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(54) REMOVAL OF MALODORANTS FROM OXYGEN-CONTAINING GAS

(71) We, CALGON CORPORATION, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, of Robinson Township, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a method and product for the removal of malodorous sulfur-containing compounds from air and other gas streams containing oxygen.

The malodorous compounds whose removal is enhanced by use of the method and product of the present invention comprise those detectable by use of dynamic olfactometer devices and procedures, for example those described in *Operating and Reference Manual: Dynamic Olfactometer Model 1000*, Chicago Scientific Inc., Bensenville, Illinois (1974), or equivalent devices and procedures. A more detailed discussion of the use of such a dynamic olfactometer is set forth hereinafter. The malodorous sulfur-containing compounds whose removal is enhanced by use of the method and product of the present invention include hydrogen sulfide, mercaptans, and organic sulfides.

Malodorous compounds, especially sulfur-containing compounds, occur in a number of environments, including petroleum storage areas, sewage treatment facilities, and pulp and paper production sites. These odor-causing compounds may be bacterial breakdown products of higher organic compounds.

Hydrogen sulfide, H₂S, is a colorless gas, denser than air, with a characteristic odor of rotten eggs. The gas is produced in coal pits, gas wells, and sulfur springs, and from decaying organic matter containing sulfur. Control of emissions of this gas, particularly from municipal sewage treatment plants, has long been considered desirable. In addition to its unpleasant odor, hydrogen sulfide is not only inflammable, but is regarded as an extremely toxic substance. Consequently ways of controlling hydrogen sulfide emissions have long been sought in a number of areas, including crude oil storage, petro-chemical refining, and paper-making.

Malodorous mercaptans, also referred to as thio alcohols or thiols, may be represented by the formula R—SH, where R represents an alkyl group of from one to eight carbon atoms. The obnoxious odor of mercaptans decreases with increasing molecular weight, and is not present where R is alkyl of nine or more carbon atoms. While only methyl and ethyl mercaptan of the said mercaptans are in the form of a gas at normally encountered ambient temperatures, the mercaptans are volatile and even extremely small concentrations are detectable by humans. In addition to methyl and ethyl mercaptan, such mercaptans are, for example, *n*-propyl mercaptan and *n*-butyl mercaptan.

Malodorous organic sulfides may be represented by the formula R-S-R', where R and R' may be the same or different and are alkyl of from one to five carbon atoms, provided that the total number of carbon atoms for R and R' does not exceed eight.

Activated carbon will physically adsorb considerable quantities of hydrogen sulfide. See, for example, U.S. Patent No. 2,967,587. See also French Patent No.

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1,443,080, which describes adsorption of hydrogen sulfide directly by activated carbon, which is then regenerated by hot inert gas or superheated steam. However, it has long been recognized that much better removal can be accomplished by using the carbon to, in effect, catalyze the oxidation of hydrogen sulfide to sulfur, based on the ability of carbon to oxidize hydrogen sulfide to elemental sulfur in the presence of oxygen. For example, a conventional process uses small amounts of ammonia added to the influent gas stream containing hydrogen sulfide and oxygen to further catalyze the reaction, the oxidation of as much as 100 percent by weight of hydrogen sulfide, based on the carbon, has been reported.

Other catalytic agents to be impregnated on activated carbon for the removal of hydrogen sulfide have been suggested. See, for example, French Patent No. 1,388,453 which describes activated carbon granules impregnated with 1% iodine (I_2) for this use. South African Patent No. 70/4611 discloses the use of silicate-impregnated activated carbon. Swinarski et al., *Chem. Stosowana*, Ser. A 9(3), 287-94 (1965), (*Chemical Abstracts*, Vol. 64, 1379c), describe the use of activated carbon treated with potassium compounds, including KOH, for hydrogen sulfide adsorption.

A problem faced in the prior art in using activated carbon for hydrogen sulfide removal has been the reduction in net adsorption capacity of the activated carbon with increasing number of adsorption cycles. That is, there is an increase in the amount of residual compositions, possibly sulfur, deposited on the activated carbon, which, in turn, results in a continuing reduction in the total adsorption capacity of the activated carbon through successive adsorption cycles. South African Patent No. 70/4611, referred to above, teaches overcoming this problem with the use of silicate-impregnated activated carbon, but also teaches that extraction with alkaline solutions is ineffective to remove the residual adsorbate. Boki, in *Shikoku Zasshi*, 30 (3), 121-8 (1974) (*Chemical Abstracts*, Vol. 81, 126300p), discloses that the adsorption capacity of activated carbons used for adsorption removal of hydrogen sulfide gas can be recovered to nearly original levels by treatment with 1% NaOH. However, it is clear that these are simply attempts to overcome the problem of decreasing net adsorption. Thus, the prior art has failed to appreciate the discovery on which the present invention is based, viz. that regeneration of used activated carbon, or treatment of unused activated carbon, with NaOH and moisture under conditions also sufficient to impregnate the carbon with 0.5 to 20% by weight of NaOH and 4 to 50% by weight of moisture, can result in an activated carbon whose capacity for removing malodorous sulfur-containing compounds is increased several-fold as compared with the normally expected capacity of unused (virgin) activated carbon. When proceeding on the basis of this discovery, the character of the adsorption by the activated carbon is apparently changed from predominantly physical adsorption to predominantly chemical reaction followed by physical adsorption.

The term "moisture" as used herein means essentially pure water, and with reference to treatment of activated carbon and its presence therein, means water present within the activated carbon structure, being held therein mechanically or by physical or chemical adsorption, or by any combination of these.

In accordance with the present invention, there is provided a method of removing malodorous sulfur-containing compounds, viz. H_2S , mercaptans and organic sulfides of formula $R-S-R'$, where each of R and R' is C_{1-8} alkyl but the total number of carbon atoms in R and R' does not exceed 8, from gas streams containing oxygen, comprising contacting said gas stream with an activated carbon impregnated with from 0.5 to 20 percent by weight of NaOH and from 4 to 50 percent by weight of moisture, as hereinbefore defined, both based on weight of dry activated carbon, the activated carbon acting as an adsorbent for the sulfur-containing compounds.

The present invention also provides an activated carbon for removal of malodorous sulfur-containing compounds, viz. H_2S , mercaptans and/or organic sulfides of the above formula, and impregnated with from 0.5 to 20 percent by weight of NaOH and from 4 to 50 percent by weight of moisture as hereinbefore defined, both based on weight of dry activated carbon.

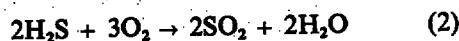
The amount of moisture present in the activated carbon that will be sufficient to produce the maximum increase in the adsorption capacity of the activated carbon for malodorous sulfur compounds, whether the activated carbon is a virgin carbon being treated initially or a loaded carbon being regenerated and impregnated, will depend on several factors, related primarily to the

characteristics of the activated carbon being treated or regenerated. Moreover, the presence of only a small amount of moisture in the NaOH-impregnated activated carbon appears to further increase the said adsorption capacity. The amount of moisture desirably present in the NaOH-impregnated carbon is from 6 to 45 percent, preferably from 10 to 40 percent by weight.

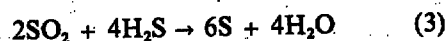
The overall reaction in which hydrogen sulfide is oxidized to elemental sulfur in the presence of activated carbon may be represented by the following equation:



However, it has been demonstrated that two other reactions can occur:



and



It has been demonstrated that the reaction (2) above is accelerated by the presence of moisture on the activated carbon. See Swinarski, A., and Siedlewski, J. *Roczniki Chemii*, 35, pp. 999-1008 (1961). It is also known that preoxidation of the carbon surface increases total hydrogen sulfide removal capacity, but at the same time also increases the proportion of sulfur oxides formed. Thus, during hydrogen sulfide removal by activated carbon, a number of potential reaction products are possible, although the primary reaction product is elemental sulfur.

The present invention is concerned both with the impregnation of unused carbon by NaOH and with the use of NaOH to regenerate activated carbon which has become loaded with, i.e., reached its efficient removal capacity for hydrogen sulfide and the other malodorous sulfur-containing compounds. The regeneration with NaOH as is already known restores the major part of the original adsorptive capacity of the spent activated carbon. However, the present invention makes use of such regeneration as a convenient method of removing adsorbate while at the same time providing a ready means of impregnation of the activated carbon with NaOH for improved adsorptive capacity for the malodorous compounds, as described hereinafter. Thus, other regeneration techniques, known in the art, might be used followed by NaOH impregnation. Such conventional regeneration techniques, useful in restoring virgin capacity prior to impregnation with NaOH and moisture, include thermal treatment and wet air oxidation.

It is well known that activated carbons used for removal of hydrogen sulfide can be regenerated for re-use by removing the adsorbed sulfur compounds, a large portion of which will be elemental sulfur when oxidizing conditions exist during the adsorption. The compounds can be removed by extracting them with a suitable organic solvent. Such materials as ammonium sulfide, carbon disulfide, xylene and toluene have proved effective regenerating media. Regeneration using ammonium sulfide as the solvent has been common. Sulfur is recovered from the solvent by distilling off the ammonium polysulfide or by steaming the solvent. Regeneration has also been accomplished using hot inert gas, superheated steam and natural gas under high pressure.

Previous regeneration methods for restoring activated carbons used to remove hydrogen sulfide suffer from a number of disadvantages. The use of organic solvents is undesirable from the standpoint of environmental pollution as well as of personnel safety, and will usually entail expensive recovery systems. Regeneration by hot gases or steam requires the expenditure of considerable amounts of energy, a clear disadvantage. A more serious detriment, perhaps, than those just discussed, is that detriment inherent in most prior activated carbons used for hydrogen sulfide removal and processes for their regeneration, which is the decrease in net adsorption capacity experienced through successive adsorption cycles. The disadvantages of these prior art activated carbons and regeneration processes have been reduced in the treatment method and resultant activated carbon of the present invention.

The treatment method and the "regeneration" method of the present invention may be regarded as essentially the same, the basic distinction being that the treatment method is performed upon virgin activated carbon, while the regeneration method is performed upon loaded activated carbon under conditions resulting in impregnation of the activated carbon with moisture and NaOH, as

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hereinafter described. Thus, the present invention includes the removal of malodorous sulfur-containing compounds where virgin-activated carbon is used initially and the loaded activated carbon resulting from removal of the said compounds is regenerated and subsequently subjected to the treatment method of the present invention. However, it is preferred to use initially an activated carbon that has been subjected to the treatment with NaOH and moisture, since the adsorption capacity of the activated carbon for malodorous compounds is thereby greatly increased.

The concentration of said malodorous compounds in the gas stream treated in accordance with the present invention is not considered critical, and concentrations resulting in as low an amount as 1.0×10^{-6} mole of the compounds passing through the activated carbon per minute can be removed by adsorption. The general effectiveness of the treated activated carbons of the present invention in removing, in particular, H_2S by adsorption has been measured in an approximate manner by establishing the time required to arrive at a breakthrough concentration of 50 parts per million by volume of H_2S in the gas passing out of the activated carbon. Such a concentration of H_2S in the outlet gas after adsorption treatment has been considered, for convenience, as indicative of nearly complete loading of the activated carbon. For methyl mercaptan, loading capacity as percent by weight of adsorbate based on weight of activated carbon, for various breakthrough levels, has been determined to establish the effectiveness of the treated activated carbons of the present invention. Enhanced removal capacity is shown by comparative determinations using virgin activated carbon.

The effectiveness of removal of malodorant compositions generally, using the treated activated carbons of the present invention, has been measured by means of a dynamic olfactometer. Such a device, and details of how to use it, are available from Chicago Scientific Inc. Other equivalent devices may be used. Basically, a dynamic olfactometer uses the human olfactory system in the form of an odor panel to perform a subjective evaluation of the odorant level. This subjective evaluation may then on the basis of statistical considerations, be used to establish an objective quantification of the odorant level. The resultant determinations serve as a basis for the detection of odors, and thus for ascertaining removal efficiencies. The test facilities include an odor evaluation room provided with odor-free air. The dynamic olfactometer device provides a stream of deodorized air at a known flow rate to an observer, with an odorant or known concentration being slowly added in ever-increasing concentrations until detected by the observer. This is the sensory perception (odor) threshold for that observer. An odor panel is then selected by screening procedures which include testing with known odorants. A sample of air to be examined for malodorant compositions is then introduced in the same manner as with the known (standard) odorant until odor perception again occurs. In addition, evaluation of the air stream containing malodorant compositions, which are of unknown make-up, is normalized by comparison with a known odorant used as standard. Results are expressed in odor units (O.U.), which represent the ratio of the volume of total air flow to the volume of malodorant (or odorant) composition air flow in the dynamic olfactometer.

The physical and chemical makeup of the gas stream from which it is desired to remove malodorant compositions, especially H_2S and other malodorous sulfur compounds, is not critical, provided that the gas contains oxygen. Typically, the malodorous compounds will be removed from air, especially from air admixed with effluent gas streams resulting from municipal waste treatment facilities, petrochemical refining plants, and so forth. The oxygen may be in very small amounts, but usually will be in an amount of at least 5 percent by volume, preferably 10 percent by volume, and particularly at least 15 percent by volume. The required oxygen content is derived most readily from air, if air comprises a sufficient portion of the gas stream being treated to provide a necessary amount of oxygen. The oxygen may, of course, be independently introduced into the gas stream being treated, if oxygen is totally absent or present in insufficient amounts. As will be appreciated, the amount of oxygen required for maximum malodorous compound adsorption in accordance with the present invention will depend on a number of factors, including the concentration and absolute amount of any one or more the malodorous compounds, especially sulfur compounds, being adsorbed from the gas stream being treated.

As is recognized, the amount of malodorant composition, especially hydrogen sulfide or other malodorous sulfur compound, adsorbed by any particular activated carbon will be a function of at least the following factors: basic degree of

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attraction of the activated carbon for the particular malodorous compound; the pore structure of the activated carbon, particularly with respect to size; the specific surface area of the activated carbon; and the surface characteristics of the activated carbon. A suitable activated carbon starting material can readily be selected. For example, it will be preferred to use an activated carbon whose pores have diameters falling, for the most part, in the range from 10 to 80 Å. It has been found particularly important to use activated carbons having high surface areas. Thus it is preferred to use BPL granular activated carbon for vapor phase applications, manufactured by the Pittsburgh Activated Carbon Company, Pittsburgh, Pennsylvania. Granular activated carbon is preferred to powder, and the size range of the granules is largely a matter of choice, although granules falling between Nos. 4 and 10 of the U.S. Sieve Series are preferred. It has also been found that flow rates of the gas stream being treated through the bed of activated carbon especially affect the breakthrough capacities of the activated carbon, as will be shown in more detail hereinafter.

The NaOH treatment of the activated carbon starting material may be carried out in any manner which effectively impregnates the activated carbon with from 0.5 percent to 20 percent by weight of NaOH, based on weight of dry activated carbon. The preferred amount of NaOH impregnated is from 1.0 to 15 and particularly from 5 to 10 percent by weight of the activated carbon. The NaOH treatment may be carried out simply by soaking the virgin or loaded activated carbon in its own volume of aqueous NaOH solution of from 5 to 60% by weight concentration. The time required to produce the required impregnation levels as described above is dependent approximately on the concentration of the NaOH solution used, and will only be as much time as is needed for the NaOH solution to penetrate the activated carbon. For example, it has been found that the BPL activated carbon is effectively impregnated in accordance with the present invention when it is soaked in its own volume of 4.8 percent by weight NaOH for only a few minutes. It will be understood that using NaOH for regeneration alone, as opposed to impregnation, requires substantially longer periods of time, as described hereinafter. These times will also tend to be dependent upon the concentration of the NaOH solution used. Other methods of impregnating the activated carbon starting material with the required quantities of NaOH and moisture can be used. For example, the NaOH solution may be passed through the activated carbon rather than being used in a static immersion treatment. However, it has been found that a preferred method of NaOH impregnation is by spray-addition in which a NaOH solution is sprayed onto the granular activated carbon being tumbled in a mixer. This method of impregnation will be described in more particular detail hereinafter.

While the NaOH regeneration of the loaded activated carbon restores the activated carbon essentially to its adsorption capacity as virgin activated carbon, it has been discovered that the presence of moisture in the activated carbon, in association with the impregnated NaOH, results in an activated carbon whose adsorption capacity for malodorous compositions, especially H₂S and other sulfur compounds, is increased as much as tenfold over the adsorption capacity of virgin activated carbon for the malodorous compounds. While the presence of moisture in virgin activated carbon effects a substantial increase in the total malodorous compound adsorption capacity of the activated carbon, as compared to dry, that is, moisture-free virgin activated carbon, the overall effect produced by combining NaOH and moisture in treatment of activated carbon, is a synergistic one, as will be demonstrated hereinafter.

The desired moisture content of the activated carbon in accordance with this invention is readily obtained by using moist air during the drying step following NaOH impregnation. Drying with air having a relative humidity of from 50 to somewhat less than 100 percent has been found sufficient to introduce the desired amount of moisture. However, moisture should not be introduced to the extent that the carbon becomes wet. Other methods of introducing the desired amount of moisture will readily suggest themselves.

The NaOH-and-moisture-impregnated activated carbons of the present invention possess advantages over ordinary activated carbons in addition to enhanced adsorptive capacity for malodorous compositions. For example, the NaOH-impregnated activated carbon can prevent the accumulation of slime on the activated carbon, thus preventing interference by the slime with its function through blocking of the activated carbon pores. And the NaOH-and-moisture-impregnated activated carbons of the present invention do not require water

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scrubbing prior to use in odor control applications, which is the case for ordinary activated carbons preparatory to such use.

The NaOH and moisture impregnated activated carbons of the present invention may, of course, be used alone in beds for the removal of malodorous compositions, including H_2S and other malodorous sulfur compounds. However, they may be advantageously used together with beds containing other activated carbons, including ordinary virgin activated carbon, as well as activated carbons impregnated with various catalytic materials. Various combinations of bed arrangements may be used. Thus, for example, a bed of ordinary virgin activated carbon may be used together with a bed of the NaOH-and-moisture-impregnated activated carbon of the present invention, either upstream (i.e., before the bed of NaOH and moisture impregnated activated carbon with respect to the effluent gas being treated) or downstream thereof.

The following examples, which include comparative data, will serve to better illustrate the treatment and regeneration methods of the present invention and the dramatic increase in malodorous-sulfur-compound-adsorption capacity produced thereby.

EXAMPLE 1.

15 ml (6.55 g.) of dry virgin 4×10 BPL activated carbon was exposed to moisture and then used to remove H_2S from a gas stream. The H_2S mass flow was 2.26×10^{-4} moles/min. The H_2S concentration of the outflow gas was monitored and the time elapsed after commencement of the sample run at which the H_2S concentration level reached 50 parts per million by volume of the outflow gas was recorded. Once this level was reached, the activated carbon was considered loaded and regeneration with subsequent impregnation was carried out. The original activated carbon sample was run through a total of 10 cycles of loading, regeneration and impregnation, during which the regeneration/impregnation procedures were varied. The NaOH was used throughout at a concentration of 33.3% by weight. It was found that the repeated regeneration procedures produced a constant "heel", or residual adsorbate, of 2.5—2.75% sulfur in the activated carbon. The details of the various regeneration procedures, as well as the results, are set out in the following table of data.

TABLE I

H₂S Adsorption and Caustic Regeneration on 4×10 BPL Carbon

Cycle No.	Carbon Pretreatment	Weight Pickup of Carbon After Pretreatment	Breakthrough Time to 50 ppm	% Loading of H ₂ S
1	Virgin carbon exposed to moisture	0.4 g. of H ₂ O	86 min.	9.5 wt-%
2	22.5-Hr. caustic wash with 7 bv* of 33.3 wt-% NaOH followed by water wash to reduce pH followed by air-drying for one hour (10 l/min)	0.35 g. of H ₂ O & residual S	202 min.	22.4 wt-%
3	15-Hr. soak in one bv of 33.3 wt-% NaOH followed by water wash to reduce pH followed by air-drying for 2 hrs. (10 l/min)	<0.25 g. of H ₂ O & residual S	110 min.	12.2 wt-%
4	Same procedure as cycle 3	<0.25 g. of H ₂ O & residual S	120 min.	13.3 wt-%
5	Same procedure as cycle 3	<0.25 g. of H ₂ O & residual S	111 min.	12.3 wt-%
6	Same procedure as cycle 3 with longer air-drying (3 hrs. at 10 l/min.)	<0.15 g. of H ₂ O & residual S	20 min.	2.2 wt-%
7	Same procedure as cycle 3 followed by exposure to air (100% RH at 25°C.) for 2 hrs. (10 l/min)	2.30 g. of H ₂ O & residual S	195 min.	21.6 wt-%
8	62-Hr. exposure to one bv of 33.3 wt-% NaOH followed by water wash to reduce pH followed by N ₂ drying followed by exposure to N ₂ (100% RH at 25°C.) for 2 hrs. (10 l/min)	2.15 g. of H ₂ O & residual S	120 min.	13.3 wt-%
9	15-Hr. exposure to one bv of 33.3 wt-% NaOH followed by draining followed by air-drying followed by exposure to air (100% RH at 25°C.) for 30 min. (10 l/min)	6.85 g. of H ₂ O & residual S & residual NaOH	130 min.	14.4 wt-%
10	Same procedure as cycle 9	„	135 min.	14.9 wt-%

* bv=bed volume.

EXAMPLE 2.

The procedures of Example 1 above were repeated, but using NaOH at 4.8% by weight concentration. In addition, the dry virgin activated carbon sample was used to remove H₂S without prior exposure to moisture; and a loaded sample regenerated/impregnated in accordance with this invention was used to remove H₂S from a gas stream containing no oxygen. The details of the various regeneration/impregnation procedures and the results thereof, as well as of the additional samples described, are set out in the following table of data:

TABLE II

Cycle No.	Carbon Pretreatment	Weight Pickup	Breakthrough Time	% H ₂ S Loading
1-A	Virgin carbon exposed to air (100% RH at 25°C.) for 4 hrs. (10 l/min)	2.60 g. of H ₂ O	85 min.	9.4 wt-%
2-A	15-Hr. soak in one bv of 4.8 wt-% NaOH followed by water wash to reduce pH, followed by air-drying for 2 hrs. (10 l/min), followed by exposure to air (100% RH at 25°C.) for 2 hrs. (10 l/min)	2.85 g. of H ₂ O & residual S	152 min.	16.8 wt-%
3-A	Same procedure as cycle 2-A	2.90 g. of H ₂ O & residual S	145 min.	16.0 wt-%
4-A	68-Hr. soak in one bv of 4.8 wt-% NaOH followed by water wash to reduce pH, followed by air-drying for 2 hrs. (10 l/min), followed by exposure to air (100% RH at 25°C.) for 2 hrs. (10 l/min)	3.0 g. of H ₂ O & residual S	155 min.	17.2 wt-%
5-A	15-Hr. soak in one bv of 4.8 wt-% NaOH followed by draining followed by air-drying (90% RH at 25°C.) for 2 hrs. (10 l/min)	3.75 g. of H ₂ O & residual S & residual NaOH	208 min.	23.0 wt-%
6-A	15-Hr. soak in one bv of 4.8 wt-% NaOH followed by draining followed by N ₂ drying (90% RH at 25°C.) for 2 hrs. (10 l/min)	3.6 g. of H ₂ O & residual S & residual NaOH	40 min. (No O ₂ in adsorbing gas stream)	4.4 wt-%
1-B	Virgin carbon	0.0 g.	18 min. (No O ₂ in adsorbing gas stream)	2.0 wt-%

The results of the above procedures whereby activated carbon is impregnated with NaOH and moisture and used to remove H₂S from a gas stream, when compared to the removal efficiency, that is, the break-through time or percent H₂S loading, of dry or moist virgin activated carbon not impregnated with NaOH, and of NaOH-impregnated activated carbon in the absence of moisture, make it clear that the combined presence of NaOH and moisture in the activated carbon results in a ten-fold increase in the H₂S removal efficiency of the activated carbon of the present invention.

EXAMPLE 3.

Experiments were carried out to determine the effect of mesh size, column size and flow rate on the H₂S removal efficiency of NaOH and moisture impregnated activated carbon. BPL activated carbon of 4 x 10 and 12 x 30 mesh was used that had been impregnated with 5% by weight of NaOH and then exposed to an 80% R.H. air stream to introduce moisture, in the amount of 18.75% by weight, into the carbon. Pure H₂S gas was diluted to 1.0% by volume with air that had been preconditioned with moisture to 80% R.H. Air flow rates were monitored by meter and the concentration of H₂S adjusted to 1.0% by comparison with a calibration standard. Breakthrough to 1 ppm of H₂S was determined using detector tubes sensitive in the 1-50 ppm range, available from Mine Safety Appliances Company, Pittsburgh, Pennsylvania. Two columns, 2.3 and 0.74 inches in diameter, were used, and flow rates of 10 and 100 linear feet per minute were maintained. The results of the investigation, showing the effect of flow rate, are illustrated in the following table of values.

TABLE III

Experiment No.	Column Diameter (in.)	Mesh Size	Flow Rate (ft./min.)	Breakthrough Time (hr.)	Weight Percent H ₂ S Loading to Breakthrough
1	2.3	4x10	100	7.5x10 ⁻²	2.80
2	..	12x30	10	7.97	30.1
3	0.74	12x30	100	3.4x10 ⁻¹	12.7
4	..	4x10	10	7.1	24.8

The values obtained show that flow rate, but not mesh size or column diameter, is an important parameter to be considered in designing adsorption systems in accordance with the present invention.

EXAMPLE 4.

Samples of virgin BPL activated carbon, BPL impregnated with 5% by weight NaOH and 8.3% by weight moisture, and BPL regenerated and impregnated with 5% by weight NaOH and 8.3% by weight moisture, all 4 x 10 mesh, were used to determine their respective adsorptive capacities for methyl mercaptan. The testing was carried out in a continuous flow system in which the column consisted of a 19 mm diameter glass column. The sample charge was 10 cc which resulted in a bed height of 72 mm. The weight of the sample charge was 4.6 g. for the virgin BPL and 5.4 g. for the 5% NaOH impregnated BPL containing 8.3% moisture. A gas mixture containing 1.3% methyl mercaptan, 10% oxygen and the balance nitrogen was passed downstream through the bed at a space velocity of 3000 bed volumes per hour. The methyl mercaptan content of the inlet and outlet gas stream was analysed by gas chromatography. All tests were run at ambient temperature and pressure. The regenerated and impregnated sample was obtained from NaOH impregnated BPL activated carbon (5% by weight) that had been previously loaded to 10% of influent (0.13% by volume) breakthrough during methyl mercaptan adsorption. The loaded carbon was regenerated with 2 bed volumes of 5% NaOH solution, drained, and then air dried at room temperature until essentially the original weight of impregnated carbon was obtained. The results of the evaluation are illustrated in the table of values below.

TABLE IV

Methyl Mercaptan Breakthrough: % of Influent	Methyl Mercaptan Adsorption: % by Wt.		
	Virgin BPL	NaOH Impregnated BPL	Regenerated and NaOH Impregnated BPL
2%	4.08	9.49	5.29
10%	6.45	16.70	9.61

EXAMPLE 5.

A preferred method of impregnating activated carbon with NaOH and moisture is by the spray-addition technique. In accordance with this method a 33% by weight aqueous solution of NaOH was sprayed onto 4 x 10 BPL activated carbon while it was being moved about in a Homart mixer. The amount of NaOH solution was chosen to provide 5% by weight of NaOH and 10% by weight of moisture in the final product. Four spray times ranging from 5.5 to 23 minutes were used in different treatments. However, subsequent performance evaluations failed to point up any distinction among the final products resulting from the differing spray times. No drying step was required.

EXAMPLE 6.

A NaOH and moisture impregnated activated carbon prepared in accordance with the procedures described in Example 2 above, but so as to contain 5% NaOH and about 12% moisture in the impregnated activated carbon, was employed to remove H₂S from vacuum filter air at an operating sewage treatment plant. For purposes of comparison, a bed of virgin BPL activated carbon was employed in the same manner. The activated carbon beds were 4 inches in diameter and 6 inches in depth. The adsorber system was attached to a slip stream on the vacuum filter exhaust. Air from the exhaust was routed through a water knockout pot and a blower prior to being split into individual streams. The flow rate for the influent gas, i.e., the vacuum filter air, was maintained at 8 cubic feet per minute for each bed. The influent gas was passed downflow through the activated carbon beds and exhausted through 1-inch ball valves and rotometers. Influent gas was sampled by means of a valve installed upstream of the adsorbers. The influent and effluent concentrations of H₂S were measured by means of Mine Safety Appliances Company H₂S detector tubes sensitive in the 1—50 ppm range, and recorded. The results of these evaluations are illustrated in the table of values below.

TABLE V

H₂S Adsorption from Sewage Treatment Plant Vacuum Filter Air

Elapsed Time (Hrs.)	H ₂ S Inlet Concentration (p.p.m.)	H ₂ S Effluent Concentration (p.p.m.)	
		NaOH and Moisture Impregnated Activated Carbon	BPL Activated Carbon
202.9	3	0	0
243.1	5	0	0
306.6	40	0	1
339.8	2	0	0
408.3	5	0	1
477.2	5	0	1
560.9	20	0	5
608.5	5	0	2
686.3	7	0	2
806.5	5	0	Failed*
1067.6	6	0	
1217.2	20	1	
1449.0	12	1	
1577.0	5	0	

* Bed ceased to function due to occlusion of activated carbon granules by microorganism deposits.

EXAMPLE 7.

The removal efficiency of NaOH and moisture impregnated activated carbon for malodorant compositions generally was evaluated by means of a dynamic olfactometer as previously described. The impregnated activated carbon was prepared as described above in Example 2, but so as to contain 5% NaOH and about 12% moisture in the impregnated activated carbon. For purposes of comparison, a bed of virgin BPL activated carbon was used in the same manner. A model 1000 dynamic olfactometer from Chicago Scientific, Inc. was used. Overall, the evaluation system was set up as described above in Example 6. The mean H₂S level in the influent air was determined to be 5.8 ppm. This value, together with the laboratory odor threshold value for H₂S permitted calculation of the H₂S contribution to the total inlet odor. This contribution was determined to be 830 odor units (O.U.) in a gas stream having a mean odor level of 5500 O.U. Thus, other malodorous compositions made a significant contribution to the total odor level. Gas chromatographic analysis revealed the presence of at least 25 compounds in addition to H₂S in the influent gas.

The odor panel was selected on the basis of screening with known odorants consisting of CH₃NH₂, H₂S, CH₃SH and (CH₃)₂S₂, and mixtures thereof. The mean standard deviation and percent standard deviation/mean were determined and utilized in selection of members of the odor panel. At least three members of the odor panel were employed for any evaluation. Odor response data was analysed by least squares linear regression analysis of the log of the odor level (expressed in odor units) versus a linearized expression of the normal probability function. Odor thresholds were determined from the linear regression curve by choosing the odor

level at which 50% of the odor panel participants were able to detect the odor. The calculated odor levels emanating from each adsorber were compared to the influent odor levels and expressed as "% odor removal" on a day to day basis. Trend analysis was conducted by plotting the log "% odor removal" versus "time" and linear regression analysis was conducted on this data. Correlation coefficients in all instances indicated that the curve fitting procedure was a reliable representation of the data to the 99.9% confidence level.

The results of these evaluations are illustrated in the following table of values.

TABLE VI

Elapsed Time (Hrs.)	Inlet Odor (O.U.)	Effluent Odor (O.U.)*	
		NaOH and Moisture Impregnated Activated Carbon	BPL Activated Carbon
94.1	2350	5.1	16.8
182.2	5151	25	34
325.1	5750	231	377
408.3	6050	130	235
528.8	2201	74	221
608.5	5401	271	1080
752.8	2261	229	453
875.2	1314	209	**
944.7	2814	281	
1067.6	>11,000	2676	
1217.2	2726	1363	
1341.0	5501	1101	
1449.4	1351	541	
1577.0	10,801	2161	

* O.U.=odor units.

** Bed ceased to function due to occlusion of activated carbon granules by microorganism deposits.

WHAT WE CLAIM IS:—

1. A method of removing malodorous sulfur-containing compounds, viz. H_2S , mercaptans and organic sulfides of formula $R-S-R'$, where each of R and R' is C_{1-8} alkyl but the total number of carbon atoms in R and R' does not exceed 8, from gas streams containing oxygen, comprising contacting said gas stream with an activated carbon impregnated with from 0.5 to 20 percent by weight of NaOH and from 4 to 50 percent by weight of moisture, as hereinbefore defined, both based on weight of dry activated carbon, the activated carbon acting as an adsorbent for the sulfur-containing compounds.

2. A method as claimed in Claim 1, in which the activated carbon is impregnated with from 5 to 10 percent by weight of NaOH and from 10 to 40 percent by weight of moisture, both based on weight of dry activated carbon.

3. A method as claimed in Claim 1 or 2 including the additional step of using NaOH to regenerate the activated carbon under conditions sufficient to also subsequently impregnate the activated carbon with NaOH and moisture in the amounts set forth in Claim 1 or 2.



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level at which 50% of the odor panel participants were able to detect the odor. The calculated odor levels emanating from each adsorber were compared to the influent odor levels and expressed as "% odor removal" on a day to day basis. Trend analysis was conducted by plotting the log "% odor removal" versus "time" and linear regression analysis was conducted on this data. Correlation coefficients in all instances indicated that the curve fitting procedure was a reliable representation of the data to the 99.9% confidence level.

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1. A method of removing malodorous sulfur-containing compounds, viz. H_2S , mercaptans and organic sulfides of formula $R-S-R'$, where each of R and R' is C_{1-8} alkyl but the total number of carbon atoms in R and R' does not exceed 8, from gas streams containing oxygen, comprising contacting said gas stream with an activated carbon impregnated with from 0.5 to 20 percent by weight of NaOH and from 4 to 50 percent by weight of moisture, as hereinbefore defined, both based on weight of dry activated carbon, the activated carbon acting as an adsorbent for the sulfur-containing compounds.

2. A method as claimed in Claim 1, in which the activated carbon is impregnated with from 5 to 10 percent by weight of NaOH and from 10 to 40 percent by weight of moisture, both based on weight of dry activated carbon.

3. A method as claimed in Claim 1 or 2 including the additional step of using NaOH to regenerate the activated carbon under conditions sufficient to also subsequently impregnate the activated carbon with NaOH and moisture in the amounts set forth in Claim 1 or 2.

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4. A method as claimed in Claim 1, 2 or 3, in which the malodorous sulfur-containing compound removed is methyl mercaptan.

5. An activated carbon for removal of malodorous sulfur-containing compounds, viz. H_2S , mercaptans and organic sulfides of the formula set forth in Claim 1, and impregnated with from 0.5 to 20 percent by weight of NaOH and from 4 to 50 percent by weight of moisture, as hereinbefore defined, both based on weight of dry activated carbon.

6. An activated carbon as claimed in Claim 5 with from 5 to 10 percent by weight of NaOH and from 10 to 40 percent by weight of moisture, both based on weight of dry activated carbon.

7. A method as claimed in Claim 1, substantially as hereinbefore described in any appropriate Example.

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