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ROOM TEMPERATURE CATALYST FOR IMPROVED INDOOR AIR QUALITY

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ABSTRACT

Solutions to problems of indoor air pollution have been confined to dilution by increased ventilation, filtration to control particulate concentrations, and masking or adsorbing objectionable odors. Hazardous gases from combustion exhaust, chemical cleaning or processing, and personal smoking habits are receiving increased study; however, practical methods of removal have not been available. Teledyne Water Pik has developed an innovative patented catalyst for removal of various noxious/toxic gaseous pollutants: carbon monoxide, ozone, oxides of sulfur and nitrogen, hydrogen sulfide, and as well as combustion gases and products of cigarette smoke. Three mechanisms of removal have been identified--catalytic oxidation, chemisorption, and chemical reaction. The superior performance of the Low Temperature Catalyst (LTC) is due to a high rate of activity over wide ranges of temperature and relative humidity. Only brief contact times are required. LTC has been incorporated into a portable air cleaner appliance designed to remove particulate, odors, and hazardous gases at room temperature.

INTRODUCTION

Since the sharp increases in oil prices of 1974, residents have been tightening up their homes to save energy. The conventional home exchanged the indoor air completely several times per hour. Today, energy efficient homes have one air exchange or so every five hours. Furthermore, because of increased cost, consumers now use alternative heating methods such as kerosene heaters, fireplace inserts, and woodburning stoves; all of which contribute to the accumulation of pollutants in a well-sealed house. Other well-known sources such as cigarettes, gas stoves, water heaters, furnaces, solvents, and pets, create the overall problem--indoor air pollution.

People spend 90 percent of their time indoors; 70 percent in residential and office environments. Indoor concentrations of some pollutants reach levels several times higher than the outside exposure limit established by the E.P.A. Teledyne Water Pik has been researching indoor air pollution for several years and has recently introduced a line of products that addresses all aspects of the problem--particulates, odors, and toxic/noxious gases.

An innovative patented catalyst has been developed for removal of hazardous gaseous pollutants. The LTC has good activity against carbon monoxide, ozone, oxides of sulfur and nitrogen, hydrogen sulfide, and other gases. Significant activity is achieved throughout broad ranges of temperature and relative humidity.

LTC CATALYST REACTION MECHANISM

Generally, the LTC is composed of copper chloride with small amounts of palladium chloride; a second copper salt has been added for stabilization of the active metal complex. This composition is supported on porous alumina, and exhibits some of the characteristics of both heterogeneous and homogeneous catalysis.[1] A certain minimum amount of water is necessary for reasonable catalytic efficiency.

Analogy to the well-known Wacker commercial process gives the following simplified reaction sequence:

$$C \equiv O + Pd^{II}Cl_2 \cdot 2H_2O \longrightarrow CO_2 + Pd^0 + 2HCl + H_2O \qquad (1)$$

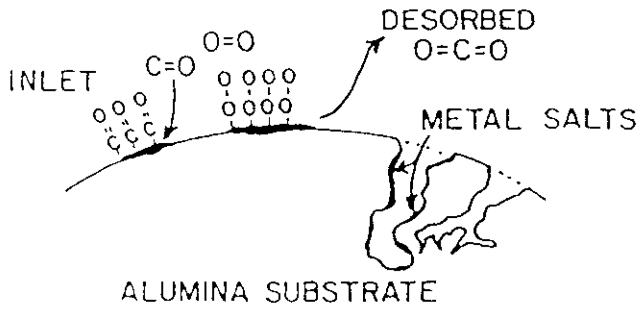
$$Pd^0 + (CU^{II}Cl_2)_2 \cdot 2H_2O \rightarrow Pd^{II}Cl_2 \cdot 2H_2O + Cu_2^ICl_2 \qquad (2)$$

$$Cu_2^ICl_2 + 2HCl + H_2O + 1/2\ O_2 \longrightarrow 2(Cu^{II}Cl_2) \cdot 2H_2O \qquad (3)$$

$$\text{Summary:} \quad C \equiv O + 1/2(O{=}O) \rightarrow O = C = O \qquad (4)$$

Research has suggested that gaseous CO bonds to an activated metal complex in solution[2,3], in addition to chemisorption of CO and O_2 gases on the active metallic surface sites. A diagram of the catalysis morphology is shown in Figure 1.

FIGURE 1



THIN FILM OF WATER AIDS SPECIES MOBILITY

Sites for chemisorption appear to be somewhat selective; thus discrete "islands" of oxygen and carbon monoxide are created. CO adsorption to the metallic surfaces occurs mainly through bridge-bonding to two metal atoms, with a lesser number of linearly-bonded molecules.[4] The considerable surface area of the large alumina pores collect most of the active metal deposits. After reaction and desorption of the carbon dioxide product, the metallic palladium is oxidized to its beginning state of Pd^{II}. The rate of catalytic activity and overall lifetime depend on a continuous cycle of oxidation/reduction between the metals.

PERFORMANCE TEST PROTOCOL

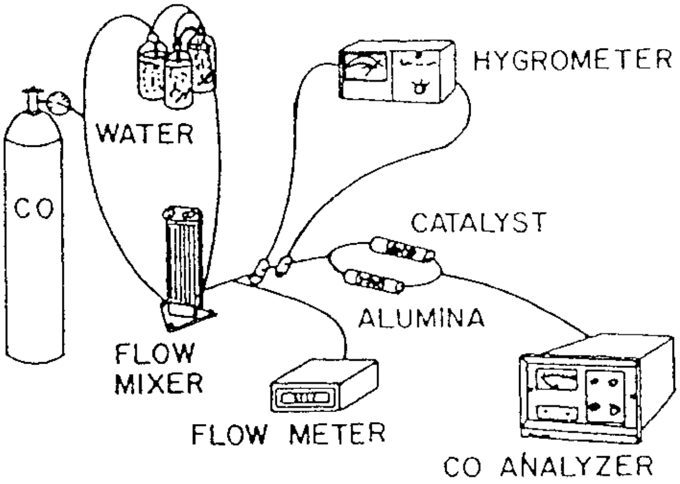
Tube Test

A diagram of one of the catalyst performance tests is shown in Figure 2. This tube test subjects about one gram of catalyst to a feed gas of known composition at ambient temperature and chosen relative humidity. Beads of catalyst are packed tightly into a tube, held in place with plugs of glass wool to prevent channeling of the gas stream. CO detection is ± 0.5 ppm by infrared adsorption. Typical feed gas is 50 ppm CO at 60 percent relative humidity, with a flow rate of 500 cc/minute. Performance is reported as a percentage of the original contaminant concentration (C_0) over six hours. It is therefore dependent on the catalyst bed configuration (indicated by the contact time), length of test, and the beginning concentration, C_0. These variables are related as follows:

$$\ln \left(\frac{C_0}{C_t}\right) = K \cdot t_c \qquad (5)$$

Where C_t is the contaminant concentration after time t, C_0 is the initial concentration, K is the reaction rate of the LTC, and t_c is the contact time. K is characteristic of the material, and thus independent of the test procedure.

FIGURE 2: TUBE TEST



Room Test

A second performance test monitors the catalyst's ability to remove contaminants according to the air cleaner product specifications. Filters of one square foot area containing about 300 grams of LTC were challenged with various gases. A filter is mounted in a duct or in the product itself, and removal rates measured in a 1152 cubic foot sealed room. Air flow rates of 250 or 300 cfm were maintained through the filters for two hours. The per pass efficiency of the filter in a sealed room may be calculated using:

$$C_t = C_o \cdot \exp\left(-\frac{FE}{V}t\right) \tag{6}$$

Where F is the flow rate (cfm), V is the room volume, and E is the per pass efficiency.

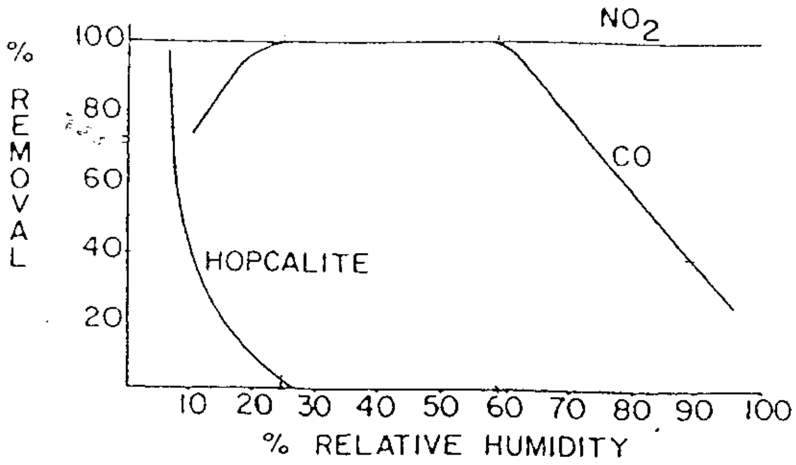
TUBE TEST RATES OF REMOVAL

Relative Humidity Dependence

Test results indicate a thin surface film of water exists on the alumina, providing a solution media. Inadequate water fixes the chemisorbed reactants to their respective "islands", causing catalytic oxidation to decrease sharply. Very high moisture content in the feed gas stream will condense in the alumina pores. As the pores fill, the gaseous reactants are forced to diffuse more slowly through the liquid phase to the active sites. Activity again falls off rather rapidly (Figure 3). This series of tube tests were conducted at 22°C, 48 ppm CO, and a contact time of 0.4 seconds.

FIGURE 3: TUBE TESTS

REMOVALS vs. % RELATIVE HUMIDITY

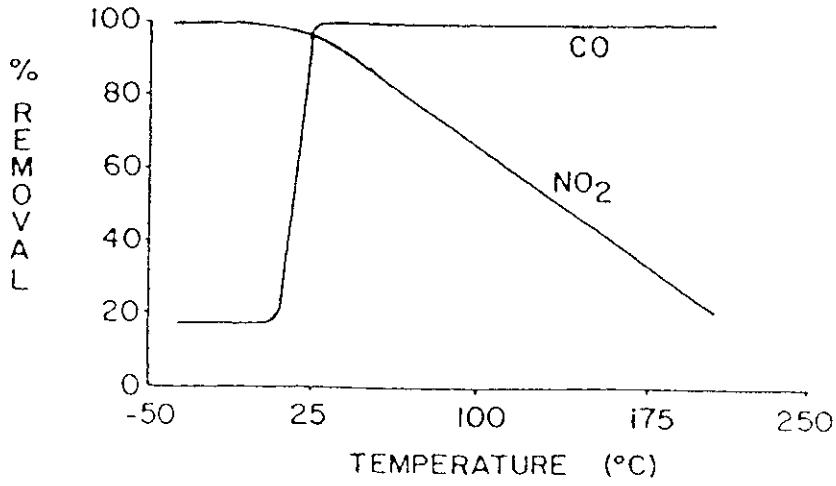


LTC activity toward NO_2 is unaffected by water content because that species is physically adsorbed on the outer surfaces as a function of temperature. For comparison, the CO removal curve for hopcalite is included on this graph. Hopcalite is a commercially available catalyst composed of approximately 78 percent MnO_2, 13 percent CuO, and traces of other metal oxides. Standard use includes safety masks for oxidizing toxic gases in mining environments and regenerating air in closed environments, such as in submarines. The removal curve shows that hopcalite is severely poisoned by water; without the use of dessicants, it is ineffective above 10 percent humidity.

Temperature Dependence

The difference between LTC's removals of adsorbed and oxidized gases is evident in a series of tube tests in Figure 4 (25 percent R.H., T_c = 0.2 sec.).

FIGURE 4: TUBE TESTS



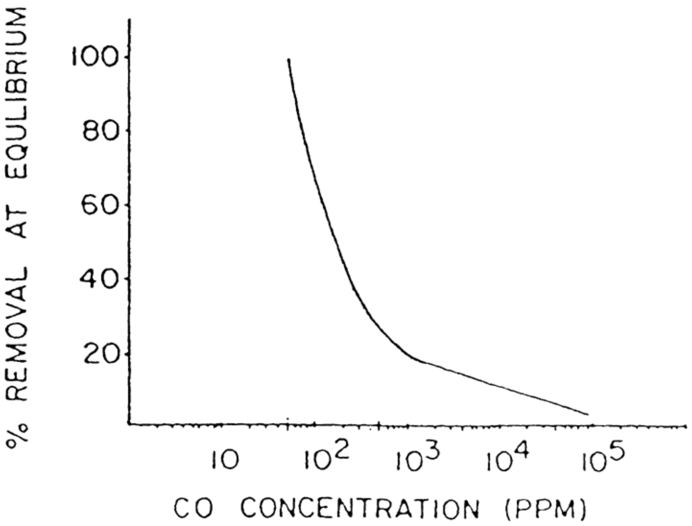
Catalytic oxidation of CO depends ultimately on the mobility of the reactive species, both in the gas and liquid phase, where diffusion is much slower. The abrupt change in oxidation rate which occurs near 20°C may be due to an autocatalytic effect. CO oxidation is exothermic, generating more than 60 kcal/mole. At low conversion rates and temperatures, the heat of reaction can dissipate so the activity remains constant near 20 percent removal. An increase in temperature causes heat to accumulate locally at reaction sites, providing enough energy to greatly increase the rate of reaction. Oxidation of CO remains near 100 percent conversion throughout ambient to 200°C temperature range.

In contrast, adsorption of NO_2 decreases as the temperature increases. That is, the equilibrium constraints become more important to the overall rate between 30°C and 90°C. Lowering the temperature, of course, favors increased adsorption. This graph shows 100 percent adsorption between approximately 30°C to -50°C (t_c = 0.2 sec.).

Gaseous Contaminants

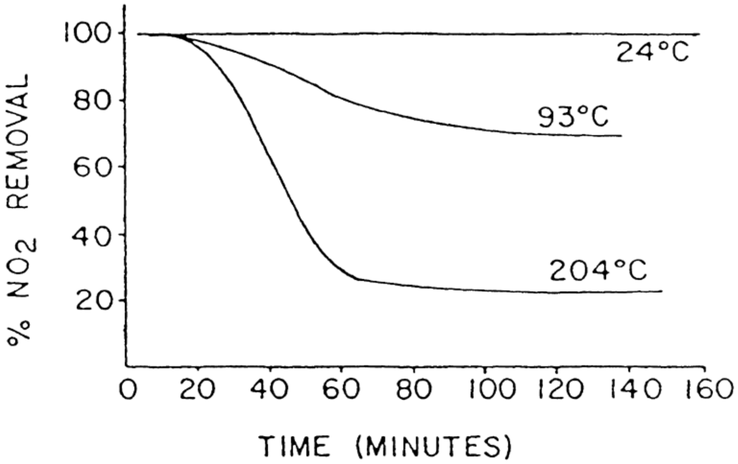
Carbon Monoxide: In addition to the humidity and temperature dependence of the oxidation reaction rate, the concentration of CO in the feed gas affects removal in a logarithmic manner. The discussion parallels that in the tube test protocol section where this behavior is described by Equation 5. Figure 5 describes the saturation of catalytic sites with increasing CO concentration. At 200 ppm, the tube test removal is 50 percent efficient (26°C, 35 percent R.H., t_c = 0.2 sec.).

FIGURE 5: TUBE TESTS



Nitrogen Oxides: NO and NO_2 are less strongly adsorbed than CO or O_2 on Pd. In fact, adsorbed NO on Pd surfaces is displaced when exposed to gaseous CO.[5] The graph of temperature dependence of catalytic process (Figure 4) is indicative of this fact. At any given temperature above about 30°C, the fraction of NO_2 removed by the catalyst is increasingly less than the fraction of CO removed. Figure 6 summarizes tube tests (t_c = 0.2 sec.) conducted at various temperatures against NO_2 contaminant gas. One-hundred percent removal rates are maintained from -40°C to above ambient. Near 90°C, the catalyst's removal efficiency for NO_2 is about 75 percent, dropping to 25 percent at 200°C.

FIGURE 6: TUBE TESTS



Sulfur Dioxide: A limited series of tube tests using a low concentration of SO_2 indicates that it is chemisorbed by the catalyst. The amount of SO_2 adsorbed is significantly greater than that experienced by the alumina substrate alone. In addition, the substrate will readily desorb SO_2, even just above room temperature. X-ray diffraction patterns suggest that SO_2 will chemisorb on Cu^{II} sites until saturation. At this point in testing, it is unclear whether or not SO_2 is subsequently oxidized to SO_3.

Hydrogen Sulfide: LTC is very reactive to H_2S, even at room temperature and low concentration. Tube tests show an irreversible conversion which results in very slow "poisoning" of the active sites. With 30 ppm H_2S tested at 400°C and a contact time of 0.2 second, some of the catalyst beads turned black after several hours of exposure. X-ray analysis indicates the formation of CuS.

APPLIANCE PERFORMANCE CURVES

LTC beads were packed into a filter one foot square by one third-inch thick. As related under room temperature protocol, these types of filters were mounted in a duct or in the air cleaner appliance to test the catalyst according to product specifications. The Instapure™ Air Filtration System was designed t provide 250 or 300 cfm air flow. The contact time for the catalyst is, therefore, reduced to only 0.02 second, an order of magnitude less than that in the tube test. All of the room tests were conducted at 40 percent relative humidit and ambient temperature.

Carbon Monoxide

Using a 300 gram catalyst filter and 250 cfm air flow, the removal curve of Figure 7 was generated over a three hour period. The initial CO concentration of 30 ppm is in the "Dangerous" category as established by EPA standards. Within an hour, this toxic concentration was reduced 50 percent by the filter. Per pass efficiency is calculated using Equation 6. Thus, an initial CO concentration of 30 ppm at an air flow rate of 250 cfm gives a filter efficiency of 14.6 percent per pass after one hour.

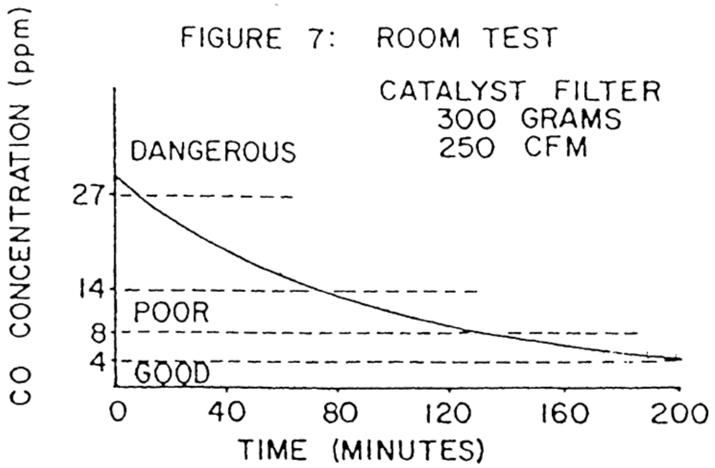


FIGURE 7: ROOM TEST

Ozone

A filter containing 300 grams of LTC was subjected to an ozone concentration of 75 ppb. At 300 cfm, the decomposition curve is summarized in Figure 8. The high reactivity of ozone molecules is reflected in the considerable rate of natural decay.

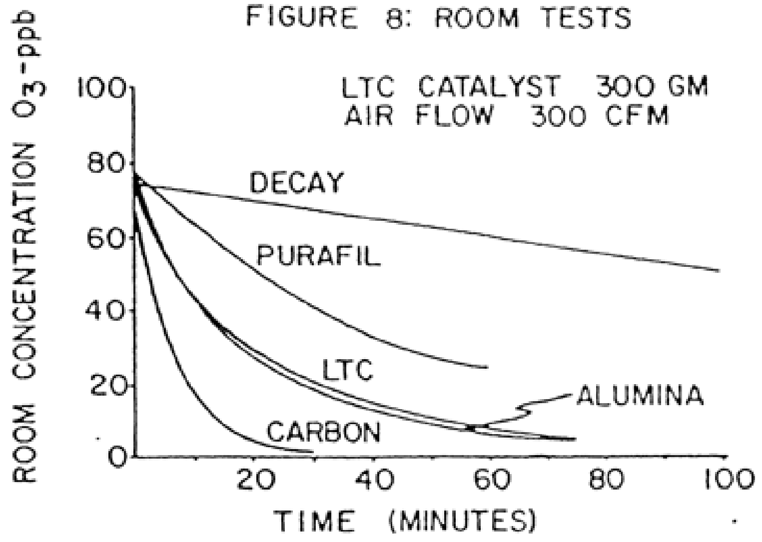


FIGURE 8: ROOM TESTS

For comparison a decomposition curve for a commercial material, Purafil (Borg-Warner Corporation, 1965), is included. Purafil consists of alumina pellets impregnated with a $KMnO_4$ solution. Although potassium permanganate is a well-known oxidizing agent, the curves show that it substantially impairs the ability of the alumina substrate to decompose ozone. The curve for the LTC catalyst on alumina is comparable to that for alumina alone. Although activated carbon significantly increases the rate of ozone decomposition, the catalyst on alumina achieves decay up to six times the natural rate. Figure 9 constitutes the room test performance of a 300 gram catalyst filter at 250 cfm air flow and 40 percent relative humidity. According to EPA standards, an "Extremely Poor" concentration of ozone is decomposed to the "Good" level after little more than an hour in the sealed room.

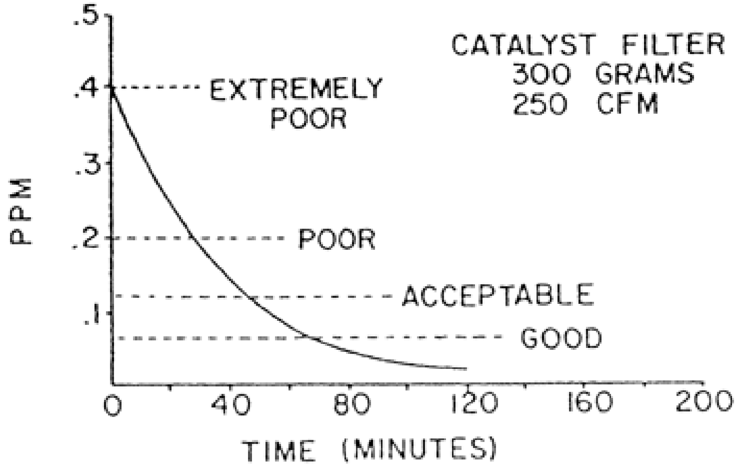
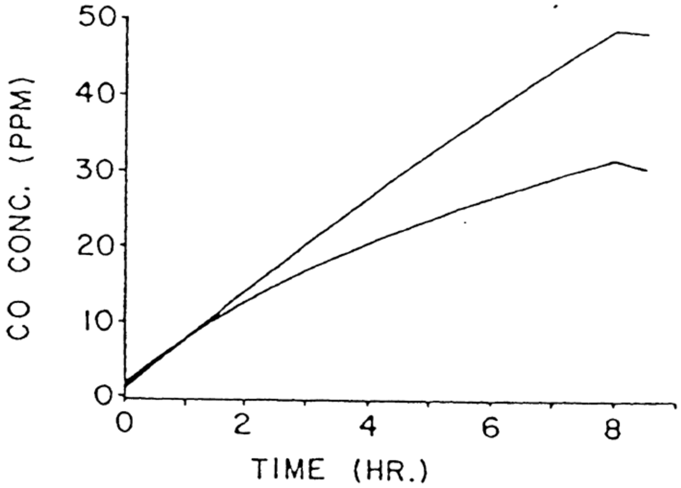


FIGURE 9: ROOM TEST

Carbon Monoxide in Cigarette Smoke

The results of carbon monoxide removal from cigarette smoke using the commercial combined particulate/carbon/catalyst filter in the appliance are summarized in Figure 9. Air flow was 300 cfm. Two cigarettes per half hour were smoked in a 1152 cubic foot sealed room to generate the upper curve ending at 48 ppm of carbon monoxide at eight hours. The same procedure was followed while running the air filtration appliance (AF-1) to generate the lower curve ending at 32 ppm of carbon monoxide at eight hours. The result is a 34 percent reduction of the initial CO concentration by this appliance.

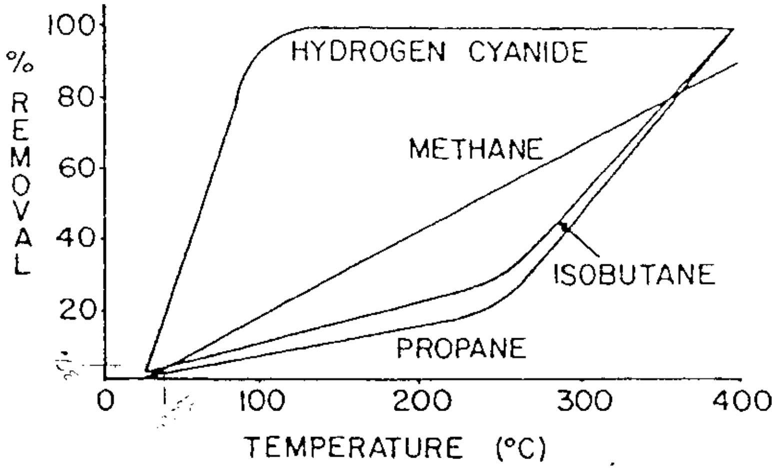
FIGURE 10



ELEVATED TEMPERATURE REMOVALS (TUBE TEST)

LTC performance (tube test) at elevated temperatures against several contaminant gases is summarized in Figure 11. HCN is the more reactive of this series because of the triply-bonded nitrogen. This high electron density bond is more readily oxidized by the catalyst than the single carbon bonds of the alkane gases. Hydrogen cyanide in a 1 percent concentration was 100 percent oxidized at temperatures greater than 100°C. For the alkane gases, oxidation rates increase steadily with higher temperatures; approaching 100 percent removal at 400°C. The reaction rate is highest for methane because of the greater reactivity of the tertiary carbon-hydrogen bond.[6]

FIGURE 11: TUBE TEST



SUMMARY

As a result of its multi-phase morphology, LTC exhibits complex behavior toward the various gaseous contaminants in this study. Since the catalysis is an oxidation/reduction couple between palladium and copper, the reactivity of the activated complex to a given gas species is a function of its bonding nature, concentration, reaction temperature, and relative humidity. Three types of reaction mechanisms are evident: oxidation, adsorption, and conventional chemical reaction (such as decomposition of ozone or formation of CuS). In the tube tests, oxidation of carbon monoxide is near 100 percent between 25 and 65 percent relative humidity, and between 20° and 400°C. About 10 to 15 percent water is necessary to facilitate mobility and thus the reaction of CO and O_2. The abrupt increase in activity at 25°C may be due to retention of the heat of oxidation (auto-catalysis). NO_2 is adsorbed by the catalyst, strongly dependent on temperature but independent of humidity. SO_2 is adsorbed until saturation, whereas H_2S forms CuS at higher temperatures. Elevated temperatures causes oxidation of HCN, methane, iso-butane, and propane in that sequence. Room tests of the Instapure™ Air Filtration appliance showed superior activity against CO, with a per pass filter efficiency of 15 percent removal. CO from cigarette smoke was diminished by 34 percent in a typical test of the appliance. Ozone was decomposed up to six times its natural rate of decay.

LTC has demonstrated superior activity against an important variety of noxious/toxic gases. It has been incorporated in a portable household air cleaner--The Instapure™ Air Filtration System--designed to remove particulate, odors, and hazardous gases at room temperatures. Removal of hazardous gases

makes this appliance effective against all major types of indoor air pollutants--certainly unique in its category. The catalytic technology is, of course, adaptable to a considerable range of commercial/industrial applications.

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