Removing Phosphine Gas in Air using Non-Impregnated Centaur® Activated Carbon

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Activated carbons containing selected metal impregnants have been used for the catalytic destruction and removal of a variety of volatile contaminants from air. Although the metal impregnated activated carbons are effective, the cost of disposal, and handling of the spent carbon, can be undesirable. Calgon Carbon Corp. has developed a new, unique activated carbon, Centaur®, which exhibits catalytic adsorption properties without metal impregnation.

Centaur can be used in many industrial applications where both physical adsorption and chemical conversion of the adsorbed contaminants are required to achieve treatment objectives.

Centaur is a bituminous coal- based activated carbon which has been specifically manufactured to enhance surface reactivity. The modified electronic character of the carbon surface is able to promote oxidation/reduction, combination/elimination, and other decomposition reactions quickly and efficiently without metal impregnation.

The removal of Phosphine from air following the fumigation of agricultural storage facilities, is one industrial application for which Centaur® Activated carbon has been found to be very effective. The removal of phosphine from air is accomplished by the decomposition of physically adsorbed phosphine, to non-toxic, strongly adsorbing phosphorus compounds via the following oxidation/reduction reactions:

$PH_3 + 2O_2 \rightarrow H_3PO_4$ (ortho phosphoric acid)

$2\,PH3 + 3O_2 \rightarrow 2H_3PO_3$ (ortho phosphorus acid)

$x\,PH_3 + 2x\,O_2 \rightarrow (HPO_3)_x + x\,H_2O$ (meta phosphoric acid)

$2x\,PH_3 + 3x\,O_2 \rightarrow (HPO_2)_{2x} + 2x\,H_2O$ (meta phosphorus acid)

A laboratory test was conducted to determine the thermodynamic capacity as well as the kinetic performance of Centaur® activated carbon for the removal of phosphine from humid air. A 25° C air stream containing 500 ppmv phosphine and 80% relative humidity was passed down flow through the Centaur activated carbon bed at a flow rate of 56.3 L/Min., equal to a linear velocity of 100 FPM. The total bed depth was separated into segments, as shown in Figure 1, to allow the measurement of the phosphine concentration throughout the 44" total carbon bed depth.

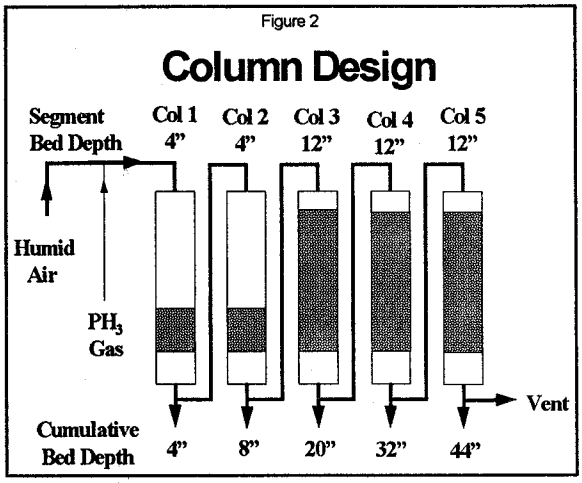

Figure 1

In essence, the segmented column design provided a test system which resulted in five phosphine breakthrough curves at different carbon bed depths at the completion of a single 43 hour test run. (See Figure 2).

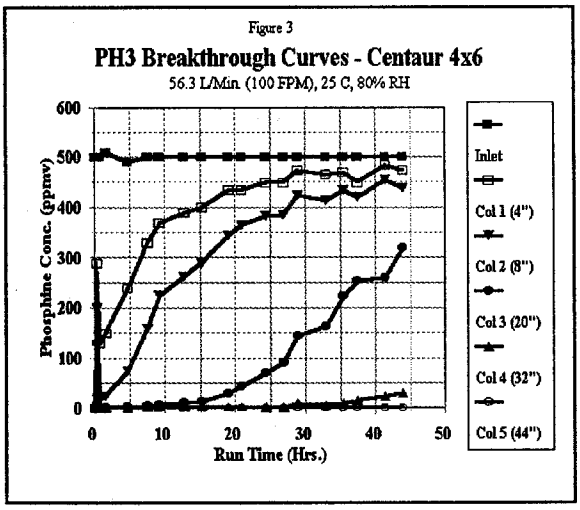

Figure 2

At approximately 30 minutes into the test run, a short-lived spike in phosphine concentration was observed in the effluent of each of the five column segments. This characteristic event, found only when beginning the operation of a virgin carbon system, has been defined as the "induction period." After 60 minutes run time, the effluent concentrations had decreased to much lower levels, and a steady state rate of removal was maintained throughout the remaining 42 hours of operation. It is believed that the induction period, a period during which the reaction rate for the decomposition of phosphine is greatly retarded, is caused by the initial slower formation of reaction intermediates, such as the P-O-P linkage of the meta phosphorus compounds.

The phosphine concentration profile through the carbon bed (Figure 2) indicates the steady state reaction/removal zone extends just beyond the 20" bed depth, equivalent to an empty bed contact time (EBCT) of 1.25 secs. Integration of the area above the breakthrough curves indicate a saturation loading of 16 wt.%, expressed as phosphine, was achieved on the Centaur activated carbon.

At the conclusion of the performance test the spent activated carbon was recovered from each column segment and analyzed to determine the reaction products adsorbed in the carbon pore structure. TG/FTIR (Thermogravimetric/Fourier transform infrared) indicated the absence of unreacted phosphine on the spent carbon, but did not reveal information concerning the molecular structure of the adsorbed phosphorus compounds.

The general composition of the spent carbon

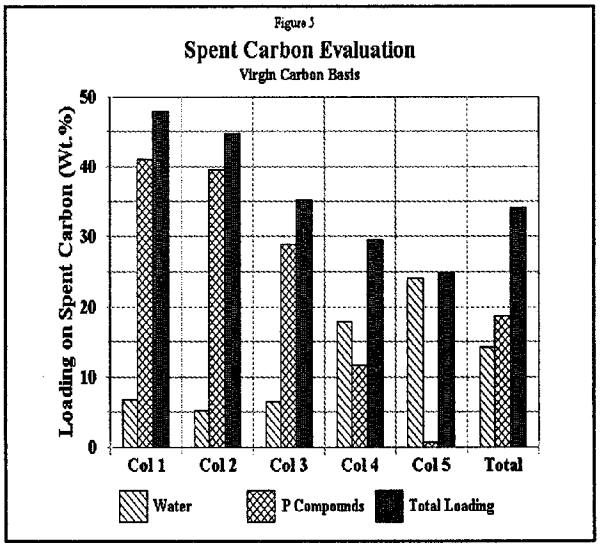

Figure 3

removed from each column segment was successfully determined gravimetrically (Figure 3). The spent carbon removed from the subsequent column segments revealed gradually diminishing loadings of phosphorus compounds. Knowing that each mole of phosphine removed in the carbon bed must generate 1 mole of phosphorus-containing compounds, it was determined that the average molecular weight of the phosphorus degradation products is 77 g/mole. Comparing this to the molecular weight of the phosphine reaction products which should be present, it is apparent that a relatively even mixture of the reaction products yield an acceptable mass balance accounting for the contaminant loading found on the spent carbon (Figure 4).

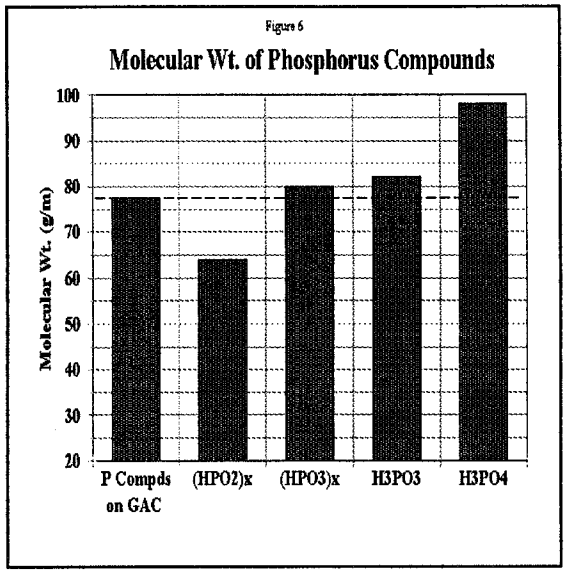

Figure 4

The above mass balance analysis is further supported by additional analyses conducted on soxhlet water extracts on the spent activated carbon as well as equilibrium solubility tests. Soxhlet water extracts, which were analyzed both by ion chromatography and ASTM D515-82 for ortho phosphate and total phosphorus, indicate the spent carbon contains a near 50/50 mixture of phosphite and phosphate ions. The equilibrium soak tests conducted on several spent carbon samples revealed that up to 40% of the initial phosphorus loading is very insoluble, consistent with the presence of the meta forms of both phosphorus and phosphoric acids existing on the spent carbon.

In final summation, the test results presented here indicate the removal and control of phosphine from air can be safely and efficiently accomplished using the catalytic enhanced Centaur activated carbon. The decomposition of the phosphine on the carbon surface to non-toxic, strongly adsorbed phosphorus compounds, results in high contaminant capacity, rapid removal kinetics, and the ability to achieve phosphine discharge concentrations below 1 ppmv. The absence of metal catalyst impregnants allows the spent activated carbon to be classified as non-hazardous, increasing the options available for disposal or thermal regeneration of the spent activated carbon.