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# Catalytic Combustion of Nuclear Submarine Atmospheric Contaminants

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A laboratory-scale catalytic reactor, which duplicates shipboard CO/H<sub>2</sub> burners with respect to catalyst, bed depth, and space velocity, was used to study the catalytic oxidation of vapors and aerosols of a number of organic compounds. Most of the compounds were substantially converted to the theoretical yield of carbon dioxide by air over hot Hopcalite catalyst at approximately 300°C. Most of the hydrocarbons were easily oxidized but methane resisted oxidation yielding only 30 percent of theoretical CO<sub>2</sub> at 400°C. As expected, oxygenated compounds were easily oxidized.

When ammonia was oxidized over Hopcalite, a 70-percent yield of nitrous oxide was obtained. This result has been shown before but the formation of nitrous oxide from pyridine, morpholine, and monoethanolamine is reported here for the first time.

The catalytic decomposition of halogen compounds ranged from slight with Freon-12 to extensive with Freon-11 and methyl chloroform. All three Freons and methyl chloroform produced acidic gases in the furnace effluent and methyl chloroform and Freon-11 formed additional organic compounds over Hopcalite.

## INTRODUCTION

The carbon monoxide levels measured by Thomas aboard the USS TROUT in December 1953 made it plain that a carbon monoxide removal system with considerable capacity must be provided if unlimited smoking were to be permitted (1). Following the evaluation of the MSA Mark V hydrogen eliminator by Thomas aboard the TROUT, a Mark V unit was set up at NRL and tested for its efficiency for carbon monoxide removal. Unfortunately, the 1:1:1 catalyst used seemed to depend upon relatively high hydrogen concentrations and the resulting high catalyst temperature for any appreciable efficiency for CO removal.

As a result of this and other experiences, the suggestion was made that Hopcalite catalyst be tried for its ability to oxidize carbon monoxide (1,2). This catalyst, an unsupported mixture of manganese and copper oxides, had been developed for the Navy during World War I by Lamb, Bray, and Frazer for use in gas masks (3). It was known that the catalyst became readily poisoned by adsorbed water vapor when operated at room temperature as in gas masks, but that the addition of small amounts of silver and cobalt

oxides prevented the water poisoning. It was also learned that the catalyst was easily poisoned by organic compounds (1) apparently because adsorption of these compounds blocked catalyst surface sites vital to catalytic action. In the hope that a higher temperature of operation would preclude water poisoning and minimize accumulation of organic material a Mark V hydrogen eliminator was loaded with Hopcalite and operated at around 260°F (127°C) for about three weeks in the laboratory. The level of CO removal remained at 80%. In the attempt to transfer the laboratory experience to a practical shipboard device it was found that an operating temperature of around 650°F (343°C) seemed to be necessary to prevent the accumulation of organic materials on the catalyst and the resulting loss in activity toward carbon monoxide. Unfortunately, at this temperature it was found that Freon-12 from leaks in the refrigeration systems decomposes to produce corrosive products. By this time the design and production of an eliminator to replace the "jury-rigged" hydrogen and carbon monoxide eliminators had been placed in the hands of the Desomatic Products Company.

## CHOICE OF MATERIALS FOR STUDY

In view of the known and suspected presence of a myriad of vapors and aerosols of many substances in nuclear submarine atmospheres, it was

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decided to undertake a systematic laboratory study of the behavior of a representative series of compounds, chiefly organic, under conditions as close to those obtained aboard ship as possible. The instance cited above, wherein higher catalyst temperature improved carbon monoxide removal but caused undesirable production of corrosive degradation products from Freon-12, served as a warning that caution must be exercised in drawing conclusions from a single observation. It was essential to learn, for instance, whether the high temperature which seemed to prevent catalyst poisoning by organic materials resulted in the complete oxidation of the organics to innocuous products such as carbon dioxide and water, or were compounds such as aldehydes and acids produced which could have a deleterious effect upon the crew and equipment.

#### Hydrocarbons

Analysis of samples of activated carbon exposed on the USS NAUTILUS during the habitability cruise in June 1956 revealed well over a hundred compounds in the water-insoluble portion of the desorbate. Hydrocarbons were found to be the most abundant by far (4). While steps were being taken toward eliminating several likely contributors to the high hydrocarbon level such as volatile components of the diesel fuel, the intemperate use of mineral spirits for cleaning machinery, and solvents from oil base paints, a study of the action of hydrocarbons in a laboratory scale catalytic reactor was started (5). Representatives of the several types of hydrocarbons, *i.e.*, normal paraffins, isoparaffins, olefins, alicyclics, aromatics, and alkyl aromatics were chosen for study because of the known differences in the ease of their noncatalyzed oxidation.

#### Oxygenated Compounds

This work was followed by a study of oxygenated compounds known or suspected to be aboard nuclear submarines (5). It was also of interest to learn whether certain compounds such as methanol which are theoretical intermediates in the oxidation reactions of hydrocarbons would prove stable in the burner or be completely oxidized to carbon dioxide and water. If oxidation intermediates such as alcohols, aldehydes, and acids should be formed from hydrocarbons or other precursors in the burner and then resist further oxidation, the result would be to produce baneful

products from relatively innocuous progenitors. Methanol itself has been used in some duplicating fluid formulations used in the ships' office although formulations containing less methanol have now been provided.

Carbitol (diethylene glycol monoethyl ether) and ethylene glycol are representative of a class of oxygenated compounds used in water-thinned paints and will doubtless be found in the atmosphere of submarines using such paints.

Cresol (ortho) is regarded as a possible hydrolytic product of the triarylphosphate (TAP) ester compressor fluids used on shipboard.

#### Nitrogen Compounds

Several nitrogenous compounds were of particular interest. The possible formation of acidic nitrogen oxides under the oxidative conditions existing within the shipboard burner was of concern because of possible toxicity and corrosion. The production of oxides of nitrogen by oxidation of ammonia is a well-known process used in the manufacture of nitric acid. In addition, the production of nitrous oxide ( $N_2O$ ) by the catalytic oxidation of ammonia has been reported (6,7) and even suggested as a means for the commercial production of nitrous oxide for use as a propellant in aerosol bombs (6). Nitrous oxide has been found to give upwards of 80% of the response of carbon monoxide on the CO channel of the Mark III shipboard analyzer. It thus appeared that recent apparent shipboard CO buildup despite use of additional CO/ $H_2$  burners might be laid to nitrous oxide formed in the CO/ $H_2$  burner.

In addition, infrared analysis of air samples taken from one operating submarine show that the air from the outlet of the CO/ $H_2$  burners was from 17% to 29% richer in nitrous oxide than the inlet air (8). Although ammonia has not been found in nuclear submarines in concentrations greater than 1 ppm, it was realized that ammonia could result from the breakdown of monoethanolamine (MEA) used in the carbon dioxide scrubbers. For this reason, both ammonia and MEA were studied for their action in the catalytic combustor. In addition, pyridine is an example of compounds having a nitrogen atom integral with an aromatic ring and hence more resistant to uncatalyzed oxidation. Morpholine is a nitrogenous compound used to adjust the pH of water-thinned paints.

### Halogen Compounds

The halogen compounds studied are used aboard nuclear submarines as refrigerants and other purposes. Freon-12 (dichlorodifluoromethane) is in wide use, and Freon-11 (trichlorofluoromethane) and Freon-114B2 (dibromotetrafluoroethane) are being used aboard some vessels. Methyl chloroform (1,1,1-trichloroethane) has been suggested as a solvent less toxic than carbon tetrachloride and has thus found some use on nuclear submarines. It has been learned recently that a proprietary contact adhesive used to apply Formica contains methyl chloroform as the major solvent (8).

### Aerosols

It was realized that some substances which have relatively low vapor pressures would not be found in the atmospheres of nuclear submarines in appreciable concentrations as vapors. Nonetheless such substances could be introduced into the atmosphere as aerosols. Such aerosols could result from oil leaks dripping on to a hot surface or from sprays from leaks in a high pressure system. At the beginning of the study of aerosols, the compound chosen for examination was dioctyl phthalate (10). This compound is used rather widely in aerosol studies as it produces stable

aerosols whose physical characteristics are well-known. It recommended itself further for our work since it is a chemical entity and thus is of unambiguous composition, which permits ready calculation of the amount of  $\text{CO}_2$  to be expected upon complete oxidation. Navy Symbol 2190 lubricating oil was chosen because it is in wide use in the Navy as a hydraulic fluid and a lubricating oil. A triarylphosphate ester fluid (TAP) was studied, as such ester mixtures have been recommended for shipboard use, because it showed good lubricant properties while possessing remarkable resistance to ignition. The particular mixture of cresylic acid phosphate esters chosen for a given application depends in part upon the viscosity characteristics desired. The fluid Cellulube 220 has a viscosity of 45.2 centi-stokes at 100°F.

### APPARATUS AND PROCEDURES

The catalytic combustion apparatus is depicted schematically in Fig. 1. The reactor unit consists of a 28-inch length of 1-1/8-inch stainless steel tubing, the lower half of which was filled with stainless steel turnings and was heated by Nichrome heating elements. By means of a continuously adjustable autotransformer it was

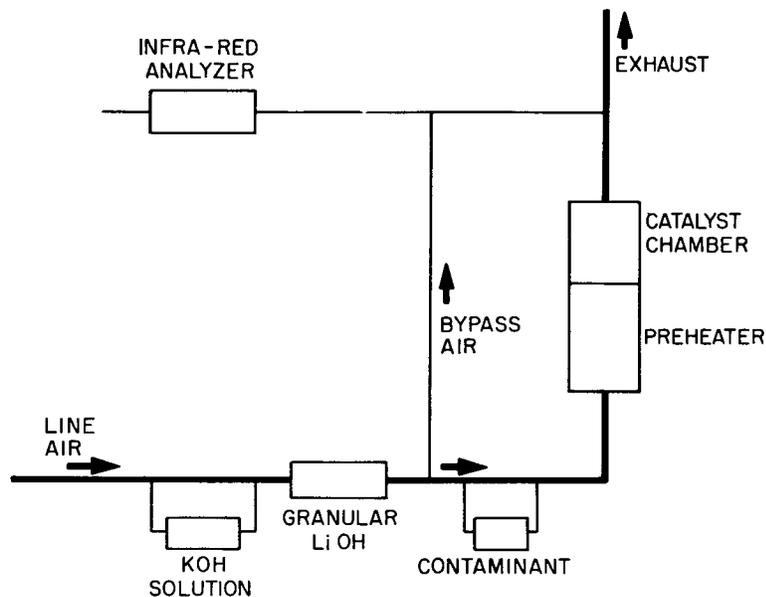


Fig. 1 - Schematic diagram of apparatus

possible to control the temperature of the air reaching the upper catalyst section of the reactor tube. This section, separated from the lower section by a circle of stainless steel screen, contained a bed of catalyst five inches long. Using a total air flow of one cubic foot per minute through the catalyst section gives a space velocity of 21,000 reciprocal hours. This duplicates the conditions of bed depth and space velocity of the 250-cfm CO/H<sub>2</sub> burner aboard many operating nuclear submarines. An iron-constantan thermocouple situated just below the catalyst bed and connected to a recording potentiometer recorded the catalyst temperature.

The catalyst used throughout this work, Hopcalite, was obtained from the Mine Safety Appliance Corporation through Navy supply channels. The catalyst, about 6-mesh size, had an apparent density of 1.0 gram per cc. Spectrographic analysis done at this Laboratory did not reveal the presence of more than traces of metals other than manganese and copper. Cobalt and silver which were added to earlier Hopcalites to prevent water poisoning were absent. Wet chemical analysis showed the catalyst to be 78.3% MnO<sub>2</sub> and 13.1% CuO with a loss on ignition of 7.9%—this loss presumably being water or chemisorbed gases.

The combustion efficiency was determined by one or more means depending chiefly upon the compound being studied and the reaction products expected. One of the most meaningful measures of the combustion efficiency is the percent of theoretical carbon dioxide obtained. The percent of theoretical carbon dioxide obtained is quite significant since carbon dioxide is one of the ultimate oxidation products of all organic compounds. In addition, the sensitivity of the analytical system is increased since most organic compounds yield more than one mole of carbon dioxide for each mole of organic compound oxidized.

The low levels of carbon dioxide encountered were readily measured by means of a Liston-Becker Model I5A nondispersive infrared analyzer which takes advantage of the strong adsorption of infrared radiation by carbon dioxide as compared to many other gases. A continuous record of the output of this instrument was made by means of a recording potentiometer. The carbon dioxide analyzer was calibrated using air

from tanks of breathing air whose carbon dioxide content was known from independent gravimetric measurement, and nitrogen was used to establish the zero point. The combustion efficiency was thus calculated by the increase in CO<sub>2</sub> content of the furnace effluent over that in the bypass air stream.

Another useful analytical technique was provided by gas chromatography. Using this system it was possible in many cases to compare the concentration of the compound of interest in the furnace effluent with that in the influent and obtain a measure of the amount of the compound disappearing. While the amount of the compound which disappears upon passage through the catalytic reactor is not necessarily the amount which is completely oxidized, gas chromatography will often reveal the formation of unexpected products by the presence of new peaks.

Because of the low concentrations of contaminants studied and the resulting low levels of CO<sub>2</sub> to be expected upon combustion, it was necessary to remove the CO<sub>2</sub> from the laboratory line air to provide sufficient sensitivity toward the CO<sub>2</sub> of combustion. It was found that unpurified line air, which contained only about 400 ppm water, was so dry that LiOH quickly lost its ability to absorb CO<sub>2</sub>. The removal of the CO<sub>2</sub> was accomplished by passing some of the inlet air through several liters of 10% aqueous potassium hydroxide and then all the air through a bed of granular lithium hydroxide. In this manner the furnace inlet air was freed of CO<sub>2</sub> and brought to 50% R.H. as desired. This purification system served well for several weeks on a single charge of LiOH.

Again, because of the low concentrations of contaminants studied, it was necessary to avoid any rubber or plastic materials of construction which were found to absorb some of the substances studied. Metal and glass were used throughout the system downstream from the point of contaminant introduction.

Known concentrations of contaminants were prepared and introduced into the furnace by several means. Gaseous substances such as methane, ethane, propane, and ammonia were admitted to the CO<sub>2</sub>-free air stream through a rotameter or soap bubble flowmeter and controlled by a fine needle valve. Because of the inadvisability of treating ammonia as an ideal gas, the approximate rate of addition of ammonia gas was controlled by the needle valve, and a measured volume of the ammonia-contaminated

furnace influent was collected and analyzed for ammonia by use of Nessler's reagent (11). During some runs both the furnace influent and effluent were examined for ammonia content. During one run the inlet ammonia concentration was regulated to a high value (352 ppm) deliberately to facilitate examination of the furnace effluent for nitrogen dioxide ( $\text{NO}_2$ ). The method of Jacobs and Hochheiser (12) for nitrogen dioxide determination was used. For the analysis of nitrous oxide, it was necessary to use a concentrating procedure because of the low concentrations of nitrous oxide sought and the limited sensitivity of the gas chromatographic equipment toward nitrous oxide. The concentration was effected by passing a measured volume, usually 2 liters, of the furnace effluent through silica gel in a gas chromatographic sampling loop immersed in a dry ice-acetone bath, then flushing the loop into the gas chromatographic instrument after heating in a hot water bath.

Substances which are liquids at room temperature, such as decane, methanol, and monoethanolamine, were introduced to the furnace from diffusers or bubblers, the choice being based upon the volatility of the liquid being studied and the concentration desired. In some cases where the volatility was quite high, it was necessary to place the diffuser in an ice bath. In such cases, vapor concentrations calculated from diffuser weight losses were unreliable because of the difficulty of obtaining accurate weight changes occurring in the diffuser wetted in an ice bath. Where such cooling was necessary, the inlet vapor concentration was compared with the furnace effluent by means of gas chromatography. Standards for gas chromatography were prepared in steel sample cylinders of about 1.7 liters capacity. The calculated amount of liquid under study was injected with a microliter syringe into an evacuated sample cylinder and the cylinder was pressurized to about 50 psig with air or with a pure gas such as nitrogen as appropriate for the optimum chromatographic results.

Aerosols were produced by means of an aerosol generator patterned after the one described by Thompson (13) and shown in Fig. 2. This generator works as follows: The fluid whose aerosol it is desired to study is placed in can B. Air at about 1.5 atmospheres is admitted through the air inlet which contains a series of peripheral jets around the lower ring. The fluid is thus subjected

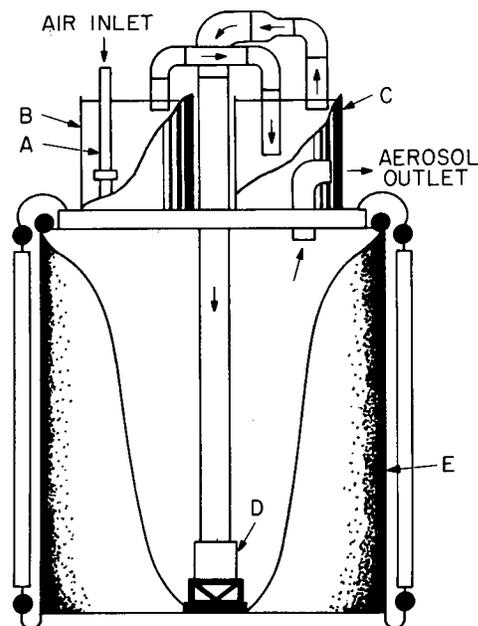


Fig. 2 - Aerosol generator

to a shearing action by the airstream which leads to the production of an aerosol. The aerosol next passes into can C where large particles settle out and thence to the jet impactor D where final particle discrimination occurs. From the jet impactor the aerosol passes out of the large can E directly into the furnace with a portion being diverted for analysis. Since the aerosol production depends upon a shearing action and hence on viscosity, it was found convenient to have can A containing the fluid at a constant temperature to permit control of the concentration of the aerosol produced.

Analysis of the aerosol concentration was accomplished by diverting a measured volume of the aerosol through previously weighed Gelman type A fiberglass filters. A second analytical filter placed in series with the first showed no weight increase indicating that all the particulate matter impinging upon the first filter was retained. On several occasions a filter was placed at the furnace exit to determine whether any aerosol survived passage through the furnace. However, no aerosol was found on the filter.

In the study of the TAP aerosol it was desired not only to determine the completeness of combustion as evidenced by the amount of carbon dioxide obtained but also to determine the fate

of the phosphorous of the ester. To further this end the original TAP ester mixture was analyzed for phosphorous as well as for carbon and hydrogen.

The mass median diameter and number diameter of the aerosols produced were determined by a light-scattering method described by Knudson and White (14). Phosphorous analyses were carried out on the original TAP fluid, reactor effluent air collected in bubblers, and aqueous extracts of catalyst granules which had been exposed to TAP aerosol. These analyses were done using the phosphomolybdate blue complex method of Carpenter *et al.* (15). In this procedure, the absorption of the phosphomolybdate complex formed from the solution being analyzed is compared with the absorption of solutions containing known amounts of inorganic phosphate, using light at 575  $m\mu$ .

The source and purity of the substances whose oxidation was studied are given in Table 1. The limits of error for data on the completeness of combustion based on  $CO_2$  measurements are  $\pm 5\%$  at low contaminant concentrations and less at higher concentrations.

## RESULTS

### Hydrocarbons

The extent of combustion of the lower molecular weight hydrocarbons is given in Table 2 and the results for the higher hydrocarbons given in Table 3. The combustion of hexane and the higher hydrocarbons is substantially complete at 300°C, while the combustion of the lower hydrocarbons is incomplete at this temperature. The rate of uncatalyzed vapor phase oxidation of hydrocarbons is known to increase as chain length increases (16).

Methane is particularly resistant to catalytic oxidation, yielding only 30% of the theoretical  $CO_2$  even at 400°C. Increasing the total air flow from one to two cubic feet per minute at 400°C diminished the extent of oxidation of methane from 27% to about 12%. The results at one and two cfm are given in Fig. 3. A tenfold increase in the methane concentration from 30 to 320 ppm did not increase the percentage of methane oxidized. During a recent investigation (17) aboard an operating nuclear submarine it was shown that one 250 cfm  $CO/H_2$  burner operating

at 600°F (315°C) was unable to prevent the buildup of atmospheric methane; the rate of methane buildup being about 10 ppm per day. When two such burners were operated at 600°F, however, the methane concentration buildup ceased and the concentration dropped markedly. Two  $CO/H_2$  burners operated at 500°F (260°C) were unable to check the methane concentration increase.

Infrared analyses of the furnace effluent during the incomplete oxidation of methane in the laboratory revealed only methane, carbon dioxide, and water. In other words, no partially oxidized intermediate products were found.

During another experiment during which the furnace temperature was lowered to a point where the oxidation of n-hexane was incomplete, comparisons of the furnace effluent and influent n-hexane concentrations were made by gas chromatography. Figure 4 shows the relationship between furnace temperature and percent theoretical carbon dioxide obtained during the combustion of n-hexane. At temperatures above 300°C where combustion is substantially complete as evidenced by the evolution of the theoretical amount of carbon dioxide, no n-hexane was detected in the furnace effluent. A similar analysis of the furnace effluent was made at a catalyst temperature of about 150°C while but 55% of the theoretical carbon dioxide was being obtained. Gas chromatography showed that the furnace effluent contained 40% to 45% of the n-hexane present in the influent, thus accounting for virtually all the n-hexane. Again, no partial oxidation products were detected.

The oxidation of 1,2,4-trimethylbenzene and 2,2-dimethylbutane was substantially complete at 350°C. The extent to which these compounds were converted to carbon dioxide dropped more rapidly as the catalyst temperature was lowered than in the case of compounds such as decane.

No significant effect of hydrocarbon concentration was found. The hydrocarbons studied were oxidized with equal facility in the concentration range 100 to 125  $\mu$  g per liter as at 20 to 30  $\mu$  g/liter.

During one experiment on the oxidation of diesel fuel totaling about three hours, the rate of introduction of the fuel fell from 130 to 75  $\mu$  g/liter, apparently indicating stripping of the volatile components by the air passing through

TABLE 1  
Substances Studied

Substance	Source	Purity
Benzene	Baker	Reagent grade
Other liquid hydrocarbons	Phillips	99 mol percent minimum purity
Gaseous hydrocarbons	Matheson	C. P.
Ethylene glycol	—	Commercial
Carbitol	—	Commercial (15 % ethylene glycol)
Methanol	Baker	Reagent grade
Cresol (ortho and para mixture)	Eastman	Practical
Triarylphosphate ester mixture	Celanese	Cellulube 220
Navy symbol 2190 lubricating oil	Navy Stock	Mixture
Freon-11	Matheson	Commercial grade
Freon-12	Matheson	Commercial grade
Freon-114B2	Dupont	Commercial grade
Methyl chloroform	Phillips and Jacob Co.	Commercial grade
Ammonia	Matheson	C. P.
Monoethanolamine	Fisher	C. P.
Pyridine	Baker	Reagent Grade
Morpholine	Fisher	Purified

the bubbler. The extent of combustion based upon the analyzed carbon content of the fuel and the actual carbon dioxide concentrations measured was  $90\% \pm 5\%$ .

The catalytic activity of Hopcalite toward n-decane and a paint thinner using vitiated air as the oxidizing agent was studied. The oxidation of n-decane at  $100\text{-}120 \mu\text{ g/l}$  and paint thinner at  $45\text{-}60 \mu\text{ g/l}$ , using air streams containing as little

as 9% oxygen, was complete showing that the  $\text{CO}/\text{H}_2$  burner will perform its function efficiently under conditions of reduced oxygen concentration in the influent air stream (5).

#### Oxygenated Compounds

Four oxygenated compounds were studied for reasons given previously and the results are given

TABLE 2  
Combustion of Lower  
Hydrocarbons over Hopcalite

Compound	Temperature (°C)	Percent of Theoretical CO <sub>2</sub> Found
Methane	400	30
	300	2
Ethane	315	12
	260	6
Propane	315	25
	260	11

in Table 4, which shows that all are completely oxidized at 350°C and all save carbitol at 300°C. Despite the incomplete combustion of methane reported above, the fact that methanol is easily oxidized at 300°C shows that methanol is not likely to be a final product in methane oxidation.

#### Nitrogen Compounds

The work of Kobe and Hosman (6) had shown that nitrous oxide is produced in 70% yield by the oxidation of ammonia over a manganese oxide-bismuth oxide catalyst at 200°C. Table 5 shows that the same yield is obtained using Hopcalite at 315°C. Zawadzki (7) shows that a number

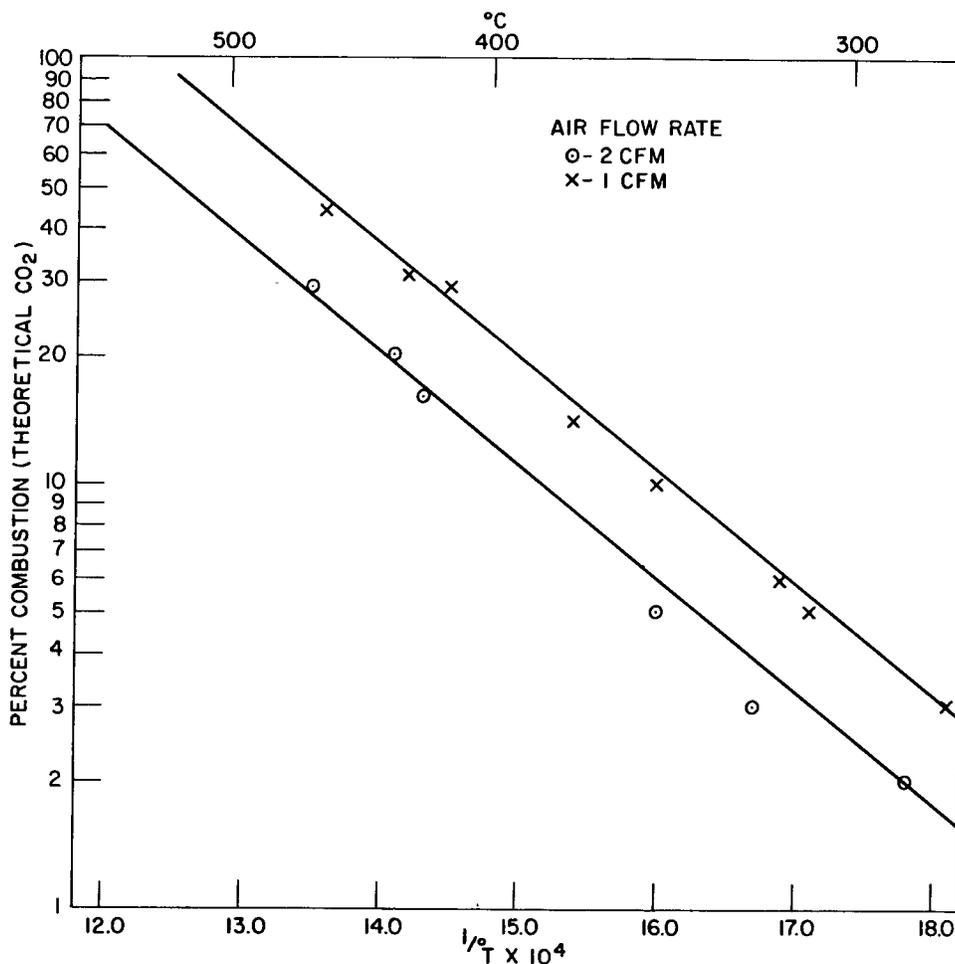


Fig. 3—Percent combustion of methane vs temperature at flowrates of 1 cfm and 2 cfm

TABLE 3  
Combustion of the Higher Hydrocarbons  
over Hopcalite

Compound	Percent of Theoretical CO <sub>2</sub> Found		
	350°C	300°C	200°C
Benzene	92	87	74
1, 2, 4-Trimethylbenzene	100	98	55
t-Butylbenzene	96	96	86
n-Hexane	97	97	77
n-Decane	96	98	89
2, 2-Dimethylbutane	98	84	40
Octene-1	94	89	83
Cyclohexane	91	—	—

of oxide mixtures, especially those containing MnO<sub>2</sub>, are active in forming nitrous oxide from ammonia in yields up to 80%. Our work indicates, as does that of Kobe and Hosman, that under otherwise identical conditions the extent of conversion of ammonia to nitrous oxide reaches a maximum at a rather moderate temperature and the conversion percentage is lowered as the catalyst temperature is raised above this value. In a separate experiment in which the inlet ammonia concentration was controlled at 352 ppm, less than 5 ppm nitrogen dioxide was measured in the furnace effluent. This indicates that the major product of the oxidation of ammonia over Hopcalite at 315°C is nitrous oxide (71%) while less than 2% of the theoretical amount of nitrogen dioxide was formed. The remainder of the ammonia was probably converted to nitrogen and water. The rather remarkable stability of nitrous oxide in the presence of hot Hopcalite

TABLE 4  
Combustion of Oxygenated Compounds over Hopcalite

Compound	Vapor Concentration		Percent of Theoretical CO <sub>2</sub>		
	(μg/l)	(ppm)	350°C	300°C	200°C
Methanol	130	97	98	98	95
Carbitol	40	7	100	82	79
Ethylene glycol	7	3	100	100	100
Cresol (ortho)	86	20	100	99	83

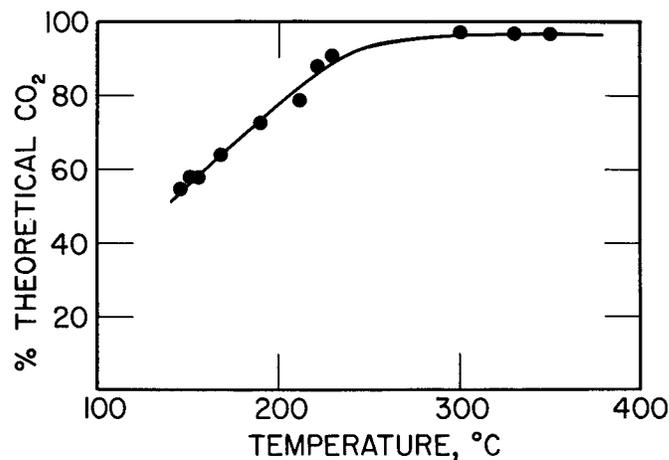


Fig. 4 — Extent of combustion of n-hexane vs temperature

was further demonstrated by passing nitrous oxide through the furnace containing Hopcalite at 315°C. Within the limits of experimental error, no measurable destruction of the nitrous oxide could be seen. It thus appears that nitrous oxide is rather easily formed from ammonia and resists destruction in the burner. These facts present the possibility that a buildup of nitrous oxide could occur aboard submarines, resulting in a serious interference with the carbon monoxide channel of the Mark III analyzer.

Although the formation of nitrous oxide by the oxidation of ammonia has been reported before, we did not find earlier reference to the formation of this product from organic progenitors (6,7). It is interesting that nitrous oxide is formed from ring compounds such as pyridine and morpholine about as readily as from a linear compound such as monoethanolamine. This suggests the possibility of the formation of nitrous oxide from nitrogenous compounds in tobacco during smoking. Nitrous oxide has been identified and semiquantitatively estimated in tobacco smoke by infrared spectroscopy (18). Analysis by Saunders (19) of carbon exposed during a 100-man fallout shelter trial, during which unlimited smoking was permitted, showed both CO and N<sub>2</sub>O in the ratio of about 25 to 1.

Since there was no attempt to maximize nitrous oxide production in this study, it may well be that conditions of temperature, space velocity, and catalyst other than those studied exist which would allow even more complete conversion of the compounds studied into nitrous oxide.

### Halogen Compounds

Some of the observations made concerning the behavior of the halogen compounds studied are given in Table 6. The extent of decomposition ranges from slight in the case of Freon-12 to virtually complete in the case of methyl chloroform. The slight decomposition of Freon-12 has been confirmed recently in shipboard studies (17). Even Freon-12, which suffered no more than 1% destruction, produced an acid reaction in the furnace effluent air. The three compounds which were extensively decomposed over Hopcalite at 315°C, Freon-114B2, Freon-11, and methyl chloroform, were studied further.

During an eight-hour run using a fresh charge of Hopcalite the apparent decomposition of

TABLE 5  
Hopcalite—Catalyzed Oxidation of  
Nitrogen Compounds

Compound	Inlet Concentration (ppm)	N <sub>2</sub> O Formed (Percent Theoretical)
Ammonia	140	70
Monoethanolamine	19	20
Morpholine	35	16
Pyridine	40	17

TABLE 6  
Hopcalite—Catalyzed\* Destruction of  
Halogen Compounds at 315°C

Compound	Extent of Destruction (Percent)
Freon-11 (CCl <sub>3</sub> F)	50
Freon-12 (CCl <sub>2</sub> F <sub>2</sub> )	< 1
Freon-114B2 (CBrF <sub>2</sub> CB <sub>2</sub> F <sub>2</sub> )	30
Methyl chloroform (CH <sub>3</sub> CCl <sub>3</sub> )	> 98

\*A strongly acid reaction of the furnace effluent to moistened universal indicator paper was obtained in all cases. A fresh charge of Hopcalite was used to study each compound.

Freon-114B2 fell from 30% to about 5%. Analysis of the furnace effluent for bromide and fluoride revealed that most of the fluoride and some of the bromide appear to be retained on the catalyst. In the case of methyl chloroform the extent of the destruction fell from 50% to 32% during the course of 6-1/2 hours. Again halogen analyses indicated partial retention of chloride and fluoride on the catalyst.

In addition to a small amount of undecomposed methyl chloroform detected in the furnace effluent, about 2% of the original concentration, gas chromatography revealed three additional products. These products and their gas chromatographic retention times are given in Table 7. Recent analyses of ships' atmosphere collected

TABLE 7  
Gas Chromatographic\* Analysis of Products from the  
Hopcalite-Catalyzed Combustion of Methyl Chloroform

Compound	Retention Time (minutes)	Amount in Effluent
Vinylidene chloride [CH <sub>2</sub> = CCl <sub>2</sub> ]	2-1/2	Considerable
Methyl chloroform [CH <sub>3</sub> CCl <sub>3</sub> ]	5	< 2%
Trichloroethylene [CHCl = CCl <sub>2</sub> ]	11	Considerable
Unidentified	16	Little

\*Beckman GC-2A Instrument, UCON HB200 Column at 70°C, He pressure, 30 psig.

in stainless steel sample bottles indicate a similar destruction of methyl chloroform and production of new organic products in the CO/H<sub>2</sub> burner (17). These analyses also show that vinylidene chloride which seems to be formed from methyl chloroform in the shipboard CO/H<sub>2</sub> burner is eventually destroyed by the burner.

Gas chromatographic analysis of the furnace effluent during the combustion of Freon-11 in the laboratory also showed traces of several other organic compounds which were not identified. It was shown that phosgene is not formed from Freon-11 under these conditions by use of a sensitive tube test which would have revealed the presence of as little as 0.1 μg (0.03 ppm) of phosgene.

During one experiment with Freon-11 during which the furnace temperature was lowered rather rapidly from 700° to 400°F (371° to 204°C), the extent of destruction of the Freon fell from 40% to about 7%. The curve is shown in Fig. 5.

It is reported that the Freons are relatively nontoxic and this study has shown that one of them is rather resistant to catalytic oxidation. Nonetheless, the production of even small amounts of halogen acids is undesirable as is the production of new organic halides whose toxic nature is not well-known since these materials may cause metal corrosion and adverse physiological reactions. For these reasons, in systems where catalytic combustion is used to cleanse the air within an ecosphere, care must be exercised in the selection of Freons or similar compounds

used and suitable means must be provided for scrubbing out possibly harmful products from the furnace effluent.

Several experiments were performed to determine whether Freon-11 and Freon-12 would suffer thermal nontoxic degradation. For these experiments the catalyst was removed from the reactor and the reactor thoroughly flushed to remove catalyst dust. When Freon-11 was passed into the empty reactor, a slightly acid reaction was obtained in the furnace effluent at temperatures as low as 232°C, but at 371°C copious quantities of acid fumes were evolved. Freon-12, on the other hand, produced no acid reaction upon thermal stressing at 371°C.

#### Aerosols

The results obtained during study of the oxidation of aerosols of several fluids are shown in Table 8. The aerosols of lubricating oil and dioctyl phthalate were completely converted to the theoretical amount of CO<sub>2</sub> at 300°C. We have no direct evidence as to whether the aerosol survives passage through the preheater section as a distinct physical state.

Initial study of the triarylphosphate aerosol (Cellulube 220) showed that CO<sub>2</sub> was being produced in greater than the calculated amount. Simultaneous measurements of the TAP aerosol concentrations showed the stream passing vertically into the furnace to have the same

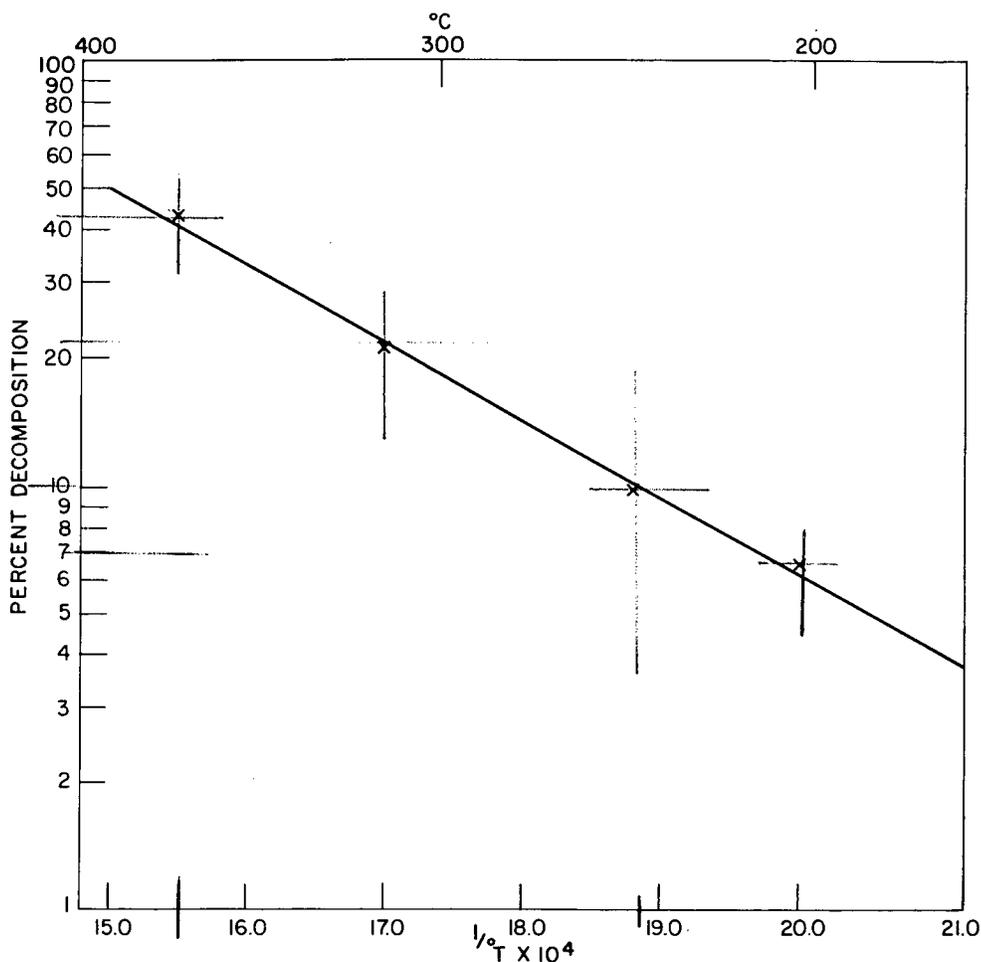


Fig. 5 - Extent of decomposition of Freon-11 vs temperature

concentration as the stream moving horizontally to the analytical filter so any anomalous results cannot be laid to anisotropy.

It was of interest to learn whether phosphorous or any of its compounds could pass through the combustor under the same conditions of operation as normally used on shipboard. Such materials as the various oxides of phosphorous would doubtlessly have a deleterious effect upon the crew and machinery. Conversely, should phosphatic material be retained upon the catalyst, a possible result would be loss of catalytic activity toward other materials. In an attempt to learn the fate of the phosphorous portion of the TAP molecule, two rather extended series of runs were made and these will be discussed separately.

During the first extended series, TAP aerosol at an average concentration of  $30 \mu\text{g}/\text{liter}$  was passed into the furnace for a total time of 40 hours. During part of the time a measured volume of the furnace air was bubbled through water. No phosphorous in any form was detected in the water. At the end of the 40-hour period the Hopcalite catalyst was removed in layers. The bottom layer of catalyst, *i.e.*, that which was first contacted by the TAP aerosol, was coated with a thin layer of gray material; the next to bottom was less gray, and so on until the sixth or topmost layer appeared the same as fresh Hopcalite. Portions of each of the six layers were extracted with hot 10% aqueous NaOH and the extracts analyzed for phosphorus by the phosphomolybdate blue procedure pre-

TABLE 8  
Combustion of Aerosols over Hopcalite at 300°C

Substance Studied	Aerosol Concentration ( $\mu\text{g/l}$ )	Extent of Conversion to $\text{CO}_2$ (percent)
Navy symbol 2190 lubricating oil	100-150	100
Diocetyl phthalate	40-100	100
Triarylphosphate	20-60	ca. 115

viously described. The analyses are summarized in Table 9. Photomicrographs of sections of catalyst granules having the highest phosphorus content showed that the surface coating is quite thin. X-ray diffraction revealed little of the chemical nature of the coating. The crystallites present are small, of the order of 100A.

TABLE 9  
Analysis of Catalyst\* Sections Exposed to TAP† Aerosol During First Extended Series

Section	Distance from Bottom of Bed (inches)	Phosphorus (percent)
1	0.0 - 0.5	0.37
2	0.5 - 1.0	0.25
3	1.0 - 2.0	0.20
4	2.0 - 3.0	0.21
5	3.0 - 3.8	0.19
6	3.8 - 5.0	0.08

\*The catalyst temperature was 315°C (600°F).

†A total of 1.8 grams of TAP aerosol were passed into the reactor during 40 hours operation.

The total phosphorus lodged on the catalyst was calculated from the weight and phosphorus content of the several layers. A value of 170 mg phosphorus was obtained as compared to the 140 mg expected from the 1.8 grams TAP used. Despite the retention of phosphatic material on the catalyst, no diminution of the catalytic activity for other materials was seen. The activity of the exposed catalyst toward n-decane and 1,2,4-trimethylbenzene was as good as fresh catalyst.

In order to produce the higher TAP aerosol concentrations desired for a second extended series of runs, it was found necessary to raise the temperature of the TAP fluid in the aerosol generator. Values for TAP aerosol concentrations produced at several generator temperatures are given in Table 10.

TABLE 10  
Concentration of TAP Aerosols Produced at Several Generator Temperatures

Generator Temperature (°C)	Aerosol Concentration Produced ( $\mu\text{g/l}$ )
30	20
35	25
40	43
45	60

During the second extended series of runs, TAP aerosol concentrations of 60  $\mu\text{g/l}$  and greater were introduced into the furnace. Under these extreme conditions some of the TAP emerged from the furnace exit as liquid TAP. The Hopcalite thus exposed to such high concentrations of TAP aerosol suffered some loss in catalytic activity toward other substances. The initial efficiency of the catalyst for the combustion of n-decane at 325°C was 62% and for 1,2,4-trimethylbenzene was 78%, as compared with values of 98% to 100% for their combustion over fresh Hopcalite. The TAP-exposed Hopcalite appeared to undergo at least a partial regeneration of its activity upon continued use for hydrocarbon combustion. During a run of several hours

duration, its activity toward n-decane rose from 62% to 80%. The catalyst was removed from the furnace and examined for organic phosphorus by Soxhlet extraction with isopropanol and for inorganic phosphorus by extraction with hot 10% aqueous NaOH. Only inorganic phosphorus was found. No phosphorus was removed from the catalyst by Soxhlet extraction with water alone.

### SUMMARY

1. Catalytic combustion studies have been conducted in the laboratory as an aid in predicting the behavior of a number of types of vapors and aerosols, chiefly organic, in the CO/H<sub>2</sub> burners used aboard nuclear submarines.

2. Using Hopcalite catalyst, an unsupported coprecipitate of copper and manganese oxides, substantially complete oxidation of the vapors of representative types of hydrocarbons, oxygenated compounds, nitrogen compounds, halogenated compounds, and aerosols of several oils was obtained at temperatures near 300°C.

3. The lower hydrocarbons, notably methane, proved resistant to oxidation; methane was oxidized only to the extent of 30% even at 400°C.

4. All the nitrogen compounds studied produced appreciable amounts of nitrous oxide (N<sub>2</sub>O). Ammonia produced nitrous oxide in 70% yield at 315°C and about 2% nitrogen dioxide. For the first time, nitrous oxide was produced from the organic nitrogen compounds pyridine, morpholine, and monoethanolamine.

5. The decomposition of organic halogen compounds, including three Freons, over Hopcalite at temperatures around 300°C ranges from slight in the case of Freon-12 to virtually complete in the case of methyl chloroform. In addition, new organic halides are formed upon the oxidation of methyl chloroform and Freon-11. There is at least a partial retention of halogen on the catalyst when Freon-114B2 and Freon-11 are oxidized.

6. Aerosols of dioctyl phthalate and lubricating oil are quantitatively oxidized by Hopcalite at 300°C. High concentrations of triarylphosphate ester (TAP) aerosol (ca. 30 μg per liter) are quantitatively oxidized at 300°C, the phosphorus is retained on the catalyst and no loss in catalytic activity toward hydrocarbons is suffered. Higher TAP aerosol concentrations (> 60 μg per liter) permits unreacted TAP liquid to emerge from the furnace. There is partial loss of catalytic activity, but the catalyst seems to undergo a partial regeneration upon continued use for hydrocarbon combustion.

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