

Methyl Chloroform in FBM Submarines

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TABLE OF CONTENTS

| | |
|---|----|
| Abstract | ii |
| Problem Status | ii |
| Authorization | ii |
| INTRODUCTION | 1 |
| HISTORICAL BACKGROUND | 2 |
| THE FBM "CORROSION" PROBLEM | 4 |
| ANALYSES FOR CHLORINATED HYDROCARBONS | 7 |
| (1) ALEXANDER HAMILTON (SSBN617) | 7 |
| (2) THOMAS JEFFERSON (SSBN618) | 8 |
| (3) TECUMSEH (SSBN628) | 8 |
| OTHER GENERAL INFORMATION | 9 |
| (1) Analysis of Bondmaster G-596 Adhesive | 9 |
| (2) Compositional Analysis of Commercial Methyl Chloroform | 9 |
| (3) Corrosive Effects of Uninhibited Methyl Chloroform | 9 |
| SUMMATION OF INFORMATION (JULY 1964) PRIOR TO FIELD TRIPS | 10 |
| FIELD TRIPS TO SHIPYARDS | 11 |
| (1) East Coast Shipyards | 11 |
| (2) Mare Island Trip | 13 |
| SUMMARY AND DISCUSSION | 15 |
| RECOMMENDATIONS | 16 |
| REFERENCES | 18 |

ABSTRACT

Chlorinated hydrocarbons, particularly methyl chloroform, have been shown to be the source of severe corrosion in many recently constructed FBM submarines. Laboratory and ship-board data show that these solvents decompose in passing through the CO/H₂ burners, yielding into the effluent air acidic products which cause corrosion of metals in the vicinity. The magnitude of the problem is underlined by the fact that in each recent FBM submarine, 1200 to 1500 gallons of adhesives have been used containing 10,000 to 12,000 pounds of methyl chloroform.

Recommendations are included in this report which will alleviate the present problem. However, the ultimate satisfactory solution is to eliminate chlorinated solvents from the materials used in the construction and operation of the nuclear submarines.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NRL Problems: C08-05, C08-18, C08-30, C08-33,
C07-01, C02-15 and R05-24B

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METHYL CHLOROFORM IN FBM SUBMARINES

INTRODUCTION

During the past two years extensive and sometimes severe corrosion has occurred in the Auxiliary Machinery Room (AMR) in a number of the advanced design Fleet Ballistic Missile (FBM) submarines. The corrosion was found to have occurred generally on unprotected metal in the vicinity of the CO/H₂ burners and often became pronounced within a few days or weeks after submerged operations began in the new submarines. Although occasional corrosion problems had been associated with the CO/H₂ burners since their first use on nuclear submarines, the increasing number of reports of severe corrosion in 608 class and 616 class FBM submarines since late 1962 indicated a new source of acid-forming material.

The Fleet Ballistic Missile Submarine is a large ship which is over 400 feet in length and 7,000 tons displacement. Within this large pressure hull are hundreds of synthetic organic materials which are necessary for construction, operation, and maintenance of the ship. Since the organic materials of construction represent tons of weight and thousands of square yards of surface, only a small percentage of occluded volatile material can represent a large reservoir of atmospheric contaminants in a sealed boat. These volatile ingredients such as solvents, monomers, plasticizers, etc., are often part of, or are applied to, these organic construction materials. Some small amounts of volatile vapors may be adsorbed later or result from deterioration of materials of construction. Many of these construction materials are specified according to performance specifications, with no requirement as to composition or residual effects. It is not surprising therefore, that atmosphere problems arise from time to time to jeopardize the operation of one or more submarines.

Continuing research on this new corrosion problem has been carried out at NRL with the cooperation of the Bureau of Ships, the U. S. N. Marine Engineering Laboratory (MEL, formerly the USNEES), and several shipyards. Information developed which implied that the presence of chlorinated hydrocarbons in the atmosphere which were decomposed in the CO/H₂ burner to yield halogen acids was probably the major cause of the corrosion. As the investigation progressed during 1964 the evidence began to point to methyl chloroform (1,1,1-trichloroethane) as the principal chlorinated hydrocarbon at fault. Armed with this knowledge, teams of investigators

from NRL, BUSHIPS and MEL visited the four shipyards which are building FBM submarines in order to gather information on the incidence of use of methyl chloroform and other suspect materials in construction and operation of these submarines. This present report outlines the historical events of the corrosion problem, the background of research pertaining to the identification of methyl chloroform as the source of corrosion, the findings of these field trips, and an analysis of the overall results with recommendations for corrective action.

HISTORICAL BACKGROUND

Chlorinated hydrocarbons have enjoyed widespread use as solvents, not only because of their excellent solubility for organic materials, but particularly because of their non-flammable characteristics. Unfortunately most chlorinated hydrocarbons are very toxic. Carbon tetrachloride, (CCl₄) once commonly used for many degreasing applications in industry and in the Navy, was recognized as a serious toxic hazard, and about ten years ago NRL was requested to search for a suitable, less hazardous substitute. The safe limit published by the American Conference of Government Industrial Hygienists in 1953 for CCl₄ in the atmosphere was 25 ppm. It is of interest that the threshold limit has since (1) been reduced to 10 ppm.

A thorough survey of available candidates for replacing CCl₄ as a nonflammable solvent was made and much pertinent information on this subject was published in an NRL report (2). It was concluded that one preferred substitute was methyl chloroform, which is much less toxic and has about the same volatility as CCl₄. It should be noted that this report also detailed minimum precautions which must be observed when handling any chlorinated solvent, especially to provide "Adequate forced ventilation of all areas where chlorinated solvents are either stored or used".

The CO/H₂ burners, which are installed in every nuclear submarine, contain a bed of heated catalyst (Hopcalite) which oxidizes carbon monoxide, hydrogen, hydrocarbons and many other organic compounds to carbon dioxide and water. Unfortunately, halogenated hydrocarbons such as Freon-12 and methyl chloroform when heated in contact with the catalyst tend to decompose to give off acidic halogenated compounds such as hydrofluoric acid (HF) and hydrochloric acid (HCl). A detailed report on the development of the CO/H₂ burner (3) recounts the search for optimum materials of construction for the burner and the

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optimum operating temperature. Lower burner temperatures were favored because less Freon-12 decomposition occurred. However, it was found that temperatures must remain high enough to prevent hydrocarbon materials from collecting on the catalyst and poison its efficiency for CO oxidation and yield "combustible" catalyst. These shipboard studies, coupled with another laboratory research program on catalytic combustion (4), led to the recommended operating temperature of 600°F as the best compromise. This temperature of 600°F is still currently in use.

Even at a nominal operating temperature of 600°F, a small fraction of any Freon-12 refrigerant in the submarine atmosphere will decompose in the CO/H₂ burner to yield fluoride and chloride and corrosion of metals, especially in the rotary heat exchanger. Laboratory studies confirmed the slight decomposition of Freon-12 to yield halogen acids (5). To counteract this corrosive effect, it was recommended that 10% by volume of lithium hydroxide (LiOH) or calcium carbonate be uniformly mixed with the Hopcalite catalyst for use in the burner (6). By utilizing these measures, corrosive effects of the burner effluent were not reported to be excessive even at fairly high concentrations of Freon-12. Major emphasis also was placed on locating and repairing leaks in the Freon systems.

In late 1961, the ETHAN ALLEN (SSBN608) submitted to the Bureau of Ships a list of items which would be useful during an FBM patrol. Information was requested as to the acceptability of these items from the viewpoint of atmospheric contamination since they were believed to contain volatile components. Among these items was a gallon of adhesive material which contained 8.5 pounds of chlorinated hydrocarbon, specifically methyl chloroform.

At the request of the Bureau of Ships, NRL studied the decomposition of methyl chloroform in the laboratory-scale Hopcalite burner (5,7). At 600°F more than 95% of this compound was decomposed with evidence of a strong acid reaction as well as free halogen in the effluent. At the same time substantial amounts of vinylidene chloride (1,1-dichloroethylene) were produced as well as a trace of trichloroethylene (1,1,2-trichloroethylene). These facts were reported by telephone to the Bureau of Ships with the recommendation that the use of volatile halogenated compounds on board nuclear submarines should be avoided where possible.

The Bureau of Ships then reported to ETHAN ALLEN that acidic products would form at the CO/H₂ burner, but if the

material were used a little at a time during a 60-day patrol, it should not present a significant hazard (8). At that time there was not believed to have been any significant use of methyl chloroform (or other chlorinated hydrocarbons) in the nuclear submarines during or following construction (9).

It was about this time (late 1961) that severe eye irritation was experienced by personnel aboard USS SNOOK (SSN592) during sea trials. This condition was traced to incorrect installation of the heaters in the lube oil purifier system (10). However, during the course of this investigation it was observed that many materials used in construction of submarines were potential sources of vapor contaminants, especially materials which undergo heating, such as materials used in lagging steam pipes and surface coatings. The information on materials which had been gathered during the SNOOK investigation, although very limited in scope, was reported (11) with the recommendation that much more information was needed in this area, in order to restrict the use of potential atmospheric pollutants. It was suggested that many deleterious solvents and other components could be excluded from nuclear submarines by developing formulations specifically designed not only to fulfill a performance demand, but also to avoid the release of irritants and other corrosive contaminants into the atmosphere.

As a direct result of the SNOOK incident, the Bureau of Ships quickly explored the possibility of initiating such a study at MEL (formerly EES), (12). The goals were primarily to identify possible irritants resulting from bake-out of laggings, coatings, etc. and to provide composition and rate of release data on volatile fractions such as paint solvents to determine how much time is required for complete solvent evaporation. It was hoped that improved formulations would result from these studies. In implementing this study by making shipboard tests, MEL became involved naturally in the "corrosion problem" which developed soon thereafter.

THE FBM "CORROSION" PROBLEM

The first indication to come to the attention of NRL of a serious corrosion problem in the new design FBM submarines was early in 1963 (13). A few months earlier it was observed in AMR of USS THOMAS JEFFERSON (SSBN618) that severe corrosion of metals was occurring in the vicinity of the discharge from the CO/H₂ burners. It was noted that SSBN618 had the first installation of the Mk3 500 CFM CO/H₂ burners. It was assumed by observers and the Bureau of Ships representatives that the origin of this problem was due to decomposition of

Freon in the burner, which in some way was being run at a higher effective temperature or in some other fashion causing a much higher than expected Freon decomposition. It was also noted that the "catalyst and marble chips" had been in place throughout much of the construction period and were, in effect, in the ventilation line during that time.

R. O. Bullock of the Bureau of Ships, Code 649 and D. D. Williams of NRL visited SSBN618 and the Newport News Shipbuilding and Drydock Co. (NNS and DD Co.) in April 1963 and confirmed the fact that severe corrosion as well as electrical failures in AMR No. 2 were continuing (14). It was believed by this team that the electrical troubles were probably due to deposits of monoethanolamine (MEA) which came from the carbon dioxide scrubbers. The metal corrosion appeared to be the result of HCl issuing from both CO/H₂ burners in unusually high concentration. The source of HCl was unknown, but it was established that it was not due to excessive Freon-12 in the atmosphere.

In May, 1963, T. Bolles of Electric Boat Division of General Dynamics Corp. (EB) discussed a similar problem by telephone with NRL personnel (J. G. Christian and J. E. Johnson). It was reported that considerable corrosion had occurred in AMR No. 2 of USS ALEXANDER HAMILTON (SSBN617) during sea trials. It was agreed that NRL would provide sampling equipment to be used by EB personnel during the fifth sea trial. Details of the analyses are reported in a later section of this report.

In March 1963, samples were taken by personnel of USS JOHN MARSHALL (SSBN611) of surface material from several pieces of equipment in AMR No. 2. These samples were received at NRL and study (15) disclosed that the source of electrical failures was probably due largely to a deposit of monoethanolamine (MEA) from CO₂ scrubbers. The MEA is a good solvent for many polymeric materials and, in addition, can form salts which are good electrical conductors. More pertinent to the present story was the conclusion that halide corrosion in the area of the CO/H₂ burner discharge was probably not due to decomposition of Freon-12 in the burner but due to some material containing chlorine alone. This was suggested by the positive tests for chloride and negative tests for fluoride, since Freon-12 should give approximately equal quantities of both chloride and fluoride. It was suggested that a survey of materials of construction might permit elimination of an appreciable source of chloride material. Also the main carbon bed, if it adsorbed chlorinated compounds during construction, might release these solvents by displacement by other materials during submergence and subsequent burner operation.

In May 1963, USNMEL received samples from USS SAM HOUSTON (SSBN609) and an inquiry concerning corrosion near the CO/H₂ burner discharge. It was deduced by MEL (16) that the deposits were due to decomposition of halogenated materials in the burner. At that time the corrosion in SSBN609 was not considered serious.

Also in May 1963, MEL personnel found significant concentrations of acid chlorides in the atmosphere of USS LAFAYETTE (SSBN616). Again this corrosive condition was blamed on burner degradation products of chlorinated hydrocarbons used in materials of construction and cleaning solvents. In a follow-up on this submarine, MEL obtained samples and made detailed analyses of corrosion products (17) which confirmed the high hydrochloric acid content in the CO/H₂ burner effluent. It was concluded that the galvanized screening which had been installed to scavenge corrosive gases from the burner effluent was grossly inadequate.

USNMEL found methyl chloroform in air samples taken in the engine rooms of three FBM submarines during saturated steam tests including: USS NATHAN HALE (SSBN623), USS WOODROW WILSON (SSBN624), and USS JAMES MADISON (SSBN627) (18). USNMEL further determined (17) from main filter carbon samples that USS SAM HOUSTON (SSBN609) and USS JOHN MARSHALL (SSBN611), had significant quantities of both methyl chloroform and HCl in the atmospheres.

In November 1963, a survey for chlorinated organic compounds was made by personnel of NNS and DD Co., Newport News, during sea trials of USS JAMES MONROE (SSBN622). The purpose of this survey (19) was to check on effectiveness of efforts to reduce contamination by chlorinated compounds and related corrosion at the CO/H₂ burner discharge. The conclusions were that the measures taken were effective.

In the spring of 1964, D. E. Field of NRL interviewed personnel of several FBM submarines at Holy Loch (20). USS GEORGE WASHINGTON (SSBN598) a well-seasoned veteran, was reported to have little or no corrosion in the AMR containing the MEA scrubbers and CO/H₂ burners. USS THOMAS EDISON (SSBN610) had experienced extensive corrosion above and around the burners. The Freon concentration had run high at times. USS THOMAS JEFFERSON (SSBN618) was still experiencing some corrosion after a year and a half. Of further interest here is the Dynel U-Lock filter sent to NRL by SSBN618 with a letter of inquiry dated 27 March 1964. This filter had received air from both the MEA scrubbers and CO/H₂ burners. Analysis showed considerable MEA carryover combined with some HCl from the burners (21).

ANALYSES FOR CHLORINATED HYDROCARBONS

Aside from Freon-12 which had been reported in nuclear boat atmospheres in concentrations as high as 1000 ppm, only occasional reports of other volatile organic compounds containing chlorine had been made (10, 22). Traces of Freon-114 and methyl chloroform had been observed. Consequently the following analytical results were viewed with great interest.

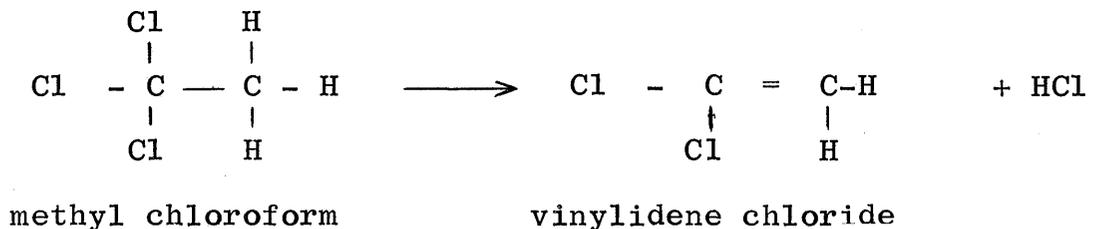
(1) ALEXANDER HAMILTON (SSBN617)

Samples of the atmosphere were collected in stainless steel bottles during the fifth sea trial. Two samples were collected from the CO/H₂ burner inlet and two from the burner outlet. The Freon-12 concentration during this time, as determined by the Mark IV Analyzer, was 8-13 ppm. The Analyzer indicated no Freon-11 and none was found in the steel bottle samples at NRL. However, considerable quantities of two chlorinated hydrocarbons were found in the bottles: methyl chloroform and vinylidene chloride ((1,1-dichloroethylene). The analytical data (23) are as follows:

Table 1
CHLORINATED HYDROCARBONS IN ATMOSPHERE OF SSBN617

| Sample No. | Burner Location | Submerg. Hours | Methyl chloroform mg/m ³ | Vinylidene Chloride ppm | Vinylidene Chloride mg/m ³ | Chloride ppm |
|------------|-----------------|----------------|-------------------------------------|-------------------------|---------------------------------------|--------------|
| 1 | Inlet | 15 | 33 | 6.1 | 6.5 | 1.6 |
| 2 | Outlet | 15 | 0.6 | 0.1 | 8.2 | 2.1 |
| 3 | Inlet | 20 | 12 | 2.2 | 2.0 | 0.5 |
| 4 | Outlet | 20 | 0.2 | 0.04 | 4.3 | 1.1 |

The data show that the methyl chloroform was nearly all destroyed in each pass through the burner. On the other hand, vinylidene chloride concentrations increased in passing through the burner. These facts fit nicely with the findings on methyl chloroform decomposition in the laboratory burner (5,7). This study showed that methyl chloroform is largely converted by the CO/H₂ burner at 600°F to vinylidene chloride and acid vapors, probably HCl. The acid may be considered as splitting off from methyl chloroform with vinylidene chloride as residue:



It is assumed that an appreciable fraction of the vinylidene chloride is further decomposed on each pass through the burner. Chemists at Electric Boat Co. reported that acid concentrations as high as 8 ppm were detected in the burner effluent at this time.

Two samples of activated carbon from the main filter of ALEXANDER HAMILTON were analyzed at NRL (24). NRL was advised by telephone that there was no main filter carbon in this submarine before and during the first two sea trials. This carbon had been installed on 20 May 1963, and removed on 26 June 1963, spanning the third through the fifth sea trials. The compressed atmosphere samples described above were also taken in the same period (fifth sea trial). The carbon samples were steam desorbed and an average of 27.5 ml. of hydrocarbon oil was recovered per 100 grams of carbon. This carbon was obviously saturated, showing the need for frequent carbon replacement during the early months.

(2) THOMAS JEFFERSON (SSBN618)

Freon levels during the early corrosion period were generally low in the SSBN618. Two samples of main filter carbon exposed during this period were received from this submarine and analyzed at NRL (23). The carbon contained 15 weight percent of organic compounds of which about 3% was methyl chloroform. Chromatographic examination of the air in a closed container of this carbon showed methyl chloroform and vinylidene chloride as major components.

(3) TECUMSEH (SSBN628)

Samples of the CO/H₂ burner influent and exhaust were collected in stainless steel bottles aboard the USS TECUMSEH during a post-shakedown cruise during June 1964. Analytical results (25) by gas chromatography for vinylidene chloride and methyl chloroform are listed below.

Table 2
CHLORINATED HYDROCARBONS IN ATMOSPHERE OF SSBN628

| Date | Burner Location | Submergence Hours | Methyl chloroform mg/m ³ | Vinylidene chloride ppm | Vinylidene chloride mg/m ³ | ppm |
|------|-----------------|-------------------|-------------------------------------|-------------------------|---------------------------------------|-----|
| 6/9 | Inlet | 20.5 | 35 | 6.2 | 8.5 | 2.1 |
| 6/9 | Outlet | 19.5 | 20 | 3.6 | 14.5 | 3.6 |
| 6/10 | Outlet | ? | 27 | 4.9 | 12.5 | 3.1 |

The burner exhaust samples appeared to be contaminated with ambient air because of the poor conversion of methyl chloroform and the presence of hydrocarbons in the samples. It is evident, however, that excessively high concentrations of these chlorinated compounds still persisted in the ship's atmosphere as late in its history as the post-shakedown cruise.

OTHER GENERAL INFORMATION

(1) Analysis of Bondmaster G-596 Adhesive

In May 1963, a sample of this adhesive was submitted to NRL for comment by the Medical Officer of USS POLLACK (SSN603). Detailed analysis of the volatiles from the adhesive showed the major component to be methyl chloroform (26). Minor components were 1,2-dichloroethane, p-dioxane, and toluene. This adhesive was stated to be used for securing decorative plastic materials to bulkheads, etc.

(2) Compositional Analysis of Commercial Methyl Chloroform

In view of the widespread occurrence of methyl chloroform in closed atmospheres, and the fact that several other chlorinated hydrocarbons of obscure origin have been found in submarine and spacecraft atmosphere, the composition of a few technical grade samples of methyl chloroform were determined at NRL (27). These samples complied with the requirements of Federal Spec. O-T-620a, 1,1,1-Trichloroethane, Technical, Inhibited (Methyl Chloroform). It was found that some samples of commercial methyl chloroform contained considerable quantities of other more toxic chlorinated hydrocarbons. For example, one sample of methyl chloroform contained 22% of 1,2-dichloroethane. This evidence emphasizes the need to know more precisely what materials are actually going into submarine construction.

(3) Corrosive Effects of Uninhibited Methyl Chloroform

Commercial methyl chloroform as marketed contains several percent of a "corrosion inhibitor", usually 1,4-dioxane or tert.-butyl alcohol. These inhibitors are soluble in water as well as in chlorinated hydrocarbons. Chlorinated solvents are often used in ultrasonic cleaning operations following which corrosion of delicate equipment by an unknown mechanism has sometimes resulted. It was discovered at NRL (28), in connection with an investigation of salvaging methods, that if the chlorinated solvent is contaminated with 1 to 2 percent water and subjected to high intensity sonic

energy such as encountered in ultrasonic cleaning, the inhibitor is separated from the solvent. This permits attack by the solvent on aluminum resulting in the generation of considerable quantities of aluminum chloride and hydrochloric acid, as well as traces of phosgene and other chlorinated hydrocarbons. Once the reaction starts it is self-accelerating and will continue until either the aluminum or the chlorinated solvent is exhausted. This process may explain many of the unexplained cases of equipment failure due to corrosion. It was recommended that no equipment containing aluminum parts should be immersed in chlorinated hydrocarbon solvents for extended periods, and that such solvents should not be used in ultrasonic equipment for cleaning delicate or critically important equipment, such as miniature ball bearings. This work also suggests the possibility that some corrosion may occur from direct reaction of methyl chloroform with metals in other situations.

SUMMATION OF INFORMATION (JULY 1964) PRIOR TO FIELD TRIPS

It has been implied from time to time in this report that measures were being taken to control the corrosion problems outlined. It is beyond the scope of this report to detail the changes in ship's equipment and operation put into effect by the Bureau of Ships, or the laboratory work being done to devise the best scrubbers for removing acids from the CO/H₂ burner effluent. It may be mentioned that serious deficiencies in the use and maintenance of the main carbon filters were found, and recommendations for better utilization of these filters were outlined by NRL (29). For example, it was recommended that carbon should not be installed during the construction period, and that carbon be replaced frequently during the first months of operation of a new submarine.

At any rate, it was known by July, 1964 that this corrosion problem was continuing in new submarines of the 608 class and especially the 616 class in spite of the several changes authorized by the Bureau of Ships. It was known further that at least some of these submarines were still experiencing significant corrosion after more than a year in service. At least seven 608 and 616 class FBM submarines had reported serious corrosion problems related to the CO/H₂ burner as recounted earlier in this report. It was also of considerable interest that by July, 1964, no ships of these classes built at Mare Island had reported such difficulty.

By this time it was known, from analyses of atmosphere samples and main carbon filter samples, that methyl chloroform

was the most likely precursor to the corrosive acids. The amounts of methyl chloroform found implied a sizable reservoir as a source of this solvent. Evidence presented at the Quarterly Progress Review on Nuclear Submarine Habitability at NRL on 16 July 1964 made it quite clear that a correlation of corrosion with methyl chloroform was likely, but the sources and amounts of methyl chloroform were uncertain.

In order to get more precise information as to the extent of the use of methyl chloroform and other chlorinated hydrocarbons during construction and operation of nuclear submarines, teams were sent in August, 1964 to the four shipyards which were involved in construction of FBM submarines.

FIELD TRIPS TO SHIPYARDS

(1) East Coast Shipyards

A team comprised of NRL, BUSHIPS, and MEL personnel made a trip (30) to three shipyards constructing FBM submarines on the East Coast (Electric Boat Co., Portsmouth Naval Shipyard, and Newport News Shipbuilding and Drydock Co.). Two days were spent in each yard consulting with Navy Supervisors of Shipbuilding, design, laboratory, shop and available nuclear submarine personnel concerning organic materials used during construction and operation of nuclear submarines. It was observed on several new FBM submarines, which had undergone sea trials or shakedown cruises, that corrosion of all unprotected metals was occurring in the vicinity of the CO/H₂ burners or within ventilation ducts from the burners' exhaust. Most of the corrosion appeared to be resulting from acidic gaseous products from the burners and to a limited extent from acidic liquid condensate from the after coolers of the burners and from particulate matter believed to be chlorinated catalyst. Consultation with the submarine medical officers and engineers revealed that little or no solvents, cleaners, bleaches, proprietary paints, adhesives, etc., were ever used on their submarines during operational periods. However, consultation with the builders revealed that large quantities of materials containing solvents such as adhesives, paints, paint removers, cleaners, etc. were used in the construction of submarines.

It soon became apparent that the largest single source of a volatile halogenated solvent was the cement used to secure hull insulation, ventilation duct insulation, chill-water

pipe insulation and, in some cases, decorative laminates. The large majority of these insulations are the unicellular, elastomeric, plastic foams specified as MIL-P-15280D, Type II. The adhesive cement is specified to be a high flash point, quick-drying, contact type which is required to pass certain performance tests. The Detail Shipbuilding Specifications specify that the adhesive meet MIL-A-18065 specification requirements and should be "Bondmaster 527" or equivalent. This adhesive and "Bondmaster 596" were used by all three shipyards for securing hull insulation (plastic foam and corkboard) and, in some cases, chill-pipe insulation, ventilation duct insulation and decorative laminates. These adhesives are used in average amounts of 1250 gallons in a FBM submarine and contain 7 to 9 pounds of methyl chloroform solvent per gallon. Although much of the methyl chloroform evaporates readily from the applied adhesive, a large amount is trapped behind the insulation when it is laid-up. Laboratory tests at NRL show that five percent of the solvent remains within an uncovered adhesive film even after 18 hours of drying under normal conditions. Since the drying period is usually less than thirty minutes for shipboard application, it seems entirely possible that five percent (or 500 pounds) of methyl chloroform is still within the insulation by the time sea trials are performed! Further evidence of trapped solvent in the hull insulation is given by positive tests for halogens from the insulation five months after its installation, and the presence of methyl chloroform in the atmosphere and carbon samples taken from several operational FBM submarines (23).

Many other adhesives are used for deck, wall, and thermal insulation coverings but, in most cases, these are water emulsions or contain nonhalogenated solvents. The only other extensive source of halogenated solvents is from the paint removers and cleaning solvents. Paint removers are essentially methylene chloride, while some cleaning solvents are methyl chloroform (Chlorothene, Inhibisol) or trichlorotrifluoroethane (Freon TF). Some 50 gallons of paint remover and 200 gallons of cleaning solvents may be used during the construction of a FBM submarine.

The crews of the submarines may use some cleaners or laundry soaps which contain minor amounts of chlorine bleach as well as some solvents for cleaning electronic gear; however, this does not appear to be a major source of halogens or halogenated compounds. Continued high concentrations of Freon in a ship's atmosphere will result in some corrosion in and around the CO-H₂ burners as well as chlorination of the catalyst.

(2) Mare Island Trip

NRL and BUSHIPS personnel made a visit (31) to the Mare Island Naval Shipyard to determine if an unreported corrosion problem also existed on FBM submarines built there, and to investigate possible sources of methyl chloroform in the atmospheres of nuclear submarines.

Personnel at the shipyard stated that there had been no appreciable corrosion on any of the FBM submarines from that yard. However, during the investigation, a verbal report from the USS DANIEL BOONE (SSBN629) indicated that there had been some corrosion in the AMR during sea trials which was attributed to MEA. There was also reportedly a communication from the ship which requested installation of a scrubber to prevent corrosion resulting from acid gases emitted from the burner. The severity of the corrosion or the most likely cause could not be determined at the time.

No methyl chloroform was reportedly used as a degreasing solvent aboard submarines during construction or operation. If a part required degreasing, the operation was carried out in the shop, and enough time allowed for the methyl chloroform to evaporate before the part was taken aboard ship.

Large quantities of methyl chloroform were used, however, in adhesive formulations. The hull insulation used during the last couple of years was Ensolite applied with Bondmaster cement G-527. In the construction of a ship of the 616 class, it was estimated that at least 50,000 sq. ft. of Ensolite were used with about 1500 gal. of Bondmaster G-527 as adhesive. The insulation was applied throughout the construction period extending essentially to the completion date. The Ensolite was first coated with a layer of adhesive in the shop and let dry. A coat was applied to the hull and allowed to dry for only about two minutes before the insulation was put in place. It was reported that the Ensolite would not adhere properly if longer drying periods were used.

Ensolite was first used at Mare Island in the construction of the ANDREW JACKSON (SSBN619). Corkboard was used initially as the hull insulation on this ship but a change to Ensolite was made during construction. It was estimated that about 60% of the insulation used was corkboard. Initially the corkboard insulation was cemented on with an adhesive containing nonchlorinated organic solvents but it proved too flammable and Bondmaster was used instead. The first use of Bondmaster on a large scale was reported to be on USS SCAMP (SSN588) in which it was used as an adhesive for corkboard. In earlier

ships corkboard was applied with adhesives containing non-chlorinated organic solvents and some water based cement. Bondmaster was well liked in the Shipyard because it was nonflammable and the cemented insulation no longer required shoring as it did with earlier adhesives.

Bondmaster cement is used also in insulating chill water pipes with polyvinyl chloride foam. It was estimated that about 50 gal. of Bondmaster G-527 and 10 gal. of Bondmaster G-596 are used for this purpose.

Formica is no longer applied with cement containing methyl chloroform at Mare Island. The adhesive used for the last several months has been Safebond, a water-based adhesive, manufactured by Minnesota Mining and Manufacturing Co. Other water-based adhesives had been used in the past for this purpose. The Formica cement used in USS STONEWALL JACKSON (SSBN634) was a water-based type and about 70 gallons was required for 1200 sq. ft. of Formica.

An inspection of SSBN634 at Mare Island revealed almost no evidence of corrosion. A lithium hydroxide filter had been installed at the outlet of each burner to scrub the acid gases from the effluent. The filter was shaped like an inverted V and held about 27 lbs. of LiOH in a bed depth of one inch. The total face area of the filter was about 10 sq. ft. The burners of the other 616 class submarines built by Mare Island also were equipped with LiOH filters, but apparently of a different design. The catalyst always contained added LiOH.

Samples of the two LiOH scrubbers in the SSBN630 were sent to NRL and analyzed for chloride by D. D. Williams, Code 6130. The contents of the filter on the forward burner, now mainly lithium carbonate, contained 2.6% lithium chloride. This burner had been used about 10 days. The after burner, which had much less use, contained about 0.6% lithium chloride in its filter. The ship's force had no way of determining when to recharge the filter with fresh LiOH. A method should be developed so that it can be changed before it absorbs enough chloride to become deliquescent.

A factor in this investigation which appeared to be very important was that both the SSBN634 and the Shipyard reported that the main carbon bed had been changed just before each sea trial. This was also true in the case of the SSBN629, and reportedly of the other submarines recently built at Mare Island.

SUMMARY AND DISCUSSION

The shipyard visits showed that there has been widespread use of cements containing methyl chloroform in the construction of recent FBM submarines. Residue of this solvent is undoubtedly the source of the methyl chloroform found by laboratory analyses of ship's atmosphere and filter carbon and other information and the source of much of the recent corrosion caused by CO/H₂ burner effluent. However, the enormous quantities actually used were astounding indeed. No less than 1200 to 1500 gallons of these cements are currently used in each FBM submarine, representing 10,000 to 12,000 pounds of methyl chloroform. Although this material is essentially all applied while the submarine is well ventilated, it is not surprising that sufficient residual solvent exists to create a corrosion problem.

It has been suggested that as much as 5% of the methyl chloroform may be still trapped in the insulation and dissolved in surface coatings, etc., when closed boat operation begins. Such a large reservoir may well evolve methyl chloroform into the submarine at such a rate that there will be appreciable corrosion potential even after a year or two, caused by decomposition of this solvent in the CO/H₂ burner. Because of this condition, the submarines which were built during this period when methyl chloroform was used in very large amounts will require installation of and careful maintenance of high-efficiency acid scrubbers. In addition, fairly frequent changes of the main filter carbon will be helpful.

It appears probable that the much lower incidence of corrosion in the Mare Island boats can be attributed to a combination of several factors. For example, on the four Mare Island FBM submarines (SSBN 619, 624, 629, and 634) each burner was equipped with an output LiOH scrubber. The catalyst always contained 10% LiOH. In addition, main filter carbon was always changed just before each sea trial while under construction at Mare Island. These measures, combined with BUSHIPS-directed changes in ducting, etc., have resulted in essentially no corrosion at Mare Island in these FBM submarines, in spite of the same potential atmospheric contamination problem as in submarines built in the East Coast shipyards. There may be other factors which were helpful at Mare Island, such as application practices, ventilation during building, ambient temperatures of submarine hulls, etc., but specific information here is lacking.

In addition to the primary corrosion which has been established as due to acids such as HCl in the burner effluent, two other sources of corrosion should be mentioned. For example, it has been reported by several sources (e.g., references 13, 15, 17) that there is evolution of chlorides of copper and manganese from the catalyst bed, especially during periods of high temperature operation (i.e., over 600°F). This material can be corrosive if not controlled. Furthermore, it is quite apparent, from the reports cited as references to this study, that condensation of monoethanolamine (MEA) on various surfaces is still a serious problem. Since MEA scrubbers will necessarily be used for several more years, a real effort should be made to bring this contamination under control. MEA contamination is potentially very serious due to its deleterious effect on electrical equipment.

RECOMMENDATIONS

1. It has been shown that methyl chloroform and other chlorinated hydrocarbons and their decomposition products have been seriously corrosive and constitute a potential health hazard in nuclear submarines. It is recommended that the Bureau of Ships eliminate the use of these solvents during construction and reiterate the restrictions on the use of these solvents by operating submarines.
2. To replace the largest single source of methyl chloroform during construction, a suitable alternative cement for hull insulation should be made available in all urgency. The Bureau of Ships should revise the present applicable specifications as soon as practicable to forbid the use of cements containing volatile organic halides.
3. In the meantime, the Bureau of Ships should require that all further use of adhesives containing chlorinated solvents should be as limited as possible, with maximum available ventilation as long as possible, and this use should be prohibited for a reasonable number of days prior to closed boat operation.
4. Restrictions should also be placed on the amounts of chlorinated hydrocarbons in other materials such as degreasers, cleaners, paint removers, etc., which might be used in later stages of construction. The Bureau of Ships should seek alternate formulations for these materials as soon as possible, with a view toward eventual elimination of these solvents.
5. The Bureau of Ships should provide instructions for the most effective use of the main carbon filters, especially for all submarines already built with adhesives based on

methyl chloroform. Carbon should be installed in the main filters only shortly before closed boat operation, and should be changed frequently in new boats. NRL will continue to provide pertinent information as it becomes available on the use of main filter carbon and on the contaminants therein.

6. Detailed information is needed on the persistence of methyl chloroform sources which are contaminating atmospheres in nuclear submarines. NRL will continue to develop such information by laboratory studies of diffusion through insulating materials, by direct analyses on shipboard, and by analyses of selected samples collected by shipboard personnel.

7. The Bureau of Ships should reiterate the need for the presence of 10% by volume of LiOH in the Hopcalite catalyst used in the CO/H₂ burners.

8. The Bureau of Ships should actively continue to support research efforts to find and develop suitable acid scrubbers for the CO/H₂ burner effluent. NRL will continue its present work on lithium carbonate and other acid scrubbers.

9. A suitable analytical device to detect acid effluent from the burners should be made available for shipboard use. NRL will continue its efforts on this problem.

10. The Bureau of Ships should critically examine the CO₂ scrubber systems to determine what design characteristics or operating deficiencies are causing excessive condensation of MEA on surfaces in the AMR-2 of recent FBM submarines. NRL will continue in an analytical capacity to monitor corrosion products and other deleterious effects which may be attributed to MEA.

11. The Bureau of Ships should provide that all materials of construction and operation in nuclear submarines be carefully reviewed in terms of both initial and residual toxicity, corrosivity, and flammability. NRL will continue to cooperate in providing analyses of selected samples of materials.

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