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Fifth Annual Progress Report

The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines

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PREVIOUS REPORTS IN THIS SERIES

"The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," R.R. Miller and V.R. Piatt, editors, NRL Report 5465, Apr. 21, 1960

"Annual Progress Report. The Present Status of Chemical Research in Atmosphere Purification and Control of Nuclear-Powered Submarines," V.R. Piatt and E.A. Ramskill, editors, NRL Report 5630, July 14, 1961

"Second Annual Progress Report. The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," V.R. Piatt and J.C. White, editors, NRL Report 5814, Aug. 29, 1962

"Third Annual Progress Report. The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," H.W. Carhart and V.R. Piatt, editors, NRL Report 6053, Dec. 31, 1963

"Fourth Annual Progress Report. The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," L. B. Lockhart and V.R. Piatt, editors, NRL Report 6251, Mar. 23, 1965

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
Summary of Progress	1
Chapter 1 - Diffusion of Methyl Chloroform	4
Chapter 2 - Chlorinated Hydrocarbons in Closed-Environment Atmospheres	8
Chapter 3 - The Mark IV Atmosphere Analyzer	13
Chapter 4 - The NRL Total Hydrocarbon Analyzer	18
Chapter 5 - Activated Carbon - Atmosphere Purification and Analysis	23
Chapter 6 - Development of Interior Paints for Nuclear Submarines	27
Chapter 7 - Review of the Electrolytic Production of Oxygen in Nuclear-Powered Submarines	33
Chapter 8 - Recent Experiments with Chlorella	40
Recommendations	49

ABSTRACT

This annual progress report supplements NRL Reports 5465 of April 21, 1960; 5630 of July 14, 1961; 5814 of August 29, 1962; 6053 of December 31, 1963; and 6251 of March 23, 1965, which provided a comprehensive review of the past and present research and development effort of the Naval Research Laboratory on the atmospheric habitability of submarines. Emphasis is at present being devoted almost exclusively to nuclear-powered submarines. Considerable progress has been made in the major efforts of developing improved methods of sampling and analysis of atmospheres, but shipboard analytical equipment continues to be of marginal quality. Problems associated with volatile chlorinated hydrocarbons in closed environments have led to their complete ban. Other topics covered in the present report include: further studies on algae as a source of oxygen (now discounted for nuclear submarines due to the excessive power requirements of the necessary light source), fire-retardant and nontoxic paints for necessary application during submergence, and a survey of oxygen sources based on a recurring need to improve the safety, reliability and logistics of the high-pressure electrolytic oxygen generator now on all FBM submarines.

PROBLEM STATUS

This is an interim report; work is continuing on all phases of the program.

AUTHORIZATION

NRL Problems C08-05, C08-18, C08-30
Project SF 018-08-03, Tasks 4092, 4093, 4094, 4095
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Fifth Annual Progress Report

The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines

Summary of Progress

As stated in previous reports of this series, both improvements and problems continue to occur in atmosphere-purification and control equipment aboard nuclear submarines. Although further major modifications are still required in the equipment, these would be less necessary yet easier to accomplish if better communication were possible among the men responsible for construction, maintenance, and operation of nuclear submarines. This series of annual reports constitutes one of the primary attempts to improve communication, as well as to establish what has been accomplished and what must still be done.

The preceding reports in this series (1-5) provided historical, status, and progress accounts on submarine air-replenishment equipment and supporting research. The present is the fifth supplemental "annual" progress report; and although nominally representing the events in calendar year 1964, it also includes the first six months and a few later events in 1965. A compendium of classified events and research during this period is being printed separately.

In the previous annual report (5), a discussion pinpointed methyl chloroform as the possible culprit in extensive corrosion aboard nuclear submarines. This conclusion was subsequently confirmed when methyl chloroform as a solvent was determined to be the main constituent in the adhesive used to apply Ensolite insulation to bulkheads (6). A mass spectrometric study has now been made (Chapter 1) of the diffusion of methyl chloroform through Ensolite and other materials, indicating that the solvent could not be ventilated outboard completely during construction, and that it could still be contributing to atmospheric difficulties for months or possibly years after the submarines became operational.

General problems with chlorinated hydrocarbons are discussed again (Chapter 2), and their indictment reemphasized from both toxicological and corrosion standpoints. Although the hazardous incident reported herein is from the spacecraft program, there is a good parallel with the submarine program, and much is to be gained by constant interchange of pertinent information.

The story about the Mark IV Atmosphere Analyzer (Chapter 3) remains the same in its overall impact: where improved infrared sources and detectors are utilized, and with the manufacturer's representative personally solving major problems, the ship's personnel become satisfied with the instrument. Conversely, when aged or obsolete parts or procedures are used, the instruments are almost totally ineffective. The dual need for improved quality control by the manufacturer and for details of usage of parts replaced or defective has limited the ability of the Navy to improve operability on the ships. The basic principle of the Mark IV continues to appear effective, but the needed improvements in the instrument seem to be lagging behind the search for more efficient substitutes.

The NRL Total Hydrocarbon Analyzer (Chapter 4) has been used successfully on operating nuclear submarines, and appears destined soon to become standard equipment. Introduction of the final version may be postponed by last-minute decisions about additional compounds such as Freons which can be measured by this versatile instrument. Most of the remaining problems are of an engineering nature.

The role and life of activated carbon in purifying submarine atmospheres (Chapter 5) has become more important since the early days of the USS NAUTILUS (SS(N)571), when the large quantities of contaminants plus an inefficient filtering system rendered the carbon ineffective within 48 hours of submergence. Now that the gross contamination is considerably lower, and since more and better carbon is used, carbon has become one of our most effective defenses against possible trouble, such as massive swamping of the atmosphere by gas leaks, painting, or accidental spillage of solvents. A general recommendation now in effect is the replacement of the main filter carbon every 20 days during submergence on new submarines or on any submarine with possible atmosphere problems. Carbon also continues to be of major assistance in analytical schemes for determining the nature of atmosphere contaminants.

In the continuing effort to lower the atmosphere contamination at the source, the development of an appropriate water-thinned paint applicable during submergence is a "must." In Chapter 6 it is shown that combining such a paint with fire-resistant properties requires sacrifices and compromises which will ultimately result in certain chemicals such as chlorine being incorporated into the paint despite the fact that these components are undesirable from an atmosphere-control standpoint. On the other hand, the chemicals giving the better fire-resistant properties generally tend to improve both the quality and appearance of the paint. Although the general composition of the paint cannot yet be estimated, most of the research is completed, and it is expected that a satisfactory paint can be formulated by 1967.

Due to the continuing maintenance and operational problems associated with the Treadwell electrolytic oxygen generator, a review has been made of the overall oxygen-supply system (Chapter 7). The Naval Ship Systems Command (formerly Bureau of Ships) has expressed continuing interest in obtaining a new and improved oxygen generator. Due to the slow development and evaluation of the Ionics, Inc., ion-exchange, ten-man prototype system for the generation of oxygen and absorption of carbon dioxide, all other promising oxygen sources should continue to be considered and/or evaluated.

The study of a photosynthetic gas exchanger using algae for oxygen production and carbon dioxide absorption (Chapter 8) has shifted from a potential system for use by nuclear submarines to an interesting subject for continued exploration, with the long-term possibility in mind. The heavy power requirement for the light sources exceeds the available power on nuclear submarines by an order of magnitude (although understandably the available power could be increased by reactor redesign if the oxygen supply were sufficiently critical, which it is not). The current NRL investigations have shed much light on the sticking of algal cells to glass and the relation of oxygen evolution to cell-to-culture-chamber thickness. Further studies are planned in the new Ocean Science and Engineering Division recently established at NRL, but progress will no longer be summarized in the annual reports until algal systems become more promising for submarine use.

Other major submarine atmosphere-control equipments not specifically covered in this report are the CO_2 scrubber, the electrostatic precipitators, and various analytical procedures. The Marine Engineering Laboratory recently has put into operation a production CO_2 scrubber for experimental purposes, and NRL began a laboratory-scale study of the CO_2 stripping system in FY 1966, but results are not yet available.

Previous NRL recommendations for stabilizing MEA (monoethanolamine) solutions in the CO_2 scrubber have not been implemented (Chapter 9, Reference 5). The sea trials (7) of the additive package containing EDTA (the tetrasodium salt of ethylenediaminetetraacetic acid) and VFS (the monosodium salt of N,N-diethanol glycine) for such stabilization of MEA solutions are not complete; although further trials might be desirable, immediate operational use of this package is recommended. The Bureau of Medicine and Surgery has lowered the maximum 60-day submergence limit of CO_2 to 0.5 percent, but major scrubber redesign or adoption of a new method may become necessary to reach the lowered

figure. No significant pattern of troubles has occurred with the electrostatic precipitators, and proper maintenance techniques appear to alleviate all troubles. The standard analytical backup facilities continue to be adequate for most purposes, with the major deficiencies still related to identical deficiencies in the major equipment, i.e., carbon monoxide and Freon measurements. The Mark V Atmosphere Analyzer, based on gas chromatography, is still in the stage of prototype construction by the Beckman Instrument Company (for initial direct distribution to submarines).

Although the above review does not appear any more alarming than previous annual reports, there is no room for complacency either in the submarines or in Navy management. The detailed reports cited in the individual chapters indicate how grave some of the problems have become, and the recommendations at the end of this report do not appear to the editors to be overstated.

Naval exchange of information about the atmospheric-habitability program and problems continues primarily through the quarterly progress reviews at NRL, to which are invited bureau, fleet, medical, Supervisor of Ship Building, and Naval shipyard personnel, and also through the NRL quarterly and annual progress reports. The establishment of the Submarine Safety Center at New London has done much to expedite follow-up activities. As NRL recommended, a new Working Group was created early in calendar year 1966 by the Bureau of Ships (now Naval Ship Systems Command) to establish more reliable acceptable limits for atmospheric contaminants as well as to establish controls on materials which should be barred from the ships.

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Chapter 1
Diffusion of Methyl Chloroform

F. E. Saalfeld and M. V. McDowell

INTRODUCTION

In addition to the long-recognized hydrocarbon contaminants from various sources, halogenated compounds have been detected in the atmosphere of some of the nuclear submarines. Corrosion found in these submarines has been attributed largely to hydrochloric acid formed on passage of air containing methyl chloroform (CH_3CCl_3) through the CO/H_2 catalytic burner. Indeed, methyl chloroform and vinylidene chloride ($CH_2{=}CCl_2$), a decomposition product of methyl chloroform, have been detected in atmospheres and main carbon filter beds in several FBM submarines that have had corrosion problems.

Studies (1) have shown that large quantities of methyl chloroform have been used during submarine construction as a major component in the solvent system of the neoprene cement used to adhere insulating and decorative materials to extensive surface areas within the ship. Information was required on the quantity of methyl chloroform that may be trapped behind the insulation or decorative panels and the rate at which it may be released to the submarine's atmosphere.

PROCEDURES

A description of the techniques required to determine diffusion rates has been given elsewhere (2). Briefly, these measurements involved placing the sample of the insulation or decorative panel, cemented to an aluminum plate with a neoprene adhesive, under a collection cell and accumulating the diffusing vapors. After a fixed period of time an aliquot of these gases was introduced into a Bendix Time-of-Flight mass spectrometer and analyzed; the remaining vapors in the cell were removed with a stream of air. This procedure was repeated at regular intervals until the methyl chloroform from the neoprene solvent could no longer be detected. Since the samples were cemented to aluminum plates, the source of methyl chloroform was constantly being depleted; thus, a steady state of mass transfer was never attained. Furthermore, since the pressure drop across the sample from the cement film was not known, the permeability coefficients themselves could not be calculated. Instead, the diffusion rate, dn/dt (lb/hr), as a function of time was calculated.

MATERIALS

The materials investigated were Ensolite (U.S. Rubber Co.), corkboard (Armstrong Cork Co.), and high-pressure Formica laminate (Formica Corp.). Ensolite, a unicellular plastic foam made of polyvinyl chloride, is supplied in production sheets either an inch or a half inch thick. Three samples of both thicknesses, 12 in. square, each cut from the center of a randomly selected production sheet, were used in these experiments.

Corkboard, a very porous material fabricated from granular cork and an appropriate binder, usually has its exposed surface area covered with a smoothing cement (Navy Formula 62-GM8010-227-1698, Mil-C-15202) before installation in the submarine. Samples

of inch-thick corkboard and the smoothing cement were obtained, and the diffusion characteristics of both the surface-covered and uncovered corkboard were investigated.

Diffusion properties of two types of decorative laminates were studied. Both were 1/16 in. thick; however, one type had aluminum foil between the laminate layers, while the second did not.

Bondmaster No. 596 cement (Pittsburgh Plate Glass Co.) was used to adhere the samples to aluminum plates. Mass spectrometric analysis of the vapors emanating from the surface of the cement film indicated the vapors to be a mixture of methyl chloroform (80 percent) and toluene (20 percent).

In these experiments none of the insulation or decorative materials were covered with decorative, pigmented paints which would further retard the diffusion rates.

RESULTS AND DISCUSSION

Data in Table 1 show the diffusion rates of methyl chloroform from Ensolite (two thicknesses) and corkboard (surface-covered and uncovered) cemented to an aluminum surface with Bondmaster No. 596 neoprene adhesive. Also shown in Table 1 is the diffusion rate of methyl chloroform from an uncovered film of the cement. The results are shown graphically in Fig. 1. Methyl chloroform did not pass through either type of high-pressure laminate material in detectable quantities.

Table 1
Rate of Diffusion of Methyl Chloroform from Ensolite and Corkboard Cemented to Aluminum Surface with Bondmaster No. 596 Neoprene Cement

Sample	Sample Thickness (in.)	Elapsed Time* (hr)	Diffusion Rate (10^{-4} lb/day-ft^2)
Ensolite, Sample E-1	1	2	0.81
		4	0.83
		5	0.67
		26	0.46
		30	0.62
		173	0.65
		2880 (120 days)	0.002
		4320 (180 days)	Not detectable
Ensolite, Sample E-5	0.5	2	10.3
		4	8.2
		5	7.2
		26	0.6
		30	0.5
		173	Not detectable
Corkboard, surface-treated Sample C-1a	1	2	0.030
		4	0.028
		5	0.035
		26	0.033
		30	0.030
		173	0.029
		2880 (120 days)	0.026
		4320 (180 days)	0.023
Corkboard, surface untreated	1	0.5	2.28
		1.0	1.80
		2.4	1.49
		3.7	1.26
		4.5	0.91
		23.6	0.12
		27.6	0.13
		96.0	0.13
Bondmaster No. 596 cement film		0.167	5.19
		0.7	1.32
		2.0	0.61
		4.5	0.31
		5.6	0.27
		23.6	0.05

*Cement-coated surfaces were brought in contact after 10 min drying period.

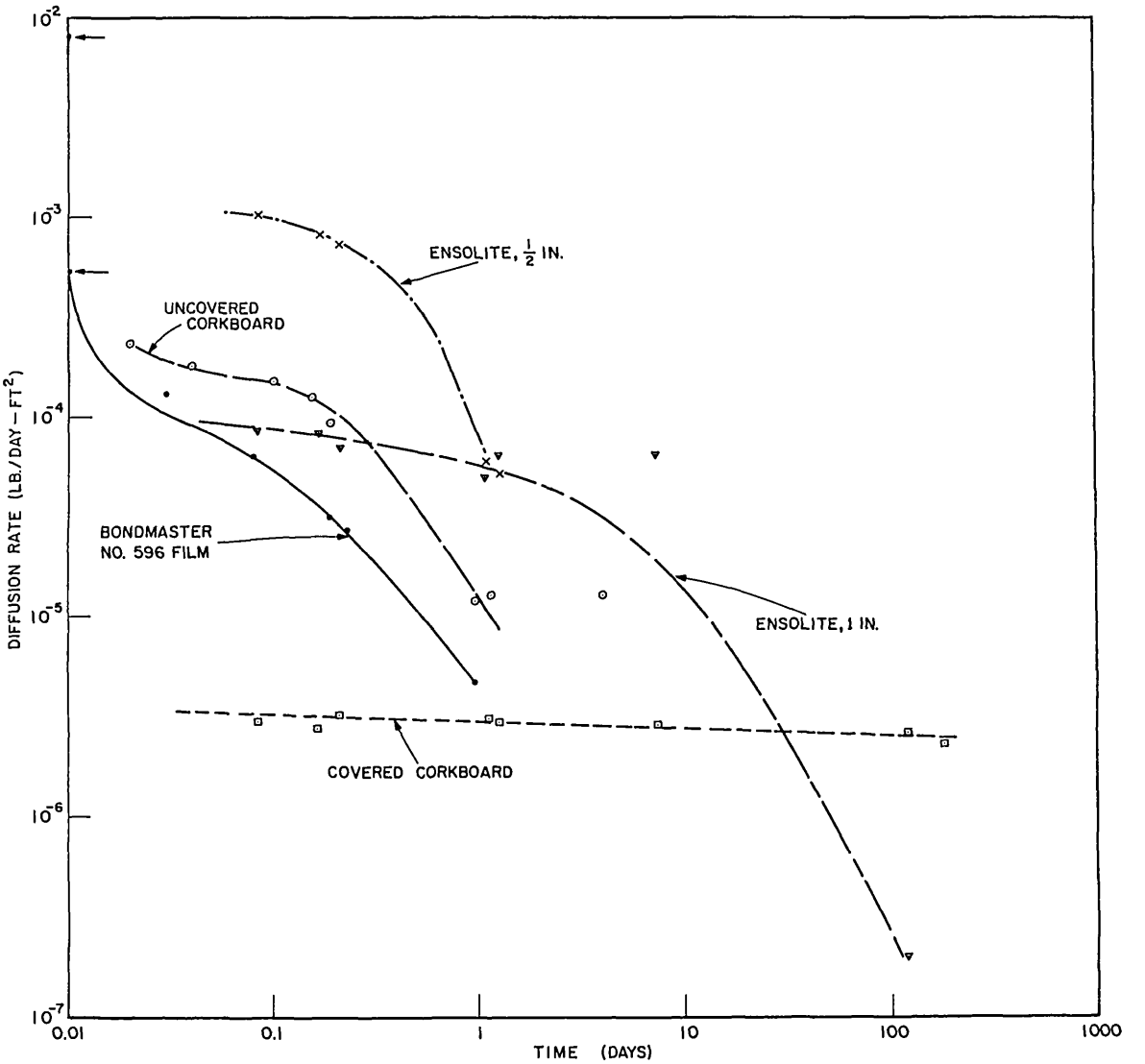

Fig. 1 - Rate of diffusion of methyl chloroform from several materials cemented with Bondmaster No. 596 adhesive (minimum detectable amount was 5.0×10^{-9} lb/day-ft^2)

With the exception of the surface-covered corkboard, all of the curves delineated in Fig. 1 have similar shapes. The uncovered Bondmaster cement film initially has a very high diffusion rate of methyl chloroform, which drops rapidly to a plateau before descending below the detectable limit of the method (5.0×10^{-9} lb/day-ft^2). Corkboard whose surface had not been covered with smoothing cement has a diffusion-rate curve similar to that of the cement film. However, the initial peak value was not observed, the plateau had a smaller slope, and the time required to reach the detectability limit was longer. Half-inch Ensolite had a curve whose shape resembled the previously discussed curves, except that the chlorinated hydrocarbon was detected diffusing from the material's surface for a longer time, and at the plateau values the rate of methyl chloroform diffusion was greater than that found for any of the other samples.

Diffusion rates of one-inch Ensolite were lower in value initially than the half-inch Ensolite and required a much greater period of time to fall below the detectable limit of

the measurement. Methyl chloroform diffused from this material at a relatively constant rate for approximately ten days before a noticeable descent in the curve was observed. One hundred and twenty days (four months) after the Ensolite had been cemented to an aluminum surface, detectable quantities of methyl chloroform were still emanating from the surface of this material.

Most unique of all the diffusion-rate curves was that of the surface-covered corkboard. It initially had a very low rate of evolution of methyl chloroform and showed no appreciable decrease in the rate during a six-month period. This result implies that the methyl chloroform trapped behind this insulating material will diffuse into the atmosphere at a slow but steady rate (about 2.5×10^{-6} lb/day-ft^2) for a very long period of time. Although it can be anticipated that this diffusion-rate curve will eventually decrease below the detectable limit, the length of time required cannot be predicted from the data.

If the area of insulation material used in submarines is assumed to be 60,000 ft^2, the amount of methyl chloroform diffusing through the surface-covered corkboard can be estimated as 0.1 lb/day, which agrees with the amount found by shipboard measurements (3). It should be noted that in the shipboard measurements the methyl chloroform was found to be diffusing from Ensolite and not from corkboard. Presumably, the shipboard measurements were made at a time before the diffusion-rate curve of Ensolite would have fallen below that of the surface-covered corkboard, and the rate of diffusion through this latter material during the shipboard measurements was below the detectability limit of the equipment used.

While the Bondmaster No. 596 cement contains methyl chloroform and toluene as solvents in approximately a 3:2 proportion, the ratio of vapor pressure of these solvents above a drying cement film is about 4:1. The mixture diffusing through surface-covered corkboard during the first week, however, contained only 10 percent toluene; after ten days the toluene could no longer be detected. Therefore, it is concluded that toluene is preferentially retained in the cement film or in the corkboard and will continue to emanate from this source at a slow rate for a long period of time.

CONCLUSIONS

The diffusion rates of methyl chloroform through insulation and decorative materials cemented to aluminum surfaces with Bondmaster No. 596 adhesive have been investigated by a mass-spectrometric technique. The measurements have shown that methyl chloroform trapped behind surface-covered corkboard diffuses into the atmosphere at a slow rate (about 2.5×10^{-6} lb/day-ft^2) for an extended length of time (more than 6 months). Inch-thick Ensolite retains methyl chloroform longer than half-inch Ensolite or corkboard whose surface has not been covered with smoothing cement. Methyl chloroform passes through uncovered corkboard faster than any other of the materials studied. No chlorinated hydrocarbon could be detected diffusing through the decorative laminates.

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Chapter 2
Chlorinated Hydrocarbons in Closed-Environment Atmospheres

R. A. Saunders

INTRODUCTION

A number of chlorinated hydrocarbons have been found in the atmospheres of environmental test chambers, Mercury spacecraft, and Polaris submarines (1,2). Some of the more common contaminants of this type are known to result from the use of cold wash solvents for cleaning or from the use of cements (3) and other formulations which contain these compounds as solvents. The origin of some of the less common chlorinated compounds which have been found in these atmospheres, however, has been something of a mystery.

These chlorinated compounds are generally present in low concentration in test-chamber and spacecraft atmospheres; since they are not likely to be decomposed by the relatively simple air-purification systems which have been used so far in these atmospheres, their presence has given little cause for concern. The situation has been more serious, however, with respect to submarine atmospheres.

SUBMARINE ATMOSPHERES

Methyl chloroform has been the chief offender in the submarine atmosphere. Large quantities of this material are used in cements for fastening decorative and insulating covering to bulkheads and pipes during the final fitting out of nuclear submarines. Most of the solvent from this cement evaporates into the ship's atmosphere at the time of application and is ventilated outboard. Significant quantities of solvent are retained for longer periods, however, and slowly diffuse into the submarine atmosphere (4). Significant quantities are also adsorbed on the ship's main charcoal beds during the application period. Later, as the carbon beds become loaded with other higher-molecular-weight air contaminants, the methyl chloroform is slowly displaced from this source also and reenters the ship's atmosphere (5).

Passage of methyl chloroform-contaminated air through the submarine CO/H_2 catalytic burners normally results in the breakdown of the solvent to form carbon dioxide, hydrochloric acid, and a trace of vinylidene chloride. The hydrochloric acid, generated slowly but continuously over a long period of time, caused appreciable corrosion damage aboard several submarines in areas surrounding the burner discharge before its identity and ultimate source were discovered.

Submarine catalytic burners operating at lower than optimum temperature (under 600°F) decompose methyl chloroform with less efficiency, producing increasing yields of vinylidene chloride and other chlorinated hydrocarbons, including trichloroethylene and tetrachloroethane. At a burner temperature of 550°F, for instance, methyl chloroform at an input concentration of a few parts per million will undergo a 10-percent conversion to vinylidene chloride and a 1-percent conversion to trichloroethylene (6).

Trichloroethylene is another common industrial cleaning solvent which, because of its low toxicity, is sometimes used in closed-environment atmospheres. Any of the chlorinated hydrocarbons are definitely undesirable in such atmospheres, however, especially those to be maintained for long periods of time, because of the possible decomposition products which might be released by the contaminant-control equipment.

SPACE-CHAMBER ATMOSPHERES

As an example of chlorinated hydrocarbons in space chambers, trichloroethylene was used as a general-purpose cleanup solvent in an environmental test chamber prior to commencement of a five-man, 30-day, simulated-flight test of an integrated life-support system. Termination of this test was necessitated after 4-1/2 days by widespread and severe vomiting among the crew. The crew was additionally afflicted with odd facial sensations, headaches, and chest pains and, following the abort, by an eruption of herpes-like sores about the mouth (7). All of these symptoms were attributed to a contaminated atmosphere by medical personnel at the scene.

Mono- and dichloroacetylene were among the many contaminants detected in that atmosphere (8). These two compounds may have been generated when their precursors, vinylidene chloride and trichloroethylene, reacted with some sodium superoxide contained in one of the units of the contaminant control system. Dichloroacetylene is known to be quite toxic and alone accounts for most of the symptoms experienced by the crew (9,10). Monochloroacetylene may have similar toxic properties. A more prolonged exposure to these two contaminants at the concentration at which they were encountered during the test could possibly have produced much more serious consequences.

SOLVENT IMPURITIES

The less common chlorinated hydrocarbons which have been found in submarine and other closed atmospheres may have resulted from the decomposition of a more common solvent in units of an air-purification system, as was shown in the examples above, or they may have been present from the first as impurities in such solvents. Commercial chlorinated solvents are known to contain appreciable quantities of certain other compounds as inhibitors and as impurities. It is becoming increasingly important to know in as much detail as possible the identity of contaminants introduced either deliberately or accidentally into closed atmospheres. Accordingly, analyses of a few of the commercial brands of methyl chloroform in the Navy supply system have been performed (11).

Analysis was made by passing the solvent through a vapor-phase chromatographic column (Ucon 50HB-2000 on 30-60 mesh Chromasorb at 100°C), which resolved the various components of the solvent as shown in the chromatogram in Fig. 2. The eluted components, represented by the various peaks of the chromatograms, were individually recovered from the effluent stream of the chromatograph in the manner described elsewhere (12). The identity of each of these components was then determined by means of its infrared and/or mass spectrum. The compositions of four solvents and the proportions of the predominant components are summarized in Table 2. Some of the less concentrated components were not identified, including a trace of component eluted at the same time as the tertiary butyl alcohol. One component of this sample, 1,1,2-trichloroethane, had a long retention time and is not shown in the chromatogram.

The quantitative data presented in Table 2 are based upon the amount of pure reference compounds required to give the same peak areas for the given column conditions. There may have been other components in the solvents examined which were not eluted from the chosen column in reasonable retention times, and therefore were not detected. Quantitative data are given only for the major constituents.

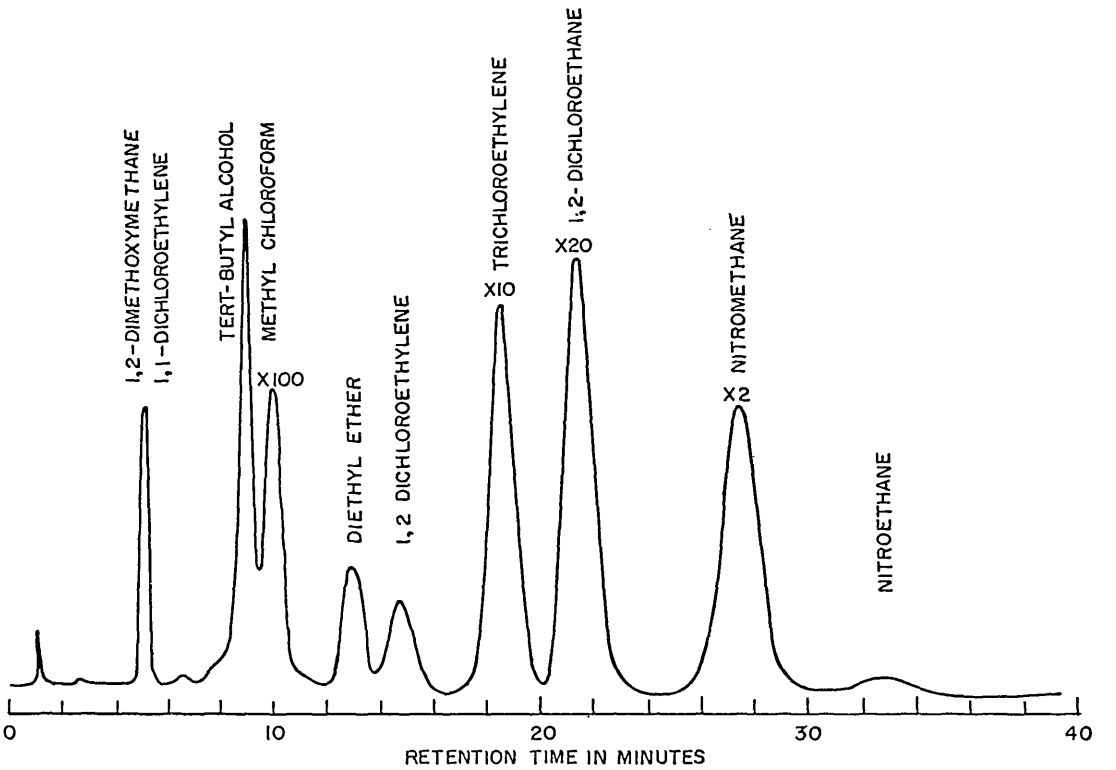

Fig. 2 - Chromatogram of methyl chloroform, brand A (see Table 2)

Table 2
Composition of Some Samples of Solvent-grade Methyl Chloroform from Commercial Sources

Compound	Composition in percent by volume			
	A*	B*	C*	D*
Chlorinated hydrocarbons				
1,1,1-trichloroethane (methyl chloroform)	65†	94†	95.5†	95†
1,2-dichloroethane (ethylene dichloride)	22.0	2.1	0.8	Trace
1,1-dichloroethylene	0.06	-	Trace	Trace
2-chlorobutane	-	Trace	-	-
1,2-dichloroethylene (acetylene dichloride)	Trace	Trace	Trace	-
1,1,2-trichloroethylene	7.6	-	-	-
1,1,2-trichloroethane (vinyl trichloride)	Trace	-	-	-
Other compounds				
sec-butyl alcohol	-	0.2	0.2	0.3
tert-butyl alcohol	3.6	-	-	-
1,4-dioxane	0	3.6	3.4	4.5
1,2-dimethoxymethane	0.24	-	-	-
diethyl ether	Trace	-	-	-
nitromethane	1.3	-	-	-
nitroethane	Trace	-	-	-

*Trade names cited in Ref. 11.
†Contribution of major component obtained by difference. Dash (-) indicates compound was not detected.

Commercial grades of methyl chloroform generally contain one or more stabilizers or inhibitors, such as p-dioxane, to prevent decomposition and the formation of hydrochloric acid. In spite of such additives, samples of methyl chloroform taken from government stock have been known to cause corrosion of metal, especially aluminum (13). Chlorinated solvents should not be used indiscriminately, therefore, for general cleaning of spacecabin components or of Polaris or other missile parts.

SUMMARY AND CONCLUSIONS

Methyl chloroform and other low-toxicity chlorinated solvents have been used in closed submarine spaces in considerable quantity, with subsequent deleterious effects on equipment. Some commercial grades of methyl chloroform have been shown to contain appreciable quantities of other more toxic chlorinated hydrocarbons. The relatively high concentrations of these components may raise the toxicity of the commercial solvent mixtures above that of pure methyl chloroform. It is obvious that the use of technical grade solvents in closed atmospheres can add several unsuspected and perhaps undesirable contaminants to the atmosphere.

Since methyl chloroform is known to decompose under certain conditions on passage through a submarine CO/H_2 catalytic burner, with the formation of additional chlorinated hydrocarbons and corrosive hydrochloric acid, and since some of the chlorinated hydrocarbons so formed might possibly react to yield more toxic substances, the use of chlorinated hydrocarbon solvents should be prohibited in closed environmental atmospheres, where catalytic burners and alkaline materials form part of the air-purification system.

An analysis of all solvent systems whose use may be necessary in submarines, spacecraft, or other analogous closed spaces, followed by restrictions on the use of those materials which contain or which might produce deleterious substances, is also recommended.

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Chapter 3
The Mark IV Atmosphere Analyzer

F. S. Thomas

INTRODUCTION

Most of the Mark IV Atmosphere Analyzers which were ordered are now in use on operating nuclear submarines. The Mark IV is the limited-objective service equipment intended to provide a continuous determination of the concentrations of the principal components of the nuclear-submarine atmosphere requiring surveillance and control. A description of the unit, together with brief reviews of early laboratory tests to which it was subjected, have been reported previously (1,2,3).

Considerable corrective maintenance was required before placing these units in operation following extended storage during construction of the submarine. This could be expected, since the equipment was new to the service personnel involved, and since any components susceptible to slow degradation were provided a long period in which such change might occur. Continuing service operation, however, has required an excessive replacement of detectors, sources, preamplifiers, and filter boxes. No requirement for the consistent replacement of other components is known.

TESTING REPLACEMENT PARTS

Only a small number of these replaced components have been returned. These were forwarded to the manufacturer under the applicable replacement warranty. It would appear that these failed parts should have been given an extensive examination. However, the only test made was a determination of their operational characteristics at the time of their return. Only those parts not conforming to the production acceptance requirements were replaceable under the warranty. These returned parts were not examined further, for reasons which will be given later.

This investigation by the manufacturer showed that somewhat less than one half of the returned parts, mainly sources and detectors, had deteriorated during operation to a point of failure. About one fourth of the parts were determined to be operationally "as-new," i.e., completely usable. These must have been replaced in error. The remaining one fourth were acceptable within the limitations of all shipboard test procedures, although somewhat outside the permissible limits of production-acceptance standards, such as in indication of linearity. These parts would be usable, although some deterioration in the quality of the analytical results would be expected.

It was concluded that any further investigation of these parts to determine the basic cause of failure was not warranted. In the period between their production and their return, so many changes had been made in design details and in preparation techniques that they did not represent current production. These changes resulted mainly from a study of parts made at the same time as those returned, and which had shown early or incipient failure during acceptance testing. Thus, any further investigation of the returned parts would be simply a repetition of previous work.

Independent laboratory testing at NRL is limited to an extremely small proportion of accepted components. Furthermore, the requirements for replacement parts have completely absorbed the production capacity for detectors, making it difficult to divert production units for laboratory testing. As observed in the laboratory, the only failure of detectors has been the gradual drift of operating characteristics, leading eventually to excessive loss of sensitivity or balance. The slow rate of this drift has permitted months of service before replacement became necessary. Initially, detector failures resulted largely from crossover sensitivity, but this defect has been completely eliminated by the optical filters on the windows of the carbon monoxide detectors and the Freon sources. Almost no gross failures of detectors have been seen in the laboratory. It is probable that the above effects resulted from slow leakage. Similar tests of sources showed only a slow increase in element resistance, except in a single instance where one source failed in less than 1000 hours. Leakage of the high-thermal-conductance gas appears to be the probable cause of deterioration. Other components in the electronic circuitry, such as preamplifiers and filter boxes, continued operable for many thousands of hours under laboratory conditions.

From the above, it appears that the continuing problem of component failure in service actually results from two causes. First, the manufacturer is still unable to attain consistently the required quality of seal needed to retain the small amount of detector fill gas for long periods, since present test methods are unable to demonstrate that such seals have been achieved in the units produced. Second, the relatively poorer results obtained in service as opposed to the laboratory results suggest that the more severe ambient conditions in the submarine are more degrading than simulated conditions in the laboratory. Recently, the operational characteristics of a group of CO_2 detectors for several Mark III analyzers were checked which were eight to ten years old. No special care had been exercised in their storage. Of the seven on hand, two showed essentially their original sensitivity to CO_2 and the absence of water-vapor sensitivity. Since the basic design of these old detectors continues into the Mark IV units, long life should be shown by an appreciable portion of the Mark IV detectors, provided the requirements of signal strength and balance in the Mark IV are not vastly more demanding.

IMPROVING DETECTORS AND SOURCES

The manufacturer has carried on, with Navy encouragement and a highly variable degree of vigor, an almost continuous in-house development program for improvement of detectors and sources, aimed especially at improving the hermetic seal and the consistency of operational characteristics of production units. Changes have included improved materials of construction, assembly techniques, and leak-detection capability, along with minor changes in design. Among many changes in the detector, a reduction of residual strains in the assembly was attained. Such strains may be important as a potential cause of both catastrophic failure, typified by cracking of the windows, or delayed initiation of slow leakage resulting from development or enlargement of minute cracks in the seals resulting in turn from a slow change in the contained gas.

This redesign of the detector appeared satisfactory in the preliminary drawing stage, as were the results from the first prototype. Most subsequent prototypes failed under the extensive tests to which they were subjected. The severity of the test conditions actually may have caused any real improvement in detector design to appear inferior. Extensive changes in personnel and organization of the manufacturer occurred at this same time. This redesign was abandoned entirely, and two concurrent approaches were followed toward improved equipment. The first consisted of further attempts to improve manufacturing and testing techniques. Secondly, a basic study of detector parameters was undertaken to form the groundwork for a new major design. Improvements in seals for the detector should also be applicable to the sources. Any significant progress toward this new major redesign has not yet been disclosed.

Recently BuShips (now Naval Ship Engineering Center) awarded a contract to Leesona-Moos Laboratories to study the present design of Mark IV detectors and sources. The objectives of this study are to create design and production criteria along with laboratory tests to insure the consistency, stability, and life of the units. Although this organization has had no previous experience with the Mark IV, they do have appreciable experience in the design and manufacture of similar infrared equipment (the positive filter method). Results to date are inconclusive.

The early return of usable analyzer components from service, as discussed previously, along with the lack of failure of preamplifiers and filter boxes in laboratory tests, suggests that service-connected conditions exist which are not duplicated in either production or laboratory tests. Incomplete or inadequate instructions would result in improper or unnecessary replacements of components as part of corrective maintenance. Examination of the instructions contained in the Technical Manual, NAVSHIPS 369-0044, Ref. (4), indicates no obvious deficiencies, although the troubleshooting charts, Fig. 7-34, in the Manual, appear to need some improvement. Revision of these charts is under study in conjunction with the development of an improved method of progressive determination of operability.

As a guide to maintenance and an aid in instruction in the use of the instrument, Beckman prepared a Detector and Source Certification Test Procedure. Evaluation of these tests and procedures at NRL indicated a need for considerable revision, to define particularly acceptable limits of variation and appropriate remedial measures. A revision of this procedure was prepared by NRL and forwarded to BuShips and subsequently to Beckman for approval of the suggested changes (5).

In order to assess more accurately the cause of failure of analyzer components in service, more comprehensive data on such failures are required. Components, particularly detectors, sources, preamplifiers, filter boxes, and electronic boards, which have been replaced in service due to change in operational characteristics, mechanical breakage, or any other cause, should be returned and studied to permit a definitive determination of the causes of service failures. The findings from such studies should define the real problem areas more accurately than the presently stipulated "shotgun" approach. All parts should be directed to NAVSEC (Naval Ship Engineering Center), Code 6649A1, and be accompanied, if possible, by a brief description of the prior history of the unit and the apparent cause of replacement.

In checking a group of sources produced in late 1964 and early 1965, it was found that the average heater-element resistance was 13.5 ohms, whereas in earlier sources this value averaged about 10 ohms. In the Technical Manual, Section 4-2-5, Section 5-4-4, and Sheet 1 of Fig. 7-34, an upper limit of 14 ohms is established for the heater-element resistance of a usable source. Sheets 2 and 3 of Fig. 7-34 each specify 11 ohms for this element. More recent sources are characterized by a higher resistance and some initial variation between sources. A small increase in resistance occurs during use, and some reasonable error is likely in the measurements. Therefore, in order not to exclude usable services the heater-element resistance values should be increased to 16 ohms.

OTHER PROBLEMS

In addition to this generalized effort toward detector and source improvement, some results from NRL's operation of its Mark IV unit are of general interest. Investigation of the relationship of the temperature-control characteristics of the oxygen channel thermostat to the oxygen indicator has continued. It has been shown that during the early operation of the present Fenwal thermostat, following either factory set or field reset, the control point drifts downward rapidly. The rate of this change appears to be dependent on the immediate prior history of the thermostat. Although the rate of change

continually decreases, the control point does not completely disappear even after a long period of time. Preliminary, favorable trials of a similar and immediately applicable thermostat made by Elmwood Sensors were informally reported by Beckman. This project on a better thermostat apparently got deferred during personnel changes at the manufacturer's plant.

Until a thermostat of proper configuration with a constant control point becomes available, no better solutions exist than the previously suggested correction chart (6). This chart could have either a nitrogen zero point set or air point set, disregarding the small error remaining in readings near the air point.

Table 2-2 of the BuShips Technical Manual provides data needed to correct hydrogen channel readouts for changes occurring in the concentration of components other than hydrogen. The values given in this table were determined for the ambient temperature and the bridge current employed in the Mark III analyzer. In the Mark IV, the H_2 bridge is located in the higher ambient temperature of the IR compartment and, due to changes in the circuitry, operates with a larger bridge current. Each of these affects the values in this table significantly. Therefore they should be changed to the following: CO_2, -4; O_2, +0.8; N_2, -0.4; H_2O, +11; and He, +68. Using these experimentally determined values, the change from dry nitrogen to dry air indicates a corrected value of 0.25 percent for H_2, dry N_2 to calibration gas as equal to +0.19 percent H_2 plus the 68-percent hydrogen equivalence of the helium concentration, and dry N_2 to room or submarine compartment air as equal to +0.37 percent H_2. This latter value is about the average of that shown by the 21 Mark IV analyzers operated at Mare Island.

Table 2-2 of NAVSHIPS369-0044

Hydrogen Analyzer Response to Various Gases

Relative Scale Deflection for 1% Gas in Air

Gas	Old Value	New Value
Hydrogen	+100	+100
Carbon Dioxide	-7.5	-4
Carbon Monoxide	-1.3	-
Oxygen	+0.6	+0.8
Nitrogen	-0.1	-0.4
Water	+6.8	+11
Helium	+64.0	+68

CONCLUSIONS

There has been considerable improvement in the production and test facilities for the preparation of Mark IV detectors and sources at the Beckman plant. Also, many minor changes in design and in production techniques have been made, all of which are intended to improve the life of these components and consistency between units. Despite this, service life of the acceptable components continues reportedly to be very short. From all available evidence, the basic cause of service failures of detectors and sources is still leakage from the sealed spaces involved. Additional information on component behavior in service, along with the return of components that have failed in use or in storage for study, would permit more effective coordination of the effort to improve these components.

A major redesign of detectors and sources by Beckman was abandoned, possibly prematurely, and the results of any further improvements have not been reported by them.

The BuShips (now NAVSEC) contract with Leesona-Moos for a study to improve detector-sources has not yet produced tangible results.

A test procedure prepared by Beckman for service certification of detectors and sources has been revised and amplified by NRL. Some of the information in this procedure is not contained in the Technical Manual and may be of appreciable aid in service maintenance of analyzers.

Experimentally determined corrections to the Technical Manual relating to source resistance and hydrogen indication corrections have been listed.

FUTURE PLANS

It is expected that NRL will continue to cooperate with NAVSEC in promoting improvement in Mark IV analyzer performance, especially with regard to detector and source life for other service-expended components as well. NRL also will attempt to obtain and verify application of the expected results of the Leesona-Moos contract. NRL will study further means of corrective maintenance and troubleshooting of the Mark IV for feasible improvement including development of diagnostic aids. The study of used and failed parts made available from the submarines through NAVSEC will be continued to determine further operational characteristics and to diagram probable cause of failures.

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Chapter 4
The NRL Total Hydrocarbon Analyzer

Walter D. Smith

INTRODUCTION

In the early history of the analysis of nuclear-submarine atmospheres, it became apparent that the organic contamination consisted of a complex mixture of constituents (1,2). The complexity of the contaminant mixtures made detailed analysis on shipboard impractical. One approach used to obtain information on the general level of organic contamination in these submarines was that of making a semiroutine sampling and analysis based on adsorption of the organic contaminants on activated carbon in the submarine, followed by analysis of desorbates in the laboratory (3). During this early period in the analysis of the atmospheres of nuclear submarines, some of the most useful data were obtained by this method.

With the advent of the Pye Gas Chromatograph, which employed an argon ionization detector of high sensitivity, direct analysis of the atmosphere in a submarine was made with some success (4). This instrument had two major limitations. The first limitation was that the desensitizing effect of water caused the detector response to vary by a factor of as much as four or five. The second limitation was the extreme variation in response to different molecular species. Even with these limitations it was established that there was present, in the submarine atmosphere, a higher concentration of hydrocarbons than that indicated by the carbon-sampling method. It is interesting to note that the carbon-sampling technique was averaging about 50 percent efficiency at the time the concentration level was approximately 150 micrograms per liter of total hydrocarbon, as determined by the Pye instrument (4).

Inherently, the carbon-sampling technique had a certain limitation that could only become greater as the contaminant levels became lower in the submarines. This limitation results from the fact that the unrecoverable material progressively constituted a more significant fraction of the relatively small quantity of adsorbed hydrocarbons. This deficiency could have been offset, in part, by increasing the sampling time, but this would have rendered the technique even less practicable. At best, carbon sampling was cumbersome and relatively time consuming, and was not applicable to an on-the-spot analysis.

It was apparent that there was a need for a method of analysis which could be used aboard ship to determine the total hydrocarbon concentration in the atmospheres of nuclear submarines. This realization led to the development of an instrument called the Total Hydrocarbon Analyzer.

INSTRUMENTATION AND PROCEDURE

The development of the Total Hydrocarbon Analyzer has been described in detail elsewhere (5). Briefly, the Total Hydrocarbon Analyzer is a gas chromatographic system which employs a flame ionization detector. This detector is highly sensitive to hydrocarbons and, to a lesser degree, is sensitive to other organic substances. It is relatively insensitive to water and other common inorganic gases, such as carbon monoxide and carbon dioxide.

The operation of the Total Hydrocarbon Analyzer uses a technique known as the "backflush." A sample of gas to be analyzed is introduced into the Analyzer in the usual fashion, with the carrier gas flowing in the normal direction. After methane and Freon-12, two of the major organic contaminants in the atmosphere of a nuclear submarine, are eluted through the chromatograph, the direction of carrier-gas flow in the column is reversed and the remaining components are regrouped and eluted as a single "lumped" peak. The area of the "backflushed" peak constitutes the measure of the total hydrocarbon content.

APPLICATION TO SHIPBOARD USE

Several models of the Total Hydrocarbon Analyzer have been designed and fabricated at NRL. These models have been used successfully on board several operating submarines (6,7). On these occasions, the Analyzer has been shown to be versatile and adaptable to the study of shipboard problems, such as determination of the efficiency for removal of various organic contaminants by the main-filter carbon beds and the CO/H_2 burners.

In order to make shipboard use of the Total Hydrocarbon Analyzer more practical, a scheme was devised for cleaning the ship's air so that it could be used as an air supply for the analyzer. Figure 3 illustrates such a scheme, in which an air supply is obtained by tapping the ship's air bank and reducing it to a suitable working pressure. The regulated air is metered into the catalytic reactor which contains a palladium-on-alumina catalyst maintained at a temperature of 600°C. The effluent air from the reactor is passed through an acid scrubber. After leaving the scrubber the purified air is split into two streams. One stream constitutes the carrier gas for the chromatograph, and the other serves as the air supply to maintain the flame for the detector.

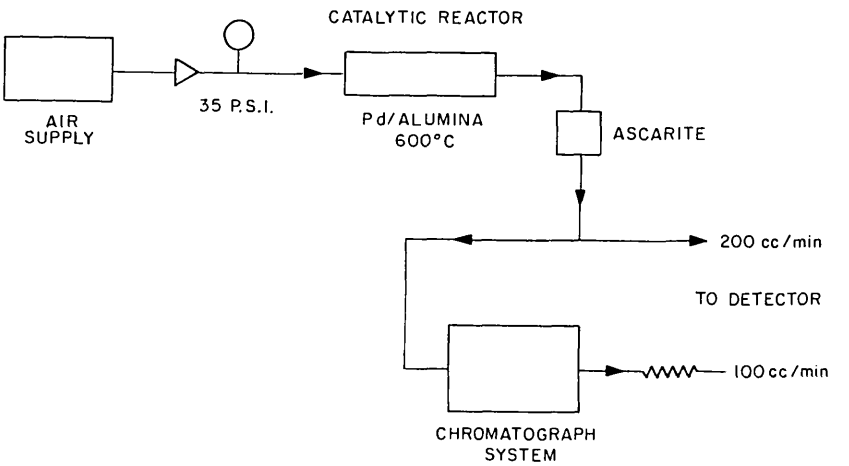

Fig. 3 - Air-purification system for the Total Hydrocarbon Analyzer

The major difficulty in cleaning the ship's air for use with the flame-ionization detector was the oxidation of methane and Freon-12. Figure 4 shows a series of three chromatograms, a through c. Chromatogram a represents the analysis of a test mixture of approximately 100 ppm each of methane and Freon-12. This mixture was used as the influent to the catalytic reactor. Chromatograms b and c show the effluent of the reactor at 500°C and 600°C respectively. It is apparent from these chromatograms that the system can remove methane and Freon-12 thoroughly from the air at 600°C.

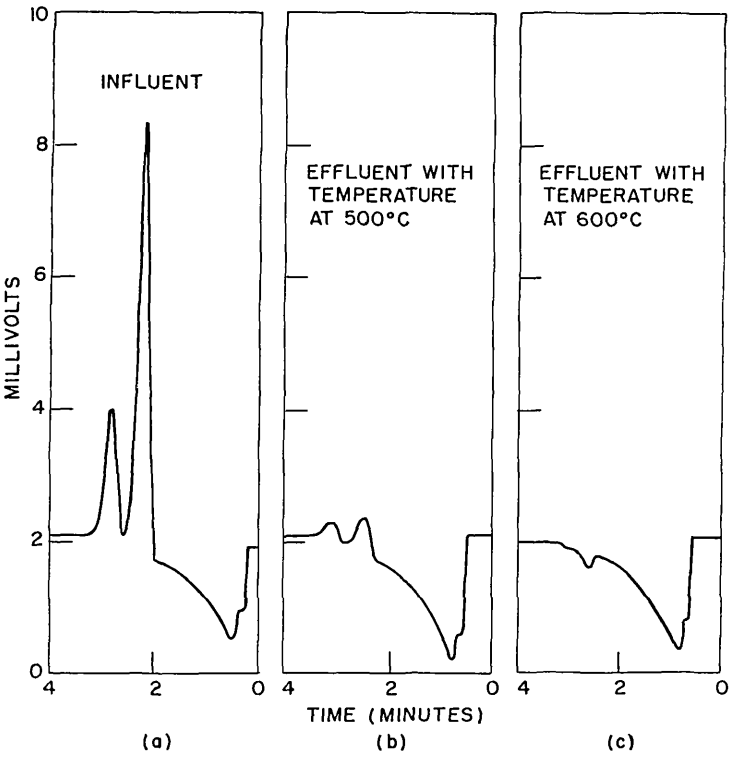

Fig. 4 - Effectiveness of removal of methane and Freon-12 from air supply for Total Hydrocarbon Analyzer

TOTAL HYDROCARBON CHROMATOGRAM

Figure 5 shows a chromatogram of an air sample from the USS SCAMP (SS(N)588). The backflushed total hydrocarbon peak is not quite symmetrical. However, the area under the curve can be determined without significant error. The methane and Freon-12 peaks are symmetrical and are sufficiently resolved that these concentrations can be determined by peak heights. The total time for this analysis was less than ten minutes. A single laboratory determination of total hydrocarbons by the carbon-sampling method requires seven hours for the desorption step alone.

COMPARISON OF TOTAL HYDROCARBON DETERMINATIONS

Table 3 shows some determinations of the total hydrocarbon contamination made aboard the SCAMP by the Total Hydrocarbon Analyzer, and comparable determinations made by the carbon-sampling method. The total hydrocarbon values as determined by the carbon-sampling method are considerably less than 50 percent of the values as determined by the Analyzer. This disparity is due largely to the unrecovered portion of the material that was adsorbed at this relatively low concentration of contaminants.

CONCLUSIONS

Sampling of atmospheric gases on submarines for later analysis in the laboratory has always been a problem. The judicious choice of equipment and techniques is paramount in obtaining a representative sample that will not change during storage and transit.

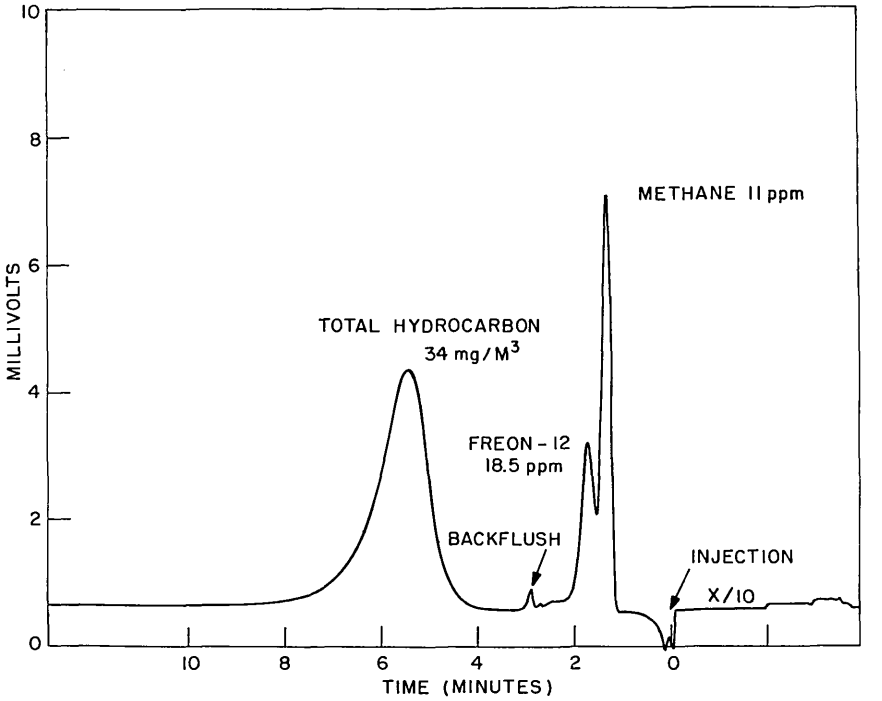

Fig. 5 - Backflush chromatogram of air sample in USS SCAMP

Table 3
Analytical Carbon Samples, USS SCAMP
(Exposure Time 12 hr in AMSLL)

Sample No.	Date	Exposure Period	No. hours Subm. at Start	Total Hydrocarbon* (mg/m^3)	Average Hydrocarbon† (mg/m^3)
1	3-12-64	0200-1400	36.0	2.0	18.5
2	3-15-64	0235-1435	108.5	8.0	16.0
3	3-16-64	0105-1305	131.0	6.0	16.0
4	3-17-64	0135-1335	155.5	4.8	18.6

*As determined by the carbon-sampling method.
†Average of concentration at the beginning and end of sampling as measured with the Total Hydrocarbon Analyzer.

The NRL Total Hydrocarbon Analyzer has been demonstrated to be suitable for shipboard operation. It fulfills a need for a method of analysis which can be used aboard ship to determine the total hydrocarbon concentration. The use of the instrument has been made more practical by devising a scheme for purifying the ship's air to make it suitable for use as an air supply for the detector.

FUTURE WORK

The usefulness of the Total Hydrocarbon Analyzer has been extended to analysis of compressed-air samples which have been collected aboard selected submarines and sent

to NRL. Further work is planned on sampling techniques to compare results obtained by the Analyzer aboard ship with such samples sent to the Laboratory. The effect of storage on compressed-air samples is particularly important, since some samples may be stored for a considerable time before analysis.

The Total Hydrocarbon Analyzer shows promise in another application. Preliminary experiments have indicated that this instrument can be effective in the analysis of specific halogenated compounds of current interest in some nuclear submarines, such as Freon-11 and methyl chloroform. Further work in this area is progressing.

The Total Hydrocarbon Analyzer will also be examined as a means for measuring the degree of saturation of the main filter carbon in the ships' ventilation systems.

As soon as certain minor modification are made in the instrument and further trials at sea are made to prove its operational capabilities, it is recommended that BuShips NAVSHIPSYSCOM procure commercial units for issue to each nuclear submarine.

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Chapter 5
Activated Carbon - Atmosphere Purification and Analysis

J. E. Johnson

INTRODUCTION

Activated carbon (charcoal) has been used in nuclear submarines in a variety of ways related to atmosphere control and purification. Activated carbon has a large surface area per unit weight or volume of the solid. Effective adsorption surface is of the order of 1500 m^2/g (seven million square feet per pound) of carbon. Another attractive feature is that activated carbon is effective in adsorbing and removing organic molecules such as hydrocarbons even from a humid gas stream. In fact, water molecules on the surface can be replaced by organic molecules. These characteristics make activated carbon useful for atmospheric filter applications and also for collecting samples of atmospheric contaminants for subsequent analysis.

ACTIVATED CARBON IN ATMOSPHERIC FILTERS

Beginning with NAUTILUS, nuclear submarines have used activated carbon as an important part of the atmosphere-purification system. This material can effectively adsorb up to 20 to 25 percent of its own weight in hydrocarbons and other organic vapors, in this way removing the vapors from the atmosphere. In submarine operation, the carbon is not regenerated, and when it is saturated (i.e., when its adsorptive capacity is exhausted), it must be replaced by fresh carbon. When properly used, activated carbon has been a major factor leading toward cleaner atmospheres on nuclear submarines.

In the early days of operation of submarines such as USS NAUTILUS, USS SEAWOLF (SS(N)575), and USS SKATE (SS(N)578), the atmosphere during submergences was so heavily contaminated with organic vapors that the carbon often was saturated within 24 to 48 hours (1). For example, in 1957, SEAWOLF had a main-filter capacity of 125 lb of activated carbon. At a concentration of 200 mg/m^3 and an air-flow rate of 1200 cfm, this carbon was exposed to 418 g/hr of organic vapors. In 24 hours this rate would amount to 10 kg, or 22 lb, which is approaching the adsorption capacity of the carbon. This situation was caused by the heavy input into the atmosphere of organic vapors from many sources. It was obvious that an exorbitant quantity of activated carbon (100 to 150 lb per day) would be needed to cope with an input of 20 to 25 lb of hydrocarbons per day, an amount equal to more than three gallons of liquid per day.

By analysis of samples of carbon from the submarines, the principal sources of contamination were identified (paint solvents, mineral spirits, diesel fuel, etc.). NRL recommended prohibition of painting while submerged and controls on amounts used aboard ship at any time. BuShips (now Naval Ship Systems Command) implemented these recommendations with an instruction to the fleet. By gradual or sporadic compliance with the instruction, the hydrocarbons and other contaminants were reduced. These cleaner submarines were able to use the filter carbon more successfully. In 1958 SEAWOLF provided

an example of the effectiveness of contamination-source control when no interior painting was permitted for three weeks prior to and throughout its record 60-day submergence. Also, USS SARGO (SS(N)583), in October 1959, by limiting painting and otherwise exercising good habitability discipline, had a maximum hydrocarbon concentration of 30 mg/m^3 during the early part of a submerged cruise from Mare Island to Pearl Harbor (2). As if to to emphasize this good control, the crew of the SARGO did some painting near the end of the cruise, which caused the atmospheric hydrocarbon concentration to rise from 20 mg/m^3 to 184 mg/m^3 within a few hours.

Today most of the nuclear submarines are cooperating in a material effort to control all known sources of contamination, with the result that it is no longer unusual to maintain the concentration below 30 mg/m^3 (3). Under these circumstances, a fresh charge of carbon will be effective for 20 days or longer. Other factors contributing to the overall cleanliness are: (a) increase in filter-bed capacity (in FBM submarines to 500 to 600 lb of carbon), and (b) increase in capacity of each CO/H_2 burner to 500 cfm.

Unfortunately, the input into the atmosphere of halogenated hydrocarbons such as methyl chloroform and Freon-11 has created new problems which have made correct practice in using carbon filters even more important. Carbon is useful in handling Freon-11 only if a strict procedure is followed (4).

CURRENT OPERATING GUIDELINES

It seems appropriate to reiterate the operating guidelines which will promote the every-day optimum use of the carbon bed.

1. Carbon should not be installed in new submarines prior to closed-boat operation. The carbon is not useful during the construction period; it soon becomes saturated, and cannot remove contaminants during subsequent closed-boat operation. In fact, such contaminated carbon can contribute harmful solvents (e.g., chlorinated hydrocarbons) to the closed-boat atmosphere. Furthermore, a carbon bed saturated with hydrocarbons is a flammability hazard which is more susceptible to ignition during construction or overhaul.

2. Fresh carbon should be installed in the main filter immediately prior to prolonged submergences. Carbon which has been exposed to the atmosphere during upkeep periods should be removed, because it will have been contaminated and rendered ineffective. It is emphasized again that such carbon can also contribute contaminants to the atmosphere. This is particularly bad during the current siege of contamination by various halogenated compounds (e.g., methyl chloroform).

3. The main-filter carbon should be replaced frequently during the first few months of operation of a newly activated submarine. Many boats have found it desirable to change carbon every 20 days of submergence during the first year of operation. Of course, carbon should be replaced earlier if unusual conditions warrant it.

4. The carbon in other applications, such as sanitary-tank filters, should be handled much the same as the main-filter carbon. Such carbon should be changed no less frequently than the main filter. Certainly fresh carbon should be used at the beginning of each cruise.

ACTIVATED CARBON FOR ATMOSPHERE SAMPLING

Activated carbon has been consistently one of the most productive sources of analytical information on the trace contaminants in atmospheres of nuclear submarines (1,5). This is true even though from time to time various analytical instruments have been

brought on board such submarines and used by NRL chemists. Several programs of sampling based on carbon samplers have been established by BuShips with NRL guidance to determine the level of trace contaminants in the submarines (6). Although these programs were useful, the value of this method lessened as the contaminant level decreased. For the past several years, sampling with special carbon canisters has been used only in special instances.

Another fruitful source of information has been carbon taken from the main filter beds. Particularly in the case of the FBM submarines, a great deal has been learned concerning the types of contamination present, together with a surprisingly good estimate of average concentrations of total trace contamination.

A unique value of activated carbon is its ability to concentrate the vapors from a large volume of atmosphere. This ability enables the analyst to obtain, by desorption of the carbon in the laboratory, useful quantities of liquid samples for detailed analysis. By this means, the characterization of contaminants by type and individual has been possible (7,8).

OTHER ANALYTICAL TECHNIQUES

In recent years the development of more sensitive analytical instruments has permitted use of other sampling and analytical methods. A total hydrocarbon analyzer (9) has been developed and is undergoing sea trials (3,10). This instrument is designed to be used aboard ship for determination of the overall organic contamination level. Its principal advantage is that answers will be obtained on shipboard for use by operating personnel.

Currently, a good deal of sampling is accomplished by pumping air from the ship's atmosphere into stainless steel bottles using a small oil-free compressor. Advantages of this method are: (a) all atmospheric components are sampled, regardless of volatility, including fixed gases; (b) samples are obtained in a few minutes; and (c) samples are immediately available, not requiring special preparation such as in the desorption of carbon.

A very promising analytical approach which may take advantage of either carbon desorbate or compressed atmosphere samples is the combination of gas chromatograph and rapid-scanning mass spectrometer (11). This equipment has been installed recently at NRL, and is now in operation. This system has the potential of providing more complete identification of the trace contaminants in submarine atmospheres than has been available before.

CONCLUSIONS AND FUTURE PLANS

Carbon will undoubtedly continue to play a strong supporting role in the analysis of submarine atmospheres, in any case, because of the potentially large amount of concentrated material it presents for analysis. It is particularly noteworthy that a sample of carbon from the main filters is a useful source of information concerning the atmosphere, and it is always available in an emergency.

Research will be continued on improved methods of analysis with carbon and on potential methods for rapid shipboard determination of the extent of saturation of the main carbon bed. Use of carbon to scavenge gross contaminants from the ship's atmospheres will continue to be monitored.

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Chapter 6
Development of Interior Paints for Nuclear Submarines

T. R. Walton

INTRODUCTION

It was shown in 1958 that much of the hydrocarbon contamination in a submarine atmosphere can be caused by paints (1). As a result, special painting instructions were developed to avoid the introduction of significant amounts of these volatile organic solvents into the atmosphere of the submarine while it is on patrol (2). Essentially all painting with organic-solvent-thinned paints must now be completed on nuclear submarines five days prior to submergence (3). During this five-day period, a maximum of one quart of organic-solvent-thinned paint per day may be used. If large areas of painting are necessary during this five-day period, then an approved proprietary water-base paint must be used. No painting should be done while on patrol.

Since it is desirable, and many times necessary, to delay most of the interior painting until the other construction and maintenance work is completed, a large amount of painting remains to be done during this five-day period. As a result, either this painting never gets completed, or large quantities of the proprietary water-base paints are used. Unfortunately these paints are quite inferior to the organic-solvent-thinned paint normally used, MIL-E-17970C (Formula 124/58) (4), and are therefore undesirable for widespread use. NRL had developed by mid-1961 a satisfactory touch-up acrylic latex paint which would be nontoxic, but which also failed to meet the latest standards for use during the critical periods (3). Thus a program was initiated at NRL during early 1964 to develop a high-quality paint for use during this five-day interval and, hopefully, even under sealed-ship conditions. This latter capability would allow much of the interior painting to be done by the ship's personnel after the submarine has departed on its patrol.

DEFINITION OF PROBLEM

Two fundamental requirements of this new paint are: (a) that it release little or no volatile organic compounds into the submarine's atmosphere during and after application, and (b) that it be self-extinguishing in its fire-retardancy performance. In general, it should have at least the minimum performance of the chlorinated alkyd paint that it is to replace. This would mean a 60° gloss between 35 and 50 percent, good leveling, so that a smooth surface which does not show brush marks is obtained, sufficient hiding power to cover an area in one coat, and the capability of withstanding abuse by moisture, abrasion, oil and grease, temperature extremes, etc. It would also be desirable for this new paint to dry to a flexible film in order that it can be used on resilient materials such as the vinyl foams applied as insulation.

APPROACH

A paint consists of four principal components: pigments, solvents, binders, and additives. The pigments are finely divided solids that provide hiding and color. The binders are oils, resins, or polymers which form the protective film and hold the pigments. The solvents are volatile liquids which provide the proper viscosity for application of the

paint. Additives are used, generally in small quantities, to improve the performance of the paint and include wetting agents, defoamers, driers, coalescing aids, and antiskinning agents.

If water is used as the solvent in place of organic liquids, the volatile organic content of the paint is eliminated or, at least, greatly reduced. Basically, there are two choices for the development of a water-base paint. The film-forming resin (pigment binder) can be a dispersion in water such as the latex or emulsion systems, or it can be a water-soluble material which converts to a water-insoluble polymer on drying. These paints can be made self-extinguishing in their fire-retardancy performance by incorporating a halogen source (either chlorine or bromine) and antimony oxide into the formulation. The halogen source can be an additive such as an inert halogenated organic compound, where its function may be considered as a fire-retardant plasticizer, or it may be added as a reactive part of the film-forming polymer. The former is represented by such materials as the chlorinated paraffins, and the latter by poly(vinyl chloride).

Since the last annual progress report (5), four principal systems have been studied: (a) a latex paint containing a chlorinated additive and antimony oxide (Sb_2O_3), (b) a paint based on a vinyl chloride/acrylic copolymer emulsion and Sb_2O_3, (c) a paint based on a convertible, water-soluble chlorinated alkyd and Sb_2O_3, and (d) a paint based on a water-soluble linseed oil derivative and containing a chlorinated additive and Sb_2O_3.

Antimony oxide has been used along with titanium dioxide in all formulations because of its remarkable property of greatly improving the effectiveness of the halogen as a fire-retardant additive. In the absence of halogen, the antimony oxide contributes nothing to fire-retardancy. This synergistic effect is illustrated in Fig. 6. All formulations were identical in the series except for the Sb_2O_3 content, which was added by replacing a part of the titanium dioxide pigment with an equivalent weight of Sb_2O_3. The ignition time is the time it takes the dried paint film on an asbestos support to ignite using a hot microburner gas flame. The burning time is the period it takes the dried paint film to burn six inches after it has been ignited and the microburner extinguished. The longer it takes to burn this six-inch length, the better the fire-retardancy performance of the paint. As the fire-retardancy performance improves, the burning film will self-extinguish itself during this six-inch burning period. As the fire-retardancy is improved further, the burning paint film will self-extinguish as soon as the source of ignition is removed (in this case, the microburner) and fail to burn any of the six-inch length.

The number of self-extinguishing samples as a function of the antimony oxide content is shown at the top of Fig. 6. It can be seen that the addition of only 0.86 wt percent of antimony oxide resulted in three out of the five samples to self-extinguish, and slowed the rate of burning of the remaining two samples for the six-inch length to 22.4 sec. This result compares to no self-extinguishment and an 18.3-sec burning time for the five paint samples containing no antimony oxide. At an antimony oxide content of 8.6 percent and higher, all samples were immediately self-extinguishing when the microburner was turned off.

DISCUSSION

The Latex/Halogenated Plasticizer Paints

The latex/halogenated plasticizer system is the most versatile of the four studied. Essentially any latex paint which has exceptionally desirable properties in terms of non-toxicity, gloss, leveling, water resistance, etc., can be converted into a fire-retardant paint by adding the antimony oxide and the halogenated plasticizer. The combined properties and performance of the modified system must be determined, however, since there is always the possibility that these additives can adversely affect the desirable characteristic of the basic paint.

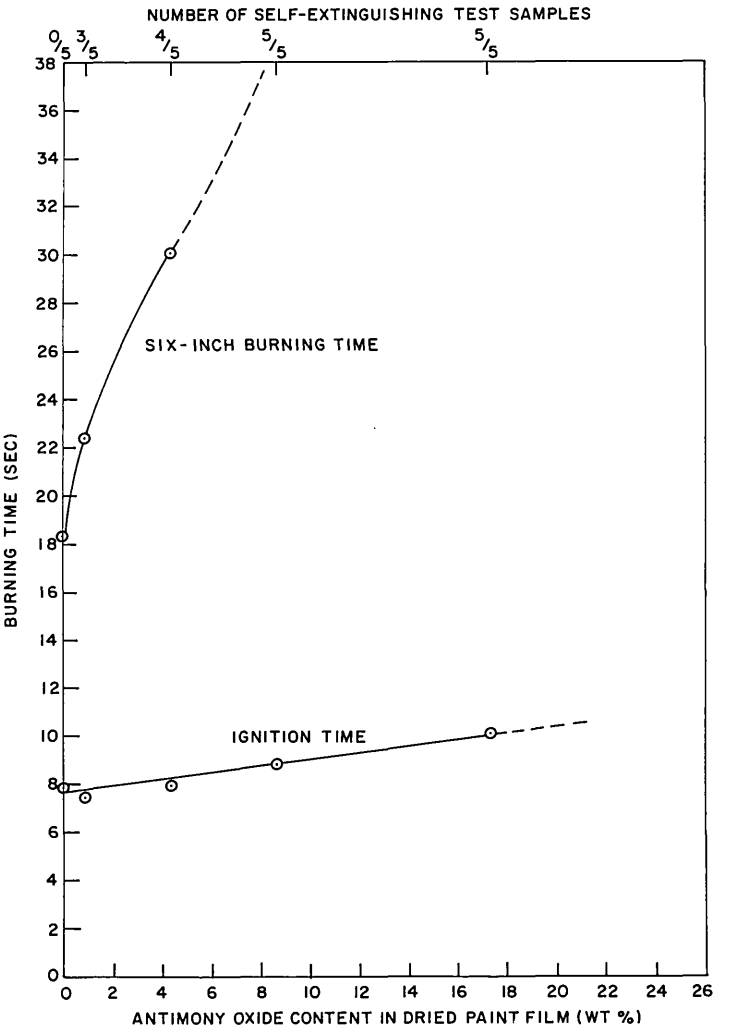

Fig. 6 - Effect of Sb_2O_3 content on fire retardancy of an acrylic latex paint containing 10.8 percent chlorine in dried paint film

Three chlorinated organic compounds have been studied as fire-retardant additives: a liquid chlorinated biphenyl containing 54 wt percent chlorine, a solid chlorinated paraffin containing 70 wt percent chlorine, and a chlorinated rubber dispersion containing 50 wt percent solids, of which 67 wt percent is chlorine. It was found that the aromatic bonded chlorine from the chlorinated biphenyl was less effective on an equal chlorine weight basis than the aliphatic bonded chlorine from the chlorinated paraffin or the chlorinated rubber. In addition, since the chlorinated biphenyl contained substantially less chlorine per gram of solid additive than the chlorinated rubber or paraffin, this additive must be used in greater percentage of the total formulation than the other two to yield an effective fire-retardant paint. At these higher levels of liquid chlorinated biphenyl, the paint remained impractically tacky.

The solid chlorinated paraffin was an effective fire-retardant additive, but some difficulty was encountered in introducing this material into the paint formulations. Proper dispersion of the chlorinated paraffin was difficult to obtain, and a number of properties of the basic latex paint were affected. This included a substantial reduction in the 60° gloss

from around 65 percent for the basic latex paint to 20 percent for the chlorinated-paraffin-modified paint. The scrub and water resistance of the modified paint was also adversely affected. Using the Gardner Model 105 Straight Line Washability and Abrasion Machine, with an abrasive soap medium, film failure occurred at around 2000 oscillations for the modified latex paint, while the basic latex paint could withstand 4000 or more oscillations. The hiding power of the modified latex paint was also reduced.

The chlorinated paraffin is a white powder which was added to the formulations during the preparation of the pigment dispersion. Microscopic examination of the TiO_2-Sb_2O_3 pigment-chlorinated paraffin dispersion indicated that the paraffin particles were only moderately distributed among the pigment particles and were much larger in size. The methods used to prepare pigment dispersion generally do not result in reduction of particle size, but, instead, mainly in breaking up and dispersing solid aggregates. It was thus felt that if the chlorinated paraffin could be predispersed into a fine-particle-size water dispersion, and added to the formulation in this form, improvement in the final paint performance could be expected. However, it was found that a chlorinated rubber dispersion was already available from a commercial source. Since the chlorinated rubber is quite similar in its chemical structure and composition to the chlorinated paraffin, it was decided to use this material rather than spend time attempting to prepare a dispersion from the chlorinated paraffin.

The fact that the dispersion contains 50 percent water was of no consequence, since most latex paints are formulated to contain approximately 50 wt percent solids anyway, and thus the addition of the chlorinated-rubber dispersion would cause no dilution. Furthermore, since the last ingredient generally to be added to the latex paint during its preparation is part of the water, this water could be just as well added as part of the chlorinated-rubber dispersion.

The versatility of the above system was even further enhanced by using this chlorinated-rubber dispersion, since now it would be possible to take an already prepared commercial or experimental paint and simply mix in the chlorine source in the form of the dispersion and the antimony oxide in the form of a concentrated paste dispersion in water, without going through the trouble of preparing the paint from the beginning.

Adding the chlorinated rubber and an antimony oxide aqueous dispersion to the basic latex paint did not affect the properties of the basic paint to the extent that the previous fire-retardant additives had. Self-extinguishing paints were obtained when the chlorine and antimony oxide content were approximately 35 and 10 wt percent, respectively, of the combustible solids in the dried paint film. Although the 60° gloss was reduced to 40 percent at these levels of fire-retardant additives, it is within the 35 to 50 percent range desired. Hiding and leveling performance of the basic latex paint were not affected; however, these properties were only fair to begin with, and further improvement would be desirable. Other performance characteristics of this paint, such as scrub and water resistance and freeze-thaw stability, remain to be evaluated.

Vinyl Chloride/Acrylic Copolymer Emulsion Paints

Because of the adverse effects encountered from the addition of the chlorinated additives to the latex paints, a paint system in which the film-forming polymer (pigment binder) contained chlorine in its structure was investigated. Initial studies with a commercially available vinyl chloride/acrylic copolymer emulsion (48 percent solids, 30 wt percent chlorine in solids) were encouraging. Paints prepared with this emulsion were immediately self-extinguishing and had 60° glosses in the 50-percent range. The scrub resistance was inferior to the organic-solvent-thinned, chlorinated alkyd paint, but better than the approved proprietary latex paints now being used. Leveling and hiding were also

inferior to the chlorinated alkyd but qualitatively similar to the proprietary latex paints. However, at the present time, it has not been possible to overcome the tendency of paints based on the emulsion to form bubbles and foam badly during their application. Although this tendency was temporarily solved with a few antifoaming agents, these additives lost their effectiveness after the paint was stored for about a week. Further efforts with this emulsion have at least temporarily been discontinued.

Convertible, Water-Soluble, Chlorinated Alkyd Paints

A paint system based on a water-soluble resin that is converted to a water-insoluble film on drying has a number of inherent advantages over a latex-type paint. Such paints generally have simple formulations compared to the complex formulation of latex paints – high gloss, good leveling, mechanical and freeze-thaw stability, and high hiding power.

Initial studies in this system were with an experimental, water-soluble, chlorinated alkyd resin from an industrial laboratory. Paints prepared with this resin have had excellent fire-retardancy, hiding, leveling, and gloss performance. Water and scrub resistance were not evaluated, because it was learned from the manufacturer that the resin solution as supplied contains approximately 30 wt percent butyl cellosolve as a co-solvent. Using the resin solution in a typical paint formulation results in a final volatile organic content of around 10 percent, much too high from toxicity considerations. Although most water-base paints contain at least 5 wt percent volatile organic solvents as coalescing aids, co-solvents, defoamers, and antifreeze agents, only those paints containing less than 5 percent volatile organic solvents have been of interest.

The manufacturer has discontinued development of this resin, and further attempts to reduce the co-solvent content cannot be expected from the company. NRL will therefore direct some effort in this direction. One water-soluble chlorinated alkyd resin has been prepared in which the co-solvent content of the final resin solution was only 15 wt percent, compared to 30 percent for the commercial resin solution. However, this particular resin was very slow drying (over 24 hours), and therefore impractical for a paint that is to be used in such an active and congested place as the interior of a nuclear-powered submarine. Work is continuing with this system to improve on water compatibility and drying time.

Water-Soluble Linseed Oil/Halogenated Plasticizer Paints

A water-soluble linseed oil which converts to a water-insoluble film on drying is commercially available. This material is described as a polyether derivative of a chemically modified linseed oil and is supplied as a solution containing 85 wt percent linseed oil and 15 wt percent of a volatile organic solvent used as a coupling agent. When this resin solution is used in the preparation of a paint, the final volatile organic content can be kept below 5 percent.

Since the modified linseed oil resin is combustible, a fire-retardant additive is necessary. A chlorinated material such as a chlorinated paraffin or wax can be dissolved in the resin solution to yield a viscous solution which on reduction with water yields what appears to be a stable oil in water emulsion.

Paints having excellent fire-retardant performance and good hiding, gloss, and leveling have been prepared from this linseed-oil solution containing 42 wt percent of a chlorinated paraffin (70 wt percent Cl). However, these paints exhibited the typical slow drying of linseed oil, taking longer than 48 hours to become tack free. Drying time was greatly reduced by replacing 43 wt percent of the linseed oil/chlorinated paraffin solids with an equivalent amount of an acrylic resin emulsion. These paints were tack free and dry to touch in less

than one hour. However, because part of the chlorinated paraffin was replaced with the combustible acrylic resin, the fire-retardancy performance was decreased. Efforts are now being directed toward bringing the chlorine content up to a more effective level by either dissolving larger amounts of the chlorinated paraffin in the linseed oil, or by adding the chlorinated-rubber dispersion previously discussed.

FUTURE WORK

Additional improvement and final laboratory evaluation of the systems discussed are needed before field testing can be started. The latex/halogenated plasticizer system requires improvement in leveling and hiding power and final evaluation of fire retardancy and scrub resistance. Since the vinyl chloride/acrylic co-polymer emulsion-based paint system needs considerable improvement in a number of areas – hiding, leveling, scrub resistance, and application properties – further work has been discontinued. The water-soluble chlorinated alkyd system depends on the preparation of a suitable film-forming resin. This preparation could involve a substantial amount of time and work, and only a minor effort will be continued in this area unless excessive problems arise with other systems. The study of the linseed oil/halogenated plasticizer system has just recently been started, and a concerted effort will be made to evaluate the system rapidly.

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Chapter 7
Review of the Electrolytic Production of Oxygen in Nuclear-Powered Submarines

J. C. White

BACKGROUND

The supply of oxygen is one of the two largest and most essential requirements in sustaining life in a nuclear-powered submarine, the other being the removal of CO_2. While many sources of breathing oxygen are normally available for use in confined atmospheres, it was apparent early to the Bureau of Ships that for the prolonged submergences expected from the nuclear submarines, oxygen could be supplied only from some type of electrolytic cell. For the initial, limited periods of submergence, large oxygen-storage flasks and/or chlorate candles (1) were adequate, but the necessary storage space for extended submergences was not available.

For these reasons BUSHIPS (now Naval Ship Systems Command) contracted with the M. H. Treadwell Company in 1953 for the development of an electrolytic oxygen generator (2). In order to avoid the possible difficulties in obtaining suitable high-pressure compressors for both hydrogen and oxygen, the decision was made at that time to develop a 3000-psi electrolytic cell system. As a result of this work, high-pressure oxygen generators have been installed on the NAUTILUS and in each of the FBM submarines and have become an essential part of their operation.

In view of the inherent difficulties involved in maintaining high-pressure hydrogen and oxygen systems, and because of a number of difficulties which have been encountered in the operation of these high-pressure electrolytic oxygen generators, it appeared worthwhile for NRL to review not only the presently used method, but other possible methods for producing oxygen in nuclear-powered submarines.

PRINCIPLES INVOLVED IN ELECTROLYTIC GENERATION OF OXYGEN

While the electrolytic generation of oxygen and hydrogen is one of the simplest and most familiar of all electrochemical processes, the basic principles involved should be briefly reviewed. In order to generate hydrogen gas by the reduction of hydrogen ions at a cathode in an electrolytic cell, the electrode material must be inactive in a chosen electrolyte so that it will not dissolve on open circuit; at the same time, because of the need for economy in power, its hydrogen overvoltage should be as low as is economically feasible. Hydrogen overvoltage can be defined as the difference in potential between the equilibrium hydrogen potential in a given solution and that which must be applied to cause a given current to flow while evolving an equivalent amount of hydrogen at that electrode. These factors are well exemplified by the noble metals, since they have a much lower hydrogen overvoltage than any of the other metals; however, their cost is very high. Nickel is often used as a compromise in alkaline solutions because it does have a relatively low hydrogen overvoltage. This potential difference, or overvoltage, is a function of both the current and the electrode material and is one of the most important factors in electrochemistry; it is also responsible for much of the heat loss in such a cell.

The electrolyte should have high conductivity and can be an acid, a base, or a salt solution, provided that its metallic ion is above hydrogen in the emf series; otherwise, instead of the reduction of hydrogen ions, the metal may be plated out on the cathode. Moreover, the anion must not be oxidized in preference to the OH^- ion.

The electrode used for oxygen evolution must be an inert material; otherwise, at the very high oxidizing potential at which it must be maintained, it will be oxidized and gradually corrode away. In some cases it is possible for a very thin oxide layer to form which will protect the underlying metal from further corrosion. Here again the noble metals are by far the best from the standpoint of stability, but their high cost prevents their use in other than very special cases. Fortunately, nickel also has very good electrode characteristics in alkaline solutions, and when oxidized, a very thin protective film is formed. For these reasons nickel is used in most practical electrolytic oxygen generators.

In this type of cell the reduction of hydrogen ions to hydrogen and oxidization of hydroxyl ions to oxygen take place in continuous fashion in an alkaline solution at almost 100 percent coulombic efficiencies. In order to reduce the power requirements, the current density on the electrodes is usually maintained as low as is economically feasible by increasing the area of the electrode, thereby reducing the voltage required. At the same time, the distance between the electrodes, which must be kept to a minimum, usually becomes a compromise between finding a diaphragm able to keep the two gases physically isolated, and avoiding an increase in the resistance to current flow through the solution path.

These factors cover essentially all the electrochemical principles involved in any type of oxygen generator. It can, therefore, be concluded that most of the remaining problems involved in obtaining a safe, useful, and reliable electrolytic oxygen generator are in design, engineering, and selection of compatible materials.

PRESENT HIGH-PRESSURE METHOD

While the early nuclear submarines were able to operate with oxygen flasks, backed up with oxygen candles, the long-submergence capability of the FBM submarine required oxygen supplied by electrolytic generators. These, as indicated previously, were developed and supplied by the M. H. Treadwell Company (2). This generator is a high-pressure electrolytic cell whose design was based largely on industrial experience in this country and in Germany. A high-pressure system was selected to eliminate the use of compressors for recharging the oxygen storage flasks and for pumping the hydrogen overboard. While high-pressure generators have been used industrially for many years, the combination of stringent requirements for both safety and submarine operation necessitated a considerable amount of development, design, and engineering.

One of the most difficult, although essential, items required for this system was sensitive and reliable control of the difference in pressure across the diaphragm that isolates the hydrogen and oxygen evolved in these cells. This requirement arises from the fact that the volume of oxygen produced is only one-half that of hydrogen. In order to prevent rupture of the diaphragm, this difference in pressure across the diaphragm must be limited to a few inches of water pressure. It was also necessary to design and develop many other safety devices to protect the other operations in the high-pressure system.

Despite various difficulties encountered in the use of these oxygen generators in the nuclear-powered submarines, they have supplied oxygen to a fleet of these submarines for several years. It should be emphasized that most of these difficulties have been caused by failures of materials and by problems of maintenance. Some of these problems have been corrected, and there has been a gradual improvement in oxygen-generator performance.

POSSIBLE NEW METHODS

Although the present Treadwell generator now appears to be performing in a reasonably satisfactory manner, because of the importance of this problem it is essential that a continuing effort be made to seek improvements by decreasing equipment size and improving simplicity, efficiency, safety, and dependability of generator operation. Since it has not been established that all of these gains can be obtained by improving (or modifying) the present Treadwell cell, it is essential that other electrochemical methods for generating oxygen be examined. Possible methods therefore will be discussed, including advantages as well as problems likely to be encountered in their submarine use.

HIGH-PRESSURE CELLS

Bipolar Type

The Bureau of Ships has supported further work on high-pressure electrolytic methods of generating oxygen. The first cell of this type is the so-called "bipolar cell" in which a group of individual electrolytic cells are arranged electrically in series within a single vessel, so that the cathode of one cell becomes the anode of the next cell, etc., for as many cells as are required. This system would not only reduce the number of high-pressure vessels required, but also the number of electrical and gas connections which must pierce the high-pressure vessel. This study was undertaken by the Treadwell Company, but it was discontinued after a number of difficult design problems were encountered.

High-Efficiency Cell

In 1964 BuShips awarded a contract to the Allis-Chalmers Company for the development of a completely new type of (although nominally a bipolar) high-pressure electrolytic oxygen generator (3) which should have a much lower power requirement, resulting in a reduced cooling requirement. The contractor is attempting to utilize electrodes which had been developed from their research on fuel cells, both in-house and under contract to several government agencies. These electrodes permit the hydrogen and oxygen to be evolved on the side of an electrode away from the electrolyte and into a gas space. This feature makes it possible to reduce the distances between the electrodes, thus requiring a lower voltage for the cell at any given current. These cells are expected to operate at about 1.7 volts, in comparison to almost 3 volts now required for the Treadwell cell. This program is proceeding in a satisfactory manner, and if it is successful could reduce the power requirements almost by half and the space requirements to less than one-third of the present system. It would, of course, retain the difficulties inherent in any high-pressure hydrogen and oxygen system.

AMBIENT-PRESSURE CELLS

A number of other methods for possible use in nuclear submarines have been studied from time to time, but since they operate at atmospheric pressure they do require high-pressure compressors to pump the hydrogen overboard and to pump oxygen into storage flasks for as long as the latter requirement exists.

Methods have been proposed which would combine H_2 and CO_2 catalytically to form a storable product. While these methods are based on industrial experience, they will require further work to adapt them for use in submarines. NASA and the Air Force have sponsored work along these lines for possible use in manned space vehicles. It should be pointed out, however, that the only reason a low-pressure oxygen generator could not now be used is the apparent lack of a compressor for expelling hydrogen from the

submarine. Even the presently available chlorate candles for oxygen could be used to augment the high-pressure oxygen-storage flasks.

The development of a suitable hydrogen compressor does not appear to be very formidable, since industry has used 15,000 lb/sq in. compressors for hydrogen for many years, and AEC has used 30,000 lb/sq in. in compressors for several years. The Electric Boat Company in the development of the split-cell oxygen generator (4,5,6) (which will be discussed later) found one commercially available compressor for hydrogen which they believed was suitable for submarine use. Later in the construction of two of these split-cell systems, scheduled for installation in the SSB(N)623 and the SSB(N)626, they procured what must have been suitable compressors. As described subsequently, these generators were not installed for other reasons.

Split-Cell System

The first of the ambient-pressure methods to be discussed was developed from an idea originating at the Naval Research Laboratory in 1953 and commonly referred to as the "split-cell" system. This idea was a by-product of the Laboratory's study of alkaline batteries, particularly the nickel oxide-cadmium type, in which the cadmium negative plate has an excellent hydrogen overvoltage characteristic which permits the cadmium hydroxide to be reduced almost completely to cadmium before hydrogen is evolved (4). This work indicated that if the nickel oxide positive electrode in an ordinary nickel oxide-cadmium storage battery is replaced by a sheet nickel electrode, a cell results in which it is possible to generate a single gas at a time, thereby eliminating the need for a diaphragm and at the same time utilizing the inherently low internal resistance of a storage battery.

When a discharged cell of this type is charged so as to reduce the cadmium hydroxide to cadmium, about 95 percent of its capacity in ampere hours is passed before any measurable amount of hydrogen is evolved at the cadmium electrode. When hydrogen evolution begins, a significant change is voltage also takes place which can be utilized for control. The detection of hydrogen at this point could also be used for the same purpose. During this time the sheet-nickel positive plate is evolving oxygen equivalent to the current that is being passed. If the current is now reversed so that the cadmium electrode is discharged to the extent of its capacity, an equivalent amount of hydrogen is generated at the sheet nickel electrode. If two of these cells, one in a discharged state and the other in a charged state, are connected in series and current passed, oxygen is generated in one cell and hydrogen in the other. If the current is reversed each time sufficient current has passed to reduce the cadmium hydroxide in one cell to cadmium and, at the same time, to oxidize the cadmium to cadmium hydroxide in the other cell, and if this step is repeated after each cycle, a continuous generation of hydrogen and oxygen will occur. Each gas evolves in pure form from separate cells, with only a brief interruption for evacuation between each cycle. This method has the capability of being put to practice in a relatively short time, since any one of a number of the different sizes of commercially available nickel-cadmium cells could be used simply by replacing the positive nickel oxide plate with sheet nickel at the time of manufacture.

Following NRL initiation and evaluation of the concept (4), BuShips awarded a contract to Electric Boat Company in 1957 to develop this idea into a system for possible submarine use (5). This study fully demonstrated the feasibility of such a system (6). Later, as a part of their proposal for the construction of the nuclear-powered submarines, SSB(N)623 and SSB(N)626, the Electric Boat Company elected to provide a split-cell system in lieu of the Treadwell system. This change was accepted by the Navy as part of the contract. Unfortunately, during the final testing of this system in 1962 just prior to installation, it was discovered that there was a long period at the beginning of each cycle in which oxygen was not generated. After considerable investigation by the Electric Boat

Company it was pointed out to them by NRL (7) that, in their search for another source of cells, they had unknowingly been supplied with partially active plates instead of inactive nickel plates, with the result that the cells behaved to some extent like a low-capacity nickel oxide-cadmium storage battery. Thus, for several minutes at the start of each cycle they were simply charging and discharging two sets of low-capacity batteries. By the time this problem had been solved, it was too late for this system to be installed in the submarines for which they had been intended, and because of their size it was not possible to install them in any of the later classes of submarines.

It still is not clear why the volume of the cells in this system was so large (about 140 cu ft) in comparison to the size (35 cu ft) which originally had been estimated by the Laboratory (4). It is probable that Electric Boat Company was very conservative in their design, because the required space was available in the submarines in which they were to have been installed. It must be concluded that if the necessary compressors can be provided (and this seems assured), this system deserves further consideration in view of its potentialities. In fact, NRL is in a position to monitor an immediate NAVSEC design contract with an appropriate manufacturer with an option to procure and install such a generator on a new submarine during construction if the space, weight and cost characteristics prove reasonable.

Sulfate-Cycle System

The sulfate-cycle system, another method for supplying electrolytic oxygen, operates at atmospheric pressure and in addition provides caustic for the absorption of CO_2 (8). The essentials of this method have been used to a limited extent in industry for many years to produce sodium hydroxide and sulfuric acid by the electrolysis of a solution of sodium sulfate (9). In 1958 NRL undertook an exploratory study to determine the feasibility of this method for absorbing CO_2 and generating oxygen in a nuclear submarine. This study demonstrated that the method is feasible provided that diaphragms can be found which will withstand the sulfuric acid produced (10). In this method an 18-percent sodium sulfate solution is electrolyzed in such a way that the products of each electrode are kept from mixing. This is accomplished by means of diaphragms which separate the hydrogen and the sodium hydroxide formed at the cathode from the oxygen and the sulfuric acid formed at the anode. The alkali formed in the cathode compartment is then used in a scrubber to remove CO_2. The carbonates thus formed along with the remaining alkali are then neutralized by the sulfuric acid being produced at the anode, to give pure CO_2 and re-forming sodium sulfate. The CO_2 is then pumped overboard, and the sodium sulfate solution returned to the cell.

Although NRL demonstrated the feasibility of this method and found a suitable diaphragm (11), work on the pilot plant was discontinued after Ionics, Inc., proposed a more promising approach utilizing an ion-exchange oxygen generator and carbon dioxide absorption (to be discussed in the next section). Previously, however, Ionics, which had been involved in the development of an ion-exchange membrane for use in the electrolytic purification of water, became interested in the sulfate cycle as a result of their development of a rigid and efficient cation-exchange membrane for the production of caustic for industrial purposes (12). The method which NRL had been investigating depended upon the uniformity of the porosity of the diaphragms to control the flow of the electrolyte from the center compartment of the cell to the anode and cathode compartments. It was believed that the use of the cation exchange membrane developed by Ionics would make it possible to use a simple flooded cell and at the same time produce the high concentrations of caustic that are required.

Ionics used these membranes in building three cells for NRL in 1960 to demonstrate the simplicity and feasibility of this method (13). Due to long periods of drying out while standing prior to evaluation, some difficulties were encountered with the anode diaphragms

which originally had been supplied with these cells, but the results did indicate that a much simpler cell could be constructed by this method (14). Essentially all but the detailed design data are available for the development of this system (15), which now appears to be more promising than the NRL version of the sulfate-cycle system.

Ionics Electrolytic Oxygen Generator System

It is quite possible that the Ionics sulfate-cycle system would have been developed much further by this time had the company not proposed a completely new system to BuShips. In this system anion and cation exchange resin beads on screens are used as an electrolyte between a series of anion and cation exchange membranes in a cell in such a way that CO_2 can be scrubbed directly from submarine air at the same time that oxygen is being generated. This method was demonstrated experimentally by Ionics in a preliminary contract (16) with BuShips and has since been developed into a ten-man prototype system which utilizes full-size plates and membranes (17). This unit was delivered in 1965 and is now being evaluated at the Marine Engineering Laboratory. If successful, this method could lead to a solution of the two most basic problems in submarine habitability.

As already indicated, the development of any of these low-pressure systems would require either the use of compressors for expelling hydrogen overboard (and perhaps for pumping the oxygen into storage) or else the elimination of hydrogen and CO_2 by some type of catalytic method, which eventually will have to be done in any case for deep-submergence submarines.

CONCLUSIONS

In considering the overall picture of electrolytic oxygen generators, it can be concluded that there is considerable room for improvement by decreasing power requirements and equipment volume, while increasing the reliability of operation and ease of maintenance of the present equipment. In each of these methods for producing oxygen, with the exception of the Electric Boat Company version of the split-cell system, the electrolytic-cell portion in the system occupies a relatively small part of the total volume, so that any real saving in space will have to be directed toward the reduction of the volume of the auxiliary units. It is, therefore, concluded that the major effort in the improvement of any of these systems should be concentrated on the reliability and safety of the components in the system as a whole, and on the reduction of the operating voltage of the cell itself in order to increase efficiency and to reduce the heat load.

In any case, the oxygen generator, which has been used on nuclear submarines for several years, will have to be used for several years to come. Vigilance in safety of operation and maintenance must therefore be continued until new equipment becomes available from the development programs that are now underway or from those yet to be initiated. While there is every indication that substantial improvements can be made in the high-pressure systems, it must be remembered that the operation of high-pressure hydrogen and oxygen equipment in submarines must always be considered to be hazardous. For this reason serious efforts must be continued toward the possible use of ambient-pressure systems, even to the extent of operating the present system or the new Allis-Chalmers system at ambient pressure, since any of these methods would require only the development of a suitable hydrogen compressor.

Certainly improvements can be expected in the other systems, particularly those which include the absorption of CO_2. Regardless of the efficiency of these methods in principle, the major problems continue to be in the field of engineering design and in the choice of materials used in construction. These factors continue to plague not only the builders of present equipment but also those who attempt to develop other systems.

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Chapter 8
Recent Experiments with Chlorella

P. J. Hannan, R. L. Shuler, C. Patouillet

INTRODUCTION

Previous reports in this series have defined the potential of mass cultures of algae as a source of oxygen for submarines as well as a means for eliminating carbon dioxide. It is sufficient to say here that the algae are reliable oxygen producers, and that the volume of an algal system would be competitive with existing systems; however, the electrical-power requirement for the lamps now available for artificial illumination is excessive. Research on algae is continuing, therefore, in those areas which may ultimately have a bearing on the use of algae as an oxygen source, and, more importantly, as a tool in the field of oceanography. The fast growth of Chlorella pyrenoidosa in mass culture makes readily available a vast source of material useful in the study of effects of various marine environments. By using gas-exchange methods as a criterion of growth, it is possible to assess these effects more quickly and more positively than with conventional oceanographic techniques.

STICKING OF CELLS TO GLASS

An early problem in the design of a photosynthetic gas exchanger for submarine use is the tendency of algal cells to stick to glass surfaces. The Sorokin strain of Chlorella used in the studies at NRL is particularly troublesome in this respect, and a strong effort has been made to determine the causes of such sticking.

Literature references to the problem are scanty, and no methods for assessing the relative tendencies of cells to stick were found. A first step, therefore, was to devise some means of making the cells stick in a controlled manner so that the effects of changes in culture conditions could be assessed.

After much experimentation, a method was devised which promoted the sticking of cells, but the phenomenon is not yet understood, and the objectives of the study are still to be reached. The method used was to siphon a bubble-free suspension of algae through a glass tube which serves as the test specimen. As shown in Fig. 7, a fresh suspension of algae produced by a mass culture unit spills into a hopper, from which it is pumped to a constant-head device, then siphoned at a constant rate back to the hopper. If the cells are of the sticky type, a measurable deposit will be left on the test specimen within several hours, and by the end of two days a heavy deposit is formed.

A positive conclusion of this study is that the sticking of cells is promoted by light and heat. In some of the early experiments a series of glass specimens, 11 mm I.D., were held together by gum rubber tubing; when the unit was disassembled it was noted that there was always less sticking to the glass underneath the rubber connectors than on the rest of the specimens. The effect was studied further by wrapping half of one specimen with black tape to exclude all light from one side, and to expose another specimen to a bright light. As expected, the area covered with the tape was almost free of any

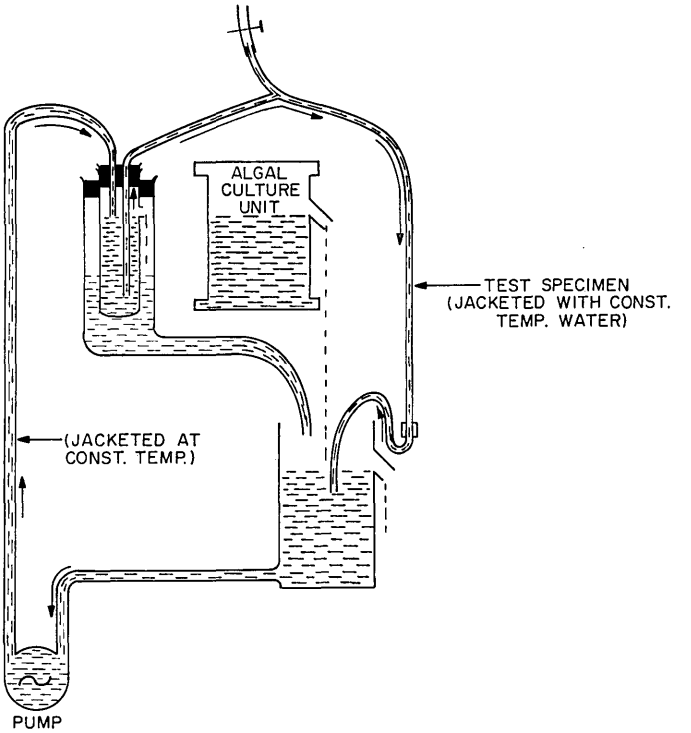

Fig. 7 - Diagram of flow to promote cell sticking

deposit, while the brightly lighted area was heavily coated by stuck cells. Inasmuch as surface heating by the bright light may have been a factor, the effect of temperature was studied by comparing two test specimens maintained at 32° and 38°C; the higher temperature appeared to promote greater sticking. This result suggests that cells may continue to grow even though stuck on the glass.

EFFECT OF BACTERIA ON STICKING OF CELLS

In a bacteria-free culture, Chlorella cells exist as single entities, but the cells produced by the six-lamp NRL unit, in which no attempt is made to exclude bacteria, are always present as large clumps. Their appearance under the microscope is that of a large bunch of grapes. If bacterial contamination causes the cells to stick to each other, it is reasonable to suspect that it is the cause of their sticking to glass. Therefore, a count of the bacterial population was made by serially diluting the suspension and plating it on nutrient agar. It was found that the normal bacterial population of the six-lamp unit was around 8×10^7 organisms per milliliter. The bacterial count of the culture medium in the supply tank was almost negligible, indicating that the algal cells or their metabolic secretions were responsible for the bacterial growth.

One method of controlling bacterial growth would be to increase the dilution rate with fresh culture medium; this would lower the algal population density and therefore the availability of nutrients for the bacteria. As shown in Fig. 8, the predicted lowering of bacterial count with increase in dilution was found, but the algal cells produced at the highest dilution rate still existed as large clumps. Dilution rates higher than that shown result in suspensions too thin to be in the linear phase of growth at the light intensity used. Therefore, dilution rate per se cannot control the problem.

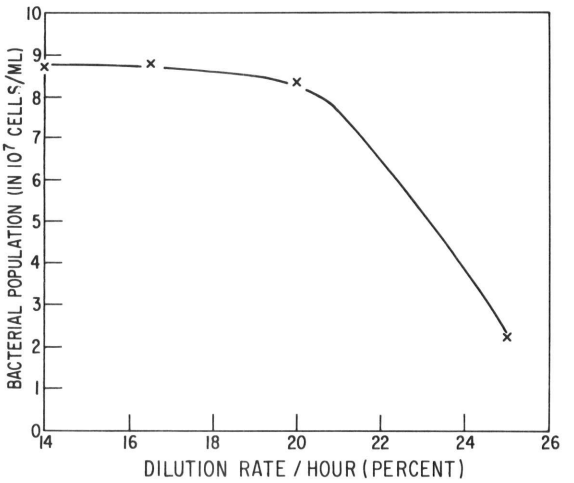

Fig. 8 - Controlling-bacterial growth by dilution

Some preliminary attempts at controlling the bacteria by antibiotics were of no avail. Streptomycin at a concentration of 80 micrograms/ml, and penicillin at 40 units/ml had no apparent effect on the bacteria. While these dosages are considerably higher than those normally used as antiseptic treatments, they undoubtedly are low in terms of dosage per bacterial cell. Concentrations higher than these were not used, partly because of the great volume (six liters) of the algal suspension being cultured. Therefore a smaller culture vessel of 350 ml volume (Fig. 9) was constructed as an assay unit in which the effects of bactericides or other additives might be studied.

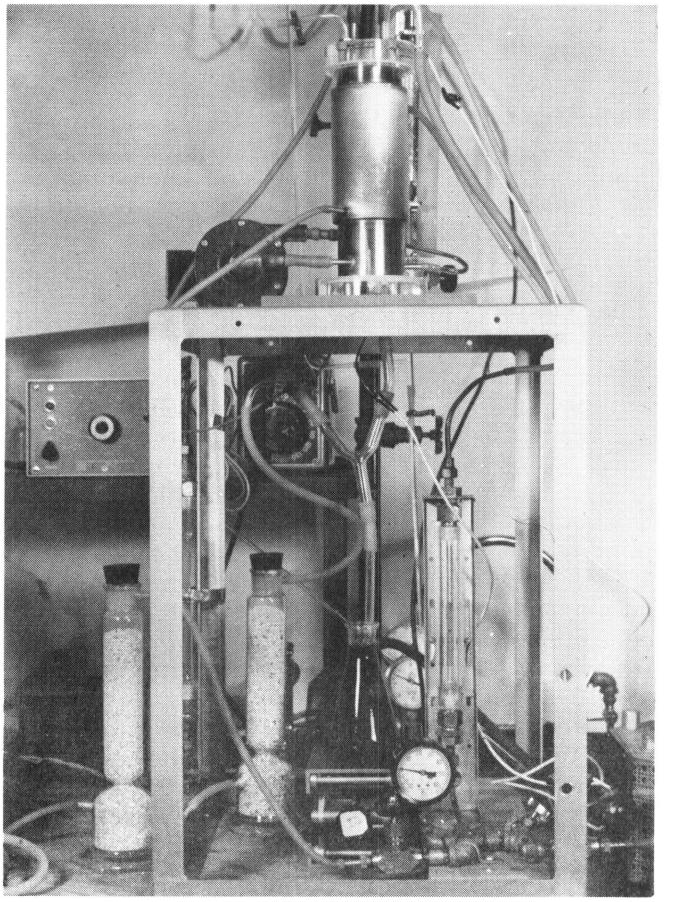

Fig. 9 - Assay unit for toxicity studies

Probably, antibiotics have little chance of success in controlling bacteria here because of the short residence time of the microorganisms in the culture vessel. At a dilution rate of 15 percent/hr, the normal rate used with the six-lamp unit, the average residence time of each cell would be only seven hours.

ASSAY UNIT

Figure 9 shows the compact assay unit mentioned previously. A G.E. Quartzline lamp is suspended through the center of the unit, surrounded by two concentric cylinders of glass and an outer jacket of stainless steel. Cooling water is passed through the inner annulus, and the outer annulus contains the algal suspension, which is swirled by the action of a small pump visible at the left of the picture.

In normal practice, a fresh supply of algal suspension is taken from the overflow of the six-lamp unit and put directly into the assay unit. A set voltage, 150 v, is applied to the lamp and a 2-percent air-CO_2 mixture is introduced at a rate of 500 cc/min. By analyzing the input and output gases for oxygen, the oxygen production of the unit is calculated. After approximately a half hour, the culture reaches a steady oxygen production which is maintained for several hours, depending on whether the culture is diluted with fresh medium. When this steady-state oxygen production has been reached, toxicants or other test materials can be added to the suspension, and the resultant change in oxygen production shows up in 15 minutes or less.

After several months' use, the metal connectors used to attach the pump to the assay unit were badly corroded and were replaced by new fittings made of 316 stainless steel. This change resulted in a total inhibition of O_2 production; in fact, oxygen was being absorbed by the system simultaneously with a slight absorption of CO_2. After several trials with identical results, the 316 stainless fittings were replaced by polyethylene and the pump was completely cleaned, but the oxygen production was still only half that normally obtained.

Multiple substitutions of various types of drain plugs, pump connections, etc., provided a variety of results which prompt diverse interpretations. The 316 stainless fittings certainly had a highly toxic effect initially, but continued use tempered the effect. Repeated washing of the unit and numerous changes in technique to pinpoint the troubles have been of little avail. The productivity of the unit has never been what it was initially with the old pot-metal fittings, though the improvement, when the fittings were put back in the assembly, was not great. The primary conclusion reached was that the structural components of an algal system play a vital chemical role in its performance, and an assay unit must be devoid of any complicating factors such as this. Therefore a new assay unit has been designed, consisting of an all-glass assembly connected to a pump made of a Bakelite housing, an impeller made of Viton, and a shaft made of titanium.

The assay unit already in use, although imperfect, was used to test the effect of structural materials. Rods 1/8 in. in diameter and 12 in. long were made of a variety of test materials: 304 and 316 stainless steel, Viton, Bakelite, nylon, brass, neoprene, Teflon, and polyethylene. The test rod was held in place above the culture until oxygen production was constant; then the test rod was pushed into the suspension and its effect on subsequent oxygen production noted. If there was a change in oxygen production, it usually appeared within 15 or 30 minutes, and a new steady state was established.

The results of these bio-assays have been variable. For example, a 304 stainless steel rod on successive tests caused 12 percent inhibition of oxygen production, and in each case the change in oxygen production was noted immediately. On a

third test with the same specimen the inhibition was the same, but its effect was delayed about a half hour. Another specimen of 304 stainless caused no change whatsoever in oxygen production, yet a spectrographic analysis of both specimens showed their gross composition to be identical except for slight changes in molybdenum and manganese content. Additions of salts of these metals at 20 ppm had no effect, moreover.

It was thought that the stainless steel jacket of the unit may be contributing somewhat to the problem; as a first step in determining its role, a culture medium containing 1 ppm iron was circulated through the unit for an hour, and aliquots were taken of the medium every 15 minutes. Each analysis showed a slightly lower amount of iron than the culture medium contained initially; therefore no dissolution of iron from the jacket was taking place.

The addition of known concentrations of metal ions (10 ppm Cr^{+++}, Ni^{++} at 5 ppm, Fe^{+++} at 5 ppm, and Cu^{++} at 5 ppm) had no effect. Copper at 10 ppm inhibited oxygen production, the degree of inhibition depending on the suspension density used.

More substantial results with algae as a bio-assay must await the construction of the metal-free unit. If a test rod of only 1/8 in. diameter can significantly affect the performance of a culture exposed to a surface area of stainless steel several orders of magnitude greater, one could expect an even greater effect in an all-glass unit.

RESPIRATION STUDIES

In the most recent report of this series (1), it was shown that the oxygen production of a culture unit was inversely related to the width of the culture chamber, the so-called culture thickness. For example, about 1.4 times more oxygen was produced by a 1.0-cm culture chamber than by a 2.2-cm culture chamber, even though more cells were present in the wider culture chamber. Because there were more cells in the 2.2-cm culture chamber, it was reasoned that their respiratory requirement for oxygen might reduce significantly the net oxygen production of the culture (that is, oxygen evolution rate not corrected for respiration). To explore this possibility, the respiration rates of various cultures have been measured under different conditions using the same culture unit.

The results of this study suggest that the respiration rates are largely determined by the rate of photosynthesis and not by the number of cells present. Thus, it appears that the influence of culture thickness on oxygen production cannot be associated with changes in the number of cells present.

Experimental Procedure

The experimental procedure was to allow a culture, usually one removed from a refrigerator after overnight storage, to grow until its oxygen evolution was constant. At this point the light was turned off and the inlet gas was diverted through Ascarite to remove all CO_2; after passage through the suspension, the oxygen content of the gas was monitored until steady (usually 30 to 40 minutes). Oxygen uptake was calculated as the product of the gas-flow rate and the difference in oxygen content of the inlet and effluent gases. For reasons to be explained later, it was of interest to know the time required for the system to achieve oxygen equilibrium after the light was turned off. For this purpose, an experiment was run with a cell-free medium, but otherwise under the same conditions used in a growth experiment. Only four minutes were required for the medium to reach oxygen equilibrium and to flush out the analytical train; after this time, there was no change in the oxygen content of the inlet and outlet gases.

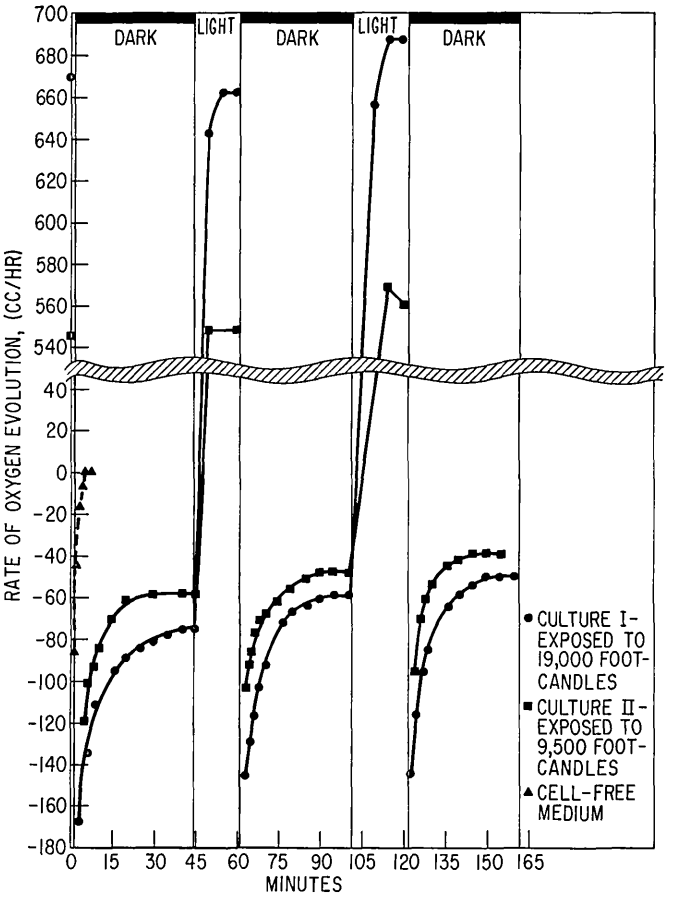

Fig. 10 - Rates of photosynthesis and respiration of two cultures as a function of time

Figure 10 illustrates the difference in respiration rates of two cultures during three light-dark sequences. Culture I was exposed to a light intensity of 19,000 foot-candles, and culture II to 9,900 foot-candles. These two suspensions contained approximately the same number of cells, but had been grown under different conditions. Culture I was taken from a refrigerator after being used previously for respiration determinations, while culture II was taken directly from a culture actively growing in another unit. Despite the big difference in the history of the two cultures, their respiration was similar: (a) a constant rate was reached at about the same time in each dark period, (b) the rate declined about 20 percent in successive dark periods, and (c) the oxygen output/oxygen uptake ratio for each light-dark sequence was about the same.

The short and almost constant time required to reach a steady respiration rate was unexpected, since longer times, several hours or more, are usually reported in the literature. However, in these and other experiments, the respiration rate reached a flat minimum in about 35 to 40 minutes.

It was thought that the decrease in the respiration rate in the last two dark periods may have been due to the inability of photosynthesis, because of the short illumination times, to produce a substance (or substances) necessary for respiration to proceed at a normal rate; another possibility would be a buildup of toxicants. The former possibility now seems unlikely, because the rate of photosynthesis was normal, or slightly enhanced, after the first dark period.

The oxygen output/oxygen uptake ratio for each light-dark sequence agreed very well for the two cultures. For culture I, the ratios were 8.9, 11.2, and 13.7 for the three light-dark periods; for culture II, the ratios were 9.4, 11.4, and 14.4. Two observations follow: (a) respiration was inhibited after the first dark period, and (b) the steady respiration rate after approximately 30 minutes in the dark is much less than that during the first few minutes of darkness. Because of the time needed to equilibrate the gas stream and the liquid medium, the oxygen uptake by the algae during the first several minutes of darkness is not known with precision, but the oxygen consumed after five minutes must be attributed to respiration.

If the respiration rate for the first several minutes of darkness is plotted against time on a logarithmic scale, a straight line is usually obtained. Figure 11 represents such a plot for the two cultures described in Fig. 10 (I and II) and five other cultures. If we assume that the extrapolated value at zero dark time represents the respiration in the light, the ratios of photosynthesis to respiration for the first light-dark sequence did not vary significantly for the seven cultures (Table 4, column 5). Thus, if the extrapolation to zero dark time is justified, the respiration rate in the light is roughly one-third of the photosynthetic rate.

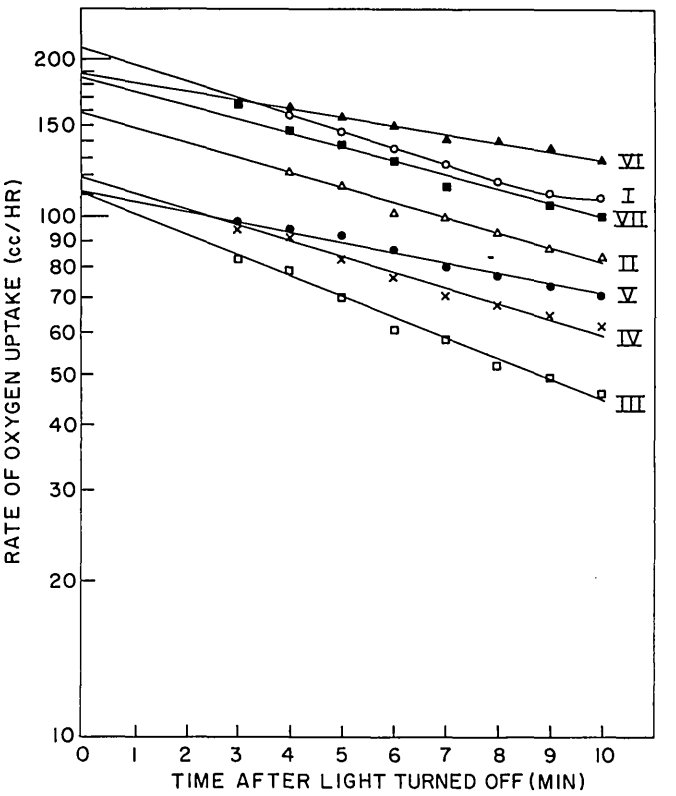

Fig. 11 - Rate of oxygen uptake as a function of time

It may also be noted (Table 4, column 8) that the ratio of the steady respiration rate (dark respiration) to the respiration rate in the light as determined by extrapolation does not differ greatly for the cultures tested. However, the oxygen consumed per cc of cells (last column) varied considerably among the cultures. Therefore, the data suggest that respiration, in the dark as well as in the light, is a function of the rate of photosynthesis, and apparently is not influenced significantly by cell concentration. This observation is

Table 4
Rates of Photosynthesis and Respiration for Several Cultures

1 Culture No.	2 Light Intensity (foot-candles)	3 Oxygen Output (cc/hr)	4 Light Resp.* (cc/hr)	5 Oxygen Output/ Light Resp.	6 Packed Cell Volume (percent)	7 Dark Resp.† (cc/hr)	8 Light/ Dark Resp. Ratio	9 Oxygen Uptake (cc/hr/cc cells)
I	19,000	670	205	3.3	1.68	75	2.7	4.5
II	9,900	546	157	3.5	1.65	58	2.7	3.5
III	6,500	359	111	3.2	0.74	43	2.6	5.8
IV	6,500	357	118	3.0	0.83	47	2.5	5.7
V	6,500	346	111	3.1	1.06	47	2.4	4.4
VI	19,000	676	189	3.6	1.32	88	2.2	6.7
VII	19,000	670	184	3.6	1.78	73	2.5	4.1

*Determined by extrapolation to zero dark time.

†Steady respiration rate in the dark.

consistent with earlier findings observed at NRL (2) that, at constant illumination, the net oxygen evolution rate is independent of cell concentration over a wide concentration range. If the rate of respiration were influenced by the number of cells, the net oxygen rate would change with cell concentration, but this effect has not been observed.

CONCLUSIONS AND FUTURE PLANS

An algal gas exchanger can be a reliable system for oxygen generation and CO_2 absorption on a nuclear submarine. However, its most serious deficiency, the high electrical power requirement of 30 to 32 kw per man, precludes further consideration at this time. These estimates are based on the use of incandescent lamps whose efficiency is only ten percent; a breakthrough in lighting technology could alter the power requirement significantly.

Certain problems would, in any case, require further investigation prior to engineering development of the system:

1. Sticking of cells. Sufficient turbulence to prevent the cells from sticking to the surface of the light jackets is difficult to achieve in large systems. The problem is not hopeless, however, because hydrophobic treatments for the glass delay the sticking, and there is a good possibility that an alga of the Anabaena species would provide the necessary oxygen production without a serious sticking problem.

2. Matching the respiratory quotient of man to the assimilatory quotient of algae. Too little or too much oxygen in the submarine atmosphere could result if these factors are not controlled properly. The proper choice of nitrogen source, or sources, for the culture medium will provide the proper O_2/CO_2 balance. This problem would not be serious, but it requires investigation.

3. Hydrocarbon vapors and aerosols. The long-term effects of typical contaminants should be investigated.

4. Re-use of culture media salvaged from cell suspensions. The quantities of minerals and urea to be added must be determined. Also, the length of time a culture medium can be used before its color affects light absorption must be determined. There seems to be little danger from the buildup of autoxicants, but a definite answer to this question must be obtained.

Since these problems and the algal gas exchanger itself no longer appear germane to the submarine-habitability program, further studies will be reported as part of the progress of the newly formed Ocean Sciences and Engineering Division of NRL.

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2. Shuler, R.L., "Some Factors Affecting the Oxygen Production by Algae in a Small Culture Unit," NRL Report 5979, Sept. 12, 1963

Recommendations

As usual, many of the recommendations from the previous annual report must be repeated. The differences are primarily in degree of emphasis, with progress in implementation partially nullified by the increase in problems due to new construction and new equipments. A few new recommendations are now added. The recommendations are addressed to the Navy Ship Engineering Center.

1. The program of determining the degradative effect of nuclear-submarine atmospheres on materials should be expanded and expedited. NRL recently acquired a rapid-scanning mass spectrometer which will be utilized in this program to a limited extent, but only as a monitor, since analytical and trouble-shooting services will keep available personnel fully occupied.

2. The Habitability Data Book, already in process of revision, should be brought up to date and so maintained.

3. Quality control must be improved in the production of the Mark IV Atmosphere Analyzer and its replacement parts, and ships and shipbuilders should be required to return faulty components to the manufacturer for replacement if still under warranty, or to the Navy Ship Engineering Center, Code 6649A1, if a warranty is not applicable. Training of shipboard personnel in operation and upkeep should also be improved.

4. Evaluation of the Ionics, Inc., prototype ion-exchange system for oxygen generation and CO_2 absorption should be expedited.

5. Major design changes are required in the CO_2 scrubber, including better quality valves and sea-water pumps, avoidance of MEA injection into the atmosphere, and provision of battery-quality makeup water. The additive package of EDTA and VFS should be standardized for use in all MEA solutions.

6. Chlorinated hydrocarbons should not be used in construction, operation, or maintenance of the submarines under any conditions in which they can be released as volatile material into the atmosphere.

7. Development of a "split-cell" oxygen-generating system for shipboard evaluation should be reinstituted. NRL is willing to extend its early effort on this problem by setting up a small-scale pilot study.

Future interests and action of NRL in the field of submarine atmospheric habitability will continue to be guided by the following considerations:

1. All research and development will continue to be performed with the view of applicability toward an integrated air-purification system.

2. Investigations will continue on: (a) refinements on the Mark IV Atmosphere Analyzer, (b) methods of air sampling and analysis, including infrared and mass spectrometry and gas chromatography, (c) the Mark V (chromatographic) Atmosphere Analyzer,

(d) the Total Hydrocarbon Analyzer, (e) the CO_2-H_2 reaction, which might eliminate the need for pumping these gases overboard, (f) a satisfactory water-thinned, nonflammable paint for application while submerged, (g) the gas-stripping mechanism in the CO_2 scrubber, (h) possible substitutes for MEA in the CO_2 scrubber, and (i) reactions, corrosion, and acid absorption in the CO-H_2 burner.

3. NRL will also continue to provide consultative services to the Naval Ship Systems Command and the Navy Ship Engineering Center as required, as well as to other Navy and government activities concerned with closed environmental systems.

4. As a continuing policy, promising research ideas will be pursued as part of NRL's program, even when there appears to be only eventual applicability to submarine needs.

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13. ABSTRACT

This annual progress report supplements NRL Reports 5465 of April 21, 1960; 5630 of July 14, 1961; 5814 of August 29, 1962; 6053 of December 31, 1963; and 6251 of March 23, 1965, which provided a comprehensive review of the past and present research and development effort of the Naval Research Laboratory on the atmospheric habitability of submarines. Emphasis is at present being devoted almost exclusively to nuclear-powered submarines. Considerable progress has been made in the major efforts of developing improved methods of sampling and analysis of atmospheres, but shipboard analytical equipment continues to be of marginal quality. Problems associated with volatile chlorinated hydrocarbons in closed environments have led to their complete ban. Other topics covered in the present report include: further studies on algae as a source of oxygen (now discounted for nuclear submarines due to the excessive power requirements of the necessary light source), fire-retardant and nontoxic paints for necessary application during submergence, and a survey of oxygen sources based on a recurring need to improve the safety, reliability and logistics of the high-pressure electrolytic oxygen generator now on all FBM submarines.

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