of activated carbon used. Moreover, hydrocarbons desorbed by steam are treated together with water to make them innocuous using a waste water disposal process such as an activated sludge treating method. Desorption using a large amount of heated air instead of steam as a purge gas involves the risk of burning activated carbon. The use of activated carbon together with gases other than air at normal temperature or incombustible nitrogen gas is prohibited by the Fire Act. However, this kind of danger can be avoided if incombustible hydrophobic silica gel is used as the adsorbent. For this reason, it is possible to use air at a high temperature (up to a maximum temperature of 250°C) as a purge gas. The concentration of gaseous hydrocarbons is limited to the value less than the explosion lower limit. This means that the concentration is preferably about 5000 ppm or less.

In the present invention, the gaseous hydrocarbons desorbed together with heated purge gases are gases suitable for burning as purge gases, as is.

Moreover, when a vacuum pump is used in combination as an auxiliary means for desorption, the larger the amount of heated air (i.e. the larger the purge coefficient), the less the load on the vacuum pump. In addition, because desorption

can be fully achieved by the use of a large amount of heated air, a degree of vacuum of about 60-150 Torr is sufficient. Because a vacuum pump is expensive, the application effect of the present invention is remarkable.

5 On the other hand, when activated carbon is used as adsorbent, there have been conventionally no desorption purge gases available other than a large amount of steam (or nitrogen gas) as mentioned above. The use of liquid water as a medium for purging has been discovered by the present inventor.

10 Injection of water to the desorption column not only can exhibit the same effect as purge gases if gasified within the desorption column by a vacuum pump, but also can exhibit the same purge effect as steam in an amount as small as one several tenths ($1/50$ to $1/60$) the amount required for steam.

15 When water is used in the present invention, a water-sealed vacuum pump is preferably used as the vacuum pump. This because concentrated hydrocarbon gases mix with sealing water and become waste water which is suitably processed by a waste water treatment unit.

20 In addition to the embodiments described above, the method of the present invention may be applied to the known PSA method, PTSA method, VSA method, VTSA method, etc. The application to these methods is also included in the scope of the present invention.

25 The present invention provides a method for concentrating and separating dilute gaseous hydrocarbons contained in waste gases and a device for performing the method.

The method and device can be applied not only to multi-component dilute hydrocarbons produced in coating processes, but also to single component dilute gases such as benzene, toluene, trichloroethylene, methyl ethyl ketone, and fluorinated hydrocarbons.

EXAMPLES

The present invention will be described in detail by way of examples. The present invention, however, is not limited to the following Examples 1 and 2.

Example 1

Figure 1 is a flow sheet for illustrating an embodiment of the method of the present invention for treating dilute gaseous hydrocarbon in waste gases. Figure 2 is a drawing showing an embodiment of a control board for monitoring and controlling operating conditions of the method shown in the flow sheet of Figure 1. Figure 3 is a longitudinal sectional view of one embodiment (Example 1) of the absorber used in the flow sheet of Figure 1.

As shown in Figure 3, the embodiment of Example 1 employs a double-cylinder absorption column 1a (1b) consisting of an inner cylinder 4a (4b) in which cooling water flows and an outer cylinder 2a (2b), provided outside the inner cylinder, in which an adsorbent layer 3a (3b) is filled. Cooling water 5 is caused to turbulently flow through the inner cylinder 4a (4b) countercurrently against the waste gases flowing through the adsorbent layer 3a (3b).

As adsorbents, particulate activated carbon ("Particulate Sirasagi #1", manufactured by Takeda Chemical Industries, Ltd.) and Y-type synthetic zeolite ("360 HUD" manufactured by Tosoh Corp.) are used. As shown in Figure 3, the adsorbent layers 3a (3b) consists of particulate activated carbon 3-1a (3-1b) and Y-type synthetic zeolite 3-2a (3-2b) provided above the particulate activated carbon in the absorption column 1a (1b). Particulate activated carbon precoated with benzene vapor is used.

10 The embodiment of Example 1 will now be explained in detail referring to Figure 1. In Figure 1, waste gases generated in a waste gas generation source (not shown in the Figure), which contain about 5000 ppm of benzene in an amount of about 20 l/minute, are fed to the adsorption column 1a after
15 compression by a blower (not shown in the Figure) which compresses the gases to less than 1 kg/cm (gauge), or without compression via a waste gas discharge pipe 11. The gas flow rate in the adsorbent layer 3a (3b) is about 10 cm/sec.

Waste gases after treatment in the adsorption step is
20 discharged from the top of the adsorption column 1a (adsorption column 1b after switching to a desorption operation) via the emission pipe 12 as clean gases (air containing 20 ppm of benzene).

The adsorption column 1a, 1b is switched alternately to
25 implement the adsorption operation and a later described desorption operation. Switching of the operation from adsorption to desorption is performed before break-through of

the adsorbent layers in the adsorption column 1a, 1b by automatically opening and closing the valves (d), (d) shown in Figure 1.

Specifically, the valves (e), (e) for switching the
5 adsorption-desorption operation is automatically opened and closed in reference to the expected break-through time and the time when the temperature (F and G) of the Y-type synthetic zeolite 3-2a (3-2b) (see Figure 3) in the adsorbent layer detected by the temperature detection board (not shown in the
10 Figure) provided in the top of the adsorbent layer stops increasing. Here, the expected break-through time means the time indicated by the CPU 22 of the adsorption model, by which the time is calculated based on the flow rate of gases at the entrance (J) and the gas concentration at the entrance (H),
15 stored in the memory 21 shown in Figure 2, and previously input into the memory (adsorption model) 23.

On the other hand, after the adsorption, the adsorbed gaseous hydrocarbons are desorbed by feeding water to the adsorption column 1a (adsorption column 1b after switching to
20 the desorption operation) via a water feed pipe 13 and, at the same time, by suction using a water-sealed vacuum pump 14 (Nash Pump, manufactured by Awamura Manufacturing Company, Ltd.).

In this Example 1, the water-sealed vacuum pump 14 is operated at about 60 Torr to reduce the pressure (to vacuum)
25 of the adsorption column 1a (switched to desorption). The water supplied is vaporized in the adsorption column 1a and used as a purge gas. The purge gas is sent to a purge exhaust gas charge

pump 15 via the water-sealed vacuum pump 14 and removed as purge exhaust gas.

Industrial water at room temperature is used for cooling of the purge exhaust gas suctioned by the water-sealed vacuum pump 14. Specifically, the purge exhaust gas is sent to a gas/liquid separator 16. The gas/liquid separator 16 is cooled by industrial water flowing through a cooling pipe (not shown in the Figure) arranged inside the column.

In this instance, benzene vapor in the purge exhaust gas is condensed together with sealing water in the gas/liquid separator 16 connected to the lower part, and separated from non-condensed gases. Water and benzene are removed and disposed using the industrial waste treating device 17.

Exhaust gases not condensed in the gas/liquid separator 16 containing residual benzene vapor are returned to the waste gas discharge pipe 11 via a return gas air pipe 18, and subjected to the adsorption treatment together with waste gases. Because of the non-condensed gases contain a high concentration residual benzene, the recycling of the entire amount to the waste gas discharge pipe 11 increases the benzene concentration in the adsorption column. Then, the time when the adsorbent layers in this adsorption column reaches break-through is predicted using the above means, based on which the switching time of the valve (e) is set and the operation is automatically switched to desorption.

A to J in Figure 1 indicate instruments for monitoring the operation, whereas (a) to (d) indicate the locations where

valves are installed for controlling the operation.

Figure 2 is a drawing showing a control board 20 for monitoring and controlling operating conditions in the method shown in the flow sheet of Figure 1. The control board 20 includes a memory 21, memory (adsorption model) 23, and CPU (calculation) 22. In Figure 2, among the data signals to be stored in the memory 21, those required at the time of adsorption/desorption switching are indicated as "X". Storage of other data signals is omitted.

Because the adsorption and desorption operations are switched in Example 1 by detection of data logger signals prior to break-through of the adsorption column, as mentioned above, it is possible to concentrate gaseous hydrocarbons in the adsorption column to several times when the concentration of the gaseous hydrocarbons is small. In addition, because of the special design of the cooling means to remove heat generated in the adsorbent layers (see Figure 3), local heating can be avoided and the temperature of the adsorbent layers is maintained almost constant during the operation.

The concentration of benzene in the gases removed to the atmosphere via the emission pipe 12 is substantially 20 ppm or less.

Example 2

Figure 4 is a longitudinal sectional view of the adsorption column used in Example 2. Figure 5 is a drawing further illustrating the adsorption column of Figure 4, wherein Figure 5(A) is a cross-section along the line A-A of Figure 4

and Figure 5(B) is an enlarged detailed illustration of part of Figure 4.

As shown in Figures 4, 5(A), and 5(B), the adsorption column 41a (41b) comprises a double layer cylinder, the outer cylinder 42a (42b) and 42a' (42b'), in which an adsorbent layer 43a (43b) is filled.

As adsorbents, pulverized activated carbon with a particle size of 0.4 mm ("HC42", manufactured by Tsurumi Coal Co., Ltd.) and Y-type synthetic zeolite with a particle size of 1.0 mm ("360 HUD" manufactured by Tosoh Corp.) are used.

As shown in Figures 4 and 5(B), the adsorbent layers 43a (43b) consist of pulverized activated carbon 43-1a (43-1b) and Y-type synthetic zeolite 43-2a (43-2b) provided above the particulate activated carbon in the absorption column 41a (41b). Pulverized activated carbon precoated with benzene vapor is used.

In Example 2, waste gases containing about 5000 ppm of benzene in the amount of 300 l/minute are treated in the same manner and under the same conditions as in Example 1, with the exception of using the absorption column 41a (41b) shown in Figures 4, 5(A), and 5(B), and using pulverized activated carbon and Y-type synthetic zeolite. The flow rate of the gas flowing in the circumference direction in the adsorbent layer 43a (43b) is 1.5 cm/sec.

In the Example 2, the concentration of benzene in the gases removed to the atmosphere via the emission pipe 12 (see Figure 1) is too small to be detected by a commercially available

portable-type HC concentration detection tube (isobutane conversion).

The results obtained in Example 2, wherein benzene contained in the gases removed to the atmosphere was too small to be detected, indicate that the method is more excellent than the method of Example 1 which reduced the concentration of benzene in the gases removed to the atmosphere to 20 ppm or less.

In addition, as can be understood, the method of Example 2 can effectively process a larger amount of waste gases of as much as 300 l/minute ($18 \text{ m}^3/\text{hour}$).

Although Example 1 of the present invention was described by way of the double-cylinder adsorption column 1a, 1b of the type shown in Figure 3, the present invention is not limited to this type of double-cylinder column, but another double-cylinder, for example, the type in which adsorbent is provided in the inner cylinder and water for cooling the adsorbent layer is circulated in the outer cylinder, or other multi-cylinder type adsorption columns can also be used.

Although Example 2 of the present invention was described by way of the multi-cylinder adsorption column of the type shown in Figures 4 and 5, the present invention is not limited to this type of multi-cylinder column, but other multi-cylinders, for example, an adsorption device made by bundling honeycomb cores with adsorbent provided therein or an adsorption device composed of layered boxes into which an adsorbent is filled, can also be used.

The present invention is not limited to the embodiments

described above. Many modifications and variations are possible without departing from the spirit and scope of the present invention.

5 INDUSTRIAL APPLICABILITY

As fully described above, according to the present invention, all or a major portion of the purge exhaust gas containing desorbed gaseous hydrocarbons is returned to the untreated waste gases, thereby increasing the concentration of hydrocarbons in the adsorbent layers (the first feature), and the operation is switched from adsorption to desorption prior to the time when the adsorption layers reach break-through conditions (the second feature), thereby ensuring safe, easy, and efficient treatment of waste gases containing dilute gaseous hydrocarbons and reduction of the content of gaseous hydrocarbons remaining in the waste gases to be discharged to atmosphere to 100 ppm or less, particularly preferably to 20 ppm or less.

The method of the present invention can remove air-polluting gaseous hydrocarbons to a level which more than meets the emission standard of "30 ppm or less" enforced by the amendment to the Air Pollution Control Law (Official Gazette dated February 6, 1997). The method can well cope with a more stringent standard, e.g. one half or less, in the future.

Moreover, a device for implementing the method of the present invention can be manufactured as an integral system movably mounted on a skid.

CLAIMS

1. A method of treating dilute gaseous hydrocarbons contained in waste gases, characterized by using a pair of adsorption devices having an adsorbent layer for alternately performing adsorption and desorption, causing waste gases containing gaseous hydrocarbons to pass through one of the adsorption devices thereby causing the gaseous hydrocarbons to be adsorbed in the adsorbent layers in the adsorption device so that waste gases substantially free from gaseous hydrocarbons are discharged to atmosphere, while switching the other adsorption device to desorption operation by which gaseous hydrocarbons adsorbed in the adsorbent layers in the adsorption device are removed by a vacuum pump and transferred to a purge exhaust gas, wherein all or a major portion of the purge exhaust gas is returned to the untreated waste gases, thereby increasing the concentration of gaseous hydrocarbons in the adsorbent layers, and switching the operation from adsorption to desorption prior to the time when the adsorption device reaches break-through conditions.

20

2. The method of treating dilute gaseous hydrocarbons contained in waste gases according to claim 1, wherein the hydrocarbons in purge exhaust gas are burned when part of the hydrocarbons is liquefied or otherwise made innocuous as an industry waste.

3. The method of treating dilute gaseous hydrocarbons



contained in waste gases according to claim 1, wherein the adsorbent layers are layers of activated carbon and/or hydrophobic silica gel, over which a synthetic zeolite layer is positioned.

5

4. The method of treating dilute gaseous hydrocarbons contained in waste gases according to any one of claims 1 to 3, wherein the adsorbents filled in or to be filled in the adsorbent layers are precoated by gaseous hydrocarbons.

10

5. The method of treating dilute gaseous hydrocarbons contained in waste gases according to any one of claims 1 to 4, wherein air or liquid water heated to above the boiling point of adsorbed hydrocarbons is used for removing the gaseous hydrocarbons adsorbed in the adsorbent layers in the adsorption device.

15

6. The method of treating dilute gaseous hydrocarbons contained in waste gases according to any one of claims 1 to 5, wherein a temperature detecting port is located on top of the absorbance layers to switch the electromagnetic valve when the temperature from the temperature detecting port no longer increases.

20

7. The method of treating dilute gaseous hydrocarbons contained in waste gases according to any one of claims 1 to 5, wherein the gas flow rate at the entrance, the hydrocarbon

25



concentration in the gas at the entrance, and a desirable hydrocarbon concentration (a hypothetical value) in the gas at the exit of the absorber during adsorption operation are input into a chip as numerical data, and the switching time is set in advance using a control simulation model installed in the chip.

8. The method of treating dilute gaseous hydrocarbons contained in waste gases according to any one of claims 1 to 7, which can reduce the hydrocarbon concentration to be discharged from the adsorption device to 100 ppm or less.

9. A device for treating dilute gaseous hydrocarbons contained in waste gases using any one of the methods described in claims 1 to 8, in which the adsorption device having adsorbent layers is a component holding the adsorbent layers, and this component is a container which can be enclosed but not sealed.

10. The device for treating dilute gaseous hydrocarbons contained in waste gases according to claim 9, wherein the adsorption device having adsorbent layers is a device containing a plurality of cylinders which encircle the adsorbent layers and through which waste gases can pass in the circumferential direction.

11. The device for treating dilute gaseous hydrocarbons contained in waste gases according to claim 10, wherein the



enclosure for the adsorbent layers is a box-type component or honeycomb-type component, and the adsorption device contains multiple layers of the component.

- 5 12. The device for treating dilute gaseous hydrocarbons contained in waste gases according any one of claims 9-11, wherein the adsorbent layer is filled with an adsorbent of fine particles with a diameter of 0.1-1 mm.

10

