



NRL/FR/6930--97-9840

Separation of Oil from Bilge Water

I. Bilge Water Characteristics and the Interaction of Bilge Water with Chemically Modified Surfaces

E. L. CHANG
J. M. CALVERT
T. KOLOSKI
R. PRICE
B. RATNA

*Laboratory for Molecular Interfacial Interactions
Center for Biomolecular Science and Engineering*

S. PUVVADA

*University of Colorado
Boulder, CO*

T. G. VARGO

*Geo-Centers
Newton Upper Falls, MA*

February 14, 1997

Approved for public release; distribution unlimited.

19970213 005

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE February 14, 1997	3. REPORT TYPE AND DATES COVERED INTERIM October 1994 to September 1995		
4. TITLE AND SUBTITLE Separation of Oil from Bilge Water I. Bilge Water Characteristics and the Interaction of Bilge Water with Chemically Modified Surfaces		5. FUNDING NUMBERS PE -0602234N 0601153N		
6. AUTHOR(S) E. L. Chang, J. M. Calvert, T. Koloski, R. Price, S. Puvvada,* B. Ratna, and T. G. Vargo**				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Washington, DC 20375-5320		8. PERFORMING ORGANIZATION REPORT NUMBER NRL/FR/6930--97-9840		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES * Department of Chemistry and Biochemistry University of Colorado Boulder, CO 80309 ** Geo-Centers Newton Upper Falls, MA 02164				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) We report on the results of a project using surface characterization and novel surface-modification techniques to address the issues of developing a minimally fouling ceramic membrane filter. We have studied the physical characteristics of a synthetic bilge water mixture, examined the surfaces of the ceramic filters for evidence of fouling, and identified several surface modifications that, under laboratory conditions, work well in prevention of foulants. These surfaces, surprisingly, include hydrophobic as well as polar coatings. For the bilge water, it was discovered that detergent, at certain concentrations, may be useful in separating and coalescing oil droplets from the bilge water. Based on the results of the studies, several strategies for optimizing the removal of oil from water are suggested.				
14. SUBJECT TERMS Bilge water Membrane filtration Oil-water separation Oily water Surface modification			15. NUMBER OF PAGES 17	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

CONTENTS

INTRODUCTION.....	1
Background.....	1
TECHNICAL APPROACH SUMMARY	2
METHODS	3
Surface-Coating Procedure.....	3
ESEM	4
ESCA	4
Light Scattering	4
Fluorescence Spectroscopy	4
RESULTS AND DISCUSSION	4
Absorbance Results of Modified Surfaces	4
ESCA Results: Adhesion of Bilge Water Components to Model Substrates.....	6
Fluorescence Results and the Relation of Suspended Oil to Detergent Concentration	7
Light-Scattering Results	9
Synopsis.....	11
SUMMARY AND CONCLUSION	13
Future Work.....	13
ACKNOWLEDGMENT.....	13
REFERENCES.....	14

SEPARATION OF OIL FROM BILGE WATER

I. BILGE WATER CHARACTERISTICS AND THE INTERACTION OF BILGE WATER WITH CHEMICALLY MODIFIED SURFACES

INTRODUCTION

Bilge water, along with gray- and blackwater, make up the bulk of shipboard wastewater. Bilge water originates from many sources: leaks, condensation, evaporation, or wash-down. Pollutants that collect in this water include transition- and heavy-metal traces, oil (from various sources), detergents, and polynuclear aromatic hydrocarbons (PAHs). Efforts are underway in the Navy to decrease the levels of these bilge water pollutants. In order to lower the oil component of bilge water, U.S. Navy ships are being equipped with oil-water separators (OWS) to reduce oil levels from 100 to about 15 ppm. The Naval Surface Warfare Center/Carderock Division (NSWCCD), Code 633, is developing a secondary oil treatment stage that will use ceramic-membrane filters to reduce the oil-in-water concentration to 5 ppm or less. However, the ceramic membranes of the commercially available filters will become fouled, leading to decreased lifetime and efficiency of the filters.

We have initiated a project to use surface characterization and novel surface-modification techniques, developed at the Naval Research Laboratory (NRL), to address the issue of fouled membranes with the expectation that using these technologies will aid both in diagnosing the nature of the fouling process and in developing new membrane filter surfaces that are much less fouling. Note, however, that neither the OWS nor a fully functional secondary system can extract heavy-metal ions or PAHs from bilge water. These systems may, however, indirectly reduce the PAH level in bilge water since most of the PAH will be solubilized into the oily phase.

This report describes the results of measurements of the interactions of modified surfaces with bilge water and of studies on the nature of the bilge water. The overall goal is to design and develop new coatings that can lessen or avoid fouling for oil-removing, ceramic-membrane filters. The initial objectives are to determine how different surfaces interact with bilge water in terms of adhesion to the prepared surfaces and to better understand some of the characteristics of the bilge water that cause the fouling. Our eventual goal is to take what has been learned in the laboratory and, working with NSWCCD, to place a low-maintenance, long-lifetime filtration system onboard Navy ships that will reduce the oil concentration in bilge water to 5 ppm or less. Achievement of these objectives will decrease logistic and maintenance requirements and will enable the deployment of naval vessels in all strategic waters. Such systems could also be transitioned to commercial shipping, since environmental regulations are enforceable against nonmilitary shipping. The technology developed should also have potential applications in oily remediation of other kinds of waste water or contaminated soils.

Background

While, historically, naval ships have sovereign immunity from maritime environmental regulations, the trend is for the naval vessels of the maritime nations to come into compliance with international agreements, such as the protocols from the MARPOL Convention (International Convention for the Prevention of Pollution from Ships). In particular, MARPOL designates "special areas" where waste discharges from ships are banned. These areas, which include the Mediterranean Sea, the Persian Gulf,

and the Black Sea, are some of the most strategically important regions of the world. Unless shipboard processes can be put into place to help vessels comply with discharge requirements [1], the U.S. Navy will inevitably be in violation of these regulations in the "special areas."

NSWCCD has identified cross-flow, ceramic-membrane filtration as the technology of choice for compliance with both local and international environmental regulations for bilge water. These inorganic filters have been successfully used for commercial separation applications since the 1970s. However, the Navy has unique requirements that may not be satisfied by any current off-the-shelf systems. To be usable aboard Navy ships, naval systems must take up minimal space, require no complex procedural steps, and need minimal maintenance. Therefore, standard practices such as back-flushing and between-cycle chemical cleaning of filters are to be avoided, if possible. Our approach is to develop a membrane surface that is nonfouling enough to obviate those procedures. Furthermore, by studying the characteristics of bilge water while developing these ceramic membrane filters, we hope to better understand how bilge water interacts with the modified surfaces. This should enable us to increase control over the parameters involved in membrane filter fouling and thereby lead to development of an overall strategy for controlling bilge water characteristics.

TECHNICAL APPROACH SUMMARY

Current systems considered for secondary purification of shipboard bilge water use cross-flow filtration to separate contaminants at the surface of the substrate and thereby allow purer water to pass through the filter (permeate). Existing filters are made of high-surface-area ceramics, which are constructed primarily of densely packed silica or microporous zirconia. The filter is formed as a long, solid tube (e.g., 13 to 36 in.) with an array of 2 or 4 mm feed channels that run the length of the tube. The surfaces of these feed channels are coated with a ceramic membrane of defined pore size (e.g., 0.005 to 1.3 μm).

To develop minimally fouling separation systems, we must examine the mechanisms that lead to fouling of the porous ceramic filters and develop chemical means for extending the lifetime of these filtration systems. We have divided the research issues associated with the development of membrane-filters for shipboard oil-water separation into three areas: the nature of fouled surfaces, the nature of the bilge water, and modification of ceramic surfaces. One aim is to discover how the surfaces are being fouled and the possible relationships between fouling and the nature and distribution of suspended oily particles. This information will then help drive the design of surface-modifying materials and methods to maximize particle/pore size mismatch.

While the primary aim of cleaning bilge water is to separate oil from water, bilge water also contains a significant amount of detergent, solvents, and PAHs. These amphophilic molecules complicate all interactions between the pollutants themselves and between pollutants and surfaces. Therefore, the situation is much more complex than a simple two-phase oil-water separation problem. The presence of the extra detergent and other compounds in bilge water is, in fact, an important factor in fouling since ceramic filtration has otherwise been shown to be highly efficient in separating mixtures of just oil and water. With feed stream oil concentration ranges from 100 to 575 ppm, the filters have decreased the concentration of oily substances in the filtrate (permeate) to between 2 and 5 ppm [2]. However, the addition of detergents and solvents decreases the filter efficiency significantly. One major effect of the detergents could be to create much smaller droplet sizes in the emulsion, down to micelles on the scale of membrane pores—thereby facilitating fouling through plug-formation. Thus, understanding how the "extraneous" additives affect oil-droplet sizes will help us control (i.e., enlarge) the droplets and thus enable us to decrease membrane/oil interactions, and thereby reduce membrane fouling.

The question of whether particle blocking or film formation is causing fouling can be partly resolved by using surface analytical techniques to monitor the buildup of contaminants on both the surface of the channels and the internal pore spaces. For example, scanning electron microscopy (SEM) could possibly distinguish between the two modes of fouling by determining whether particles are embedded in the pores that line the channel surfaces, or whether a relatively continuous organic deposit exists that would be characteristic of the gradual buildup of an oily film on an initially clean surface. Of course, both mechanisms could also coexist. Surface analysis by X-ray photoelectron spectroscopy (XPS) or energy dispersive spectrometry (EDS) would give additional insight into the elemental composition of deposits in both the interior of the channels and the microporous regions as a function of time in use.

NRL has developed techniques for permanent, covalent bonding of organosilane self-assembled monolayer (SAM) films to a wide range of oxide surfaces (e.g., silicon oxide, aluminum oxide, tungsten oxide, titanium oxide, platinum oxide). Improvements in the nonfouling performance of filter surfaces may be achieved by chemically coating the channel surfaces with these materials to eliminate surface tension matching or mismatching at the interface of the porous membrane.

To date, we have used Environmental SEM (ESEM) and Electron Spectroscopy for Chemical Analysis (ESCA) to characterize the fouled filter-surfaces, and have physically analyzed the foulants. Surface modifications that use silanization to produce surface functional groups, such as phenyl, hydrocarbon, fluorocarbon, and others were performed to create a panel of modified surfaces that spanned a wide range of hydrophobicity, as determined by contact angle measurements. Finally, we used light-scattering and fluorescence spectroscopy to characterize the size and distribution of the oily suspensions. The details of the experiments, the results, and a discussion of the data follow.

METHODS

Surface-Coating Procedure

Cleaning

Fused-silica slides were used for laboratory testing of surface interaction with synthetic bilge water. The slides were immersed in MeOH/HCl (1:1, v/v) for 30 min. The slides were rinsed twice in deionized (DI) water and then immersed in H₂SO₄ (conc) for 30 min. After again rinsing twice in DI water, they were dried with an N₂ stream.

Silanization

The following silanes were used: N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (EDA), octadecyltrichlorosilane (OTS), tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane (13-FT), hexamethyldisilane (HMDS), (p-chloromethyl)phenyltrichlorosilane (UTF-24), 11-Phenylundecyltrichlorosilane (Ph-11), polyethylene glycol (PEG), and 3-sulfonatopropyltrimethoxysilane (sulfonate). For the trichlorosilanes (e.g., 13-FT, OTS), the substrates were immersed in a 1% solution of the silane in anhydrous toluene for 5 to 7 min inside a glovebag or glovebox. The substrates were then rinsed twice with fresh toluene and baked at 120°C for 5 min. The water contact angles on fused-silica were 120° and 105° for 13-FT and OTS, respectively. For trimethoxysilanes, a slightly different procedure was used: a drop of acetic acid was added to a 94:4:1 mixture of methanol:water:silane. The substrates were immersed in this solution for 20 to 30 min on the benchtop and rinsed in methanol twice before baking at 120°C.

ESEM

Scanning electron microscopy was performed with an ElectroScan Corporation ESEM Model 2020 (Wilmington, MA). Scans were taken at 20 kV at a working distance of 6.44 mm and pressure of 4.9 T. No coatings of samples were necessary.

ESCA

Electron Spectroscopy for Chemical Analysis was done for surface-modified fused-silica slides that were immersed in a synthetic bilge water mixture for 18 h and 30 d. Spectra were taken at a 45° angle with a 1.46 min acquisition time.

Light Scattering

A Coulter instrument (N4MD, Hialeah, FL) was used to make the photon correlation spectroscopy measurements. Data were analyzed with a histogram method and for total scattered intensity. Samples were either vortexed or sonicated for 10 min. The effect of the oil/detergent ratio on the particle size was studied both by titrating aliquots of oil into a 250 ppm detergent/water mixture and aliquots of detergent into a 1000 ppm oil/water mixture.

Fluorescence Spectroscopy

Calibration of Bilge Oil Fluorescence

Fluorescence concentration standards for the bilge oil were prepared by serial dilutions, from 1:27 to 1:64000, with dodecane. The excitation wavelength was set to 360 nm, and emission was then scanned from 350 nm to 700 nm on an SLM 8000 Fluorimeter (SLM-Aminco, Urbana, IL). Dodecane had no intrinsic fluorescence under these conditions.

Preparation of Bilge Oil/Detergent Mixtures

We prepared 1000 ppm bilge oil/water samples by adding 50 mg of oil to 50 mL of 18 M Ω , 0.2 μ m filtered water. Aliquots from a stock detergent solution of 50,000 ppm were added to individual oil/water samples to obtain the desired detergent concentration. The samples were then sonicated for 5 min in a bath sonicator. Fluorescence was recorded from 370 to 450 nm and the averaged peak region of 388 to 392 nm was calculated. Oil fluorescence did not shift in the presence of water and detergent. The detergent itself had no measurable signature in this region until about 1800 ppm detergent.

RESULTS AND DISCUSSION

Absorbance Results of Modified Surfaces

The modified surfaces span a wide range of hydrophobicity, as determined by their contact angles. The plain fused-silica surface had been cleaned by the above described procedure and exhibited the lowest (most hydrophilic) contact angle. EDA and sulfonate are positively and negatively charged surfaces, respectively, while the others span a wide range of polarity and hydrophobicity. The most hydrophobic surface is 13-FT, which is significantly more hydrophobic than Teflon™ ($\eta = 120^\circ$ vs 108°). Table 1 gives the contact angles for the coatings.

Table 1 — Contact Angles

	Fused-Silica	EDA	Sulfonate	PEG	UTF-24	Ph-11	HMDS	OTS	13-FT
Contact Angle (°)	15°	25°	35°	50°	65°	70°	75°	105°	120°

We used UV absorbance to monitor the adsorption of material on the modified surfaces. Figure 1 shows the individual spectra of the detergent and oil. After only 18 h, the different surfaces have separated themselves into a range of differential adsorptivities with 13-FT the lowest and Ph-11 the highest (Fig. 2). After 30 d, only four surfaces still showed relatively clean surfaces: cleaned silica, sulfonate, OTS, and 13-FT (Fig. 3). The 13-FT- and OTS-modified slides showed the lowest absorbances, while the cleaned silica and sulfonate slides were slightly higher.

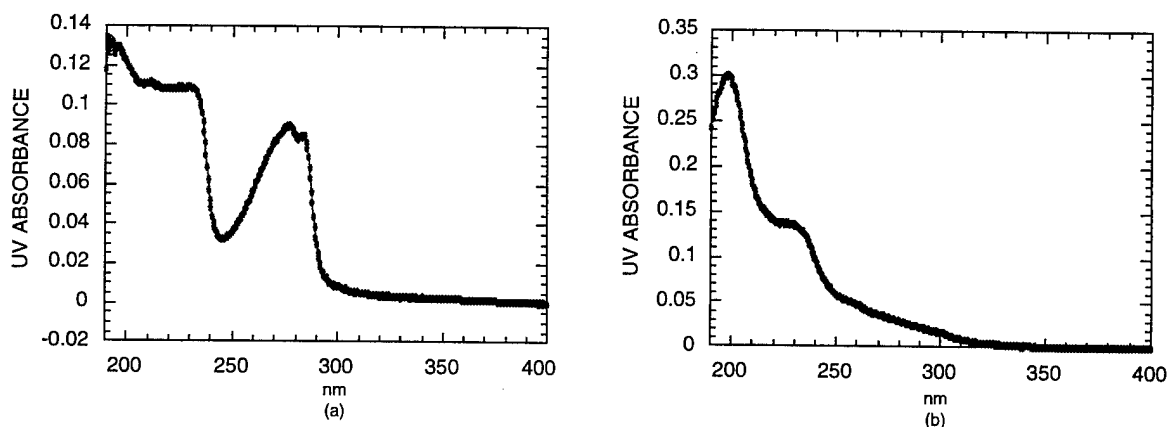


Fig. 1 — Adsorption on fused silica of (a) detergent film and (b) oil film

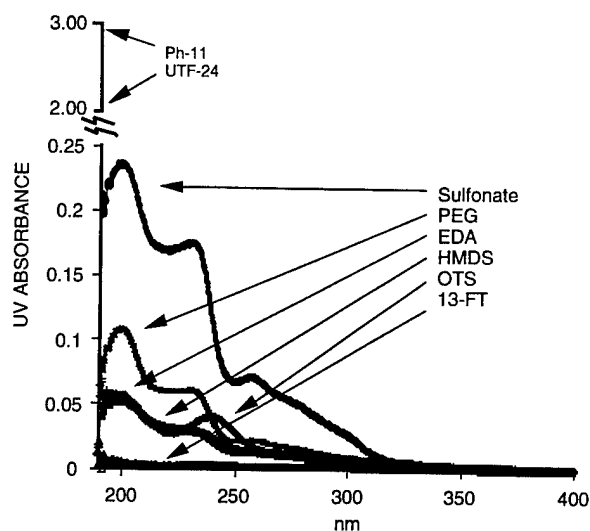


Fig. 2 — Modified surfaces after 18 h

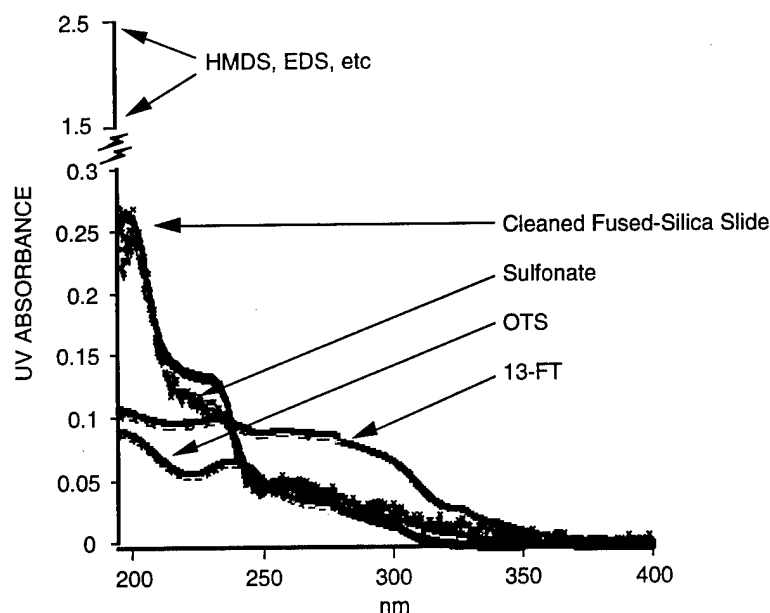


Fig. 3 — Modified surfaces after 30 d

ESCA Results: Adhesion of Bilge Water Components to Model Substrates

ESCA was used to analyze several model surfaces that were exposed to a solution containing the components found in typical bilge water filtering environments. Specifically, seven different surfaces (listed in Table 2) were studied with the intention of determining if and how ESCA analysis might be used to study the adsorption and adhesion of foulants to bilge water filters. Table 2 lists the atomic ratios that were calculated from core level photoelectron signals obtained via the ESCA analyses. We determined that most of the material adsorbed from solution onto the model surfaces consisted mainly of oxygen, free hydrocarbons, and $-\text{SO}_3^-\text{Na}^+$, which most likely originated from the detergent portion of the simulated bilge water mix. Since the signal from the sulfonate was small, we could assume that the oxygen signal measured on these substrates originated mainly from the substrate, with only minor contribution from the adsorbed film. Thus, we used the ratio of the sulfur 2p to oxygen 1s photoelectron signals to provide a relative measure of the amount of adsorbed material. Table 2 shows no detectable adsorption of foulant to either cleaned fused silica or the OTS treated fused silica (i.e., ESCA did not detect sulfur). Only trace amounts of sulfur were measured on the 13-FT coated substrate, and the sulfur/oxygen (S/O) ratios calculated for the other substrates indicated large amounts of adsorbed foulants. These results correlate well with the UV-VIS results reported below. The sulfur/carbon (S/C) ratios calculated for the samples that showed large amounts of surface adsorbed material were the same within experimental error. This indicates that the materials that adsorbed to these surfaces are compositionally similar.

Table 2 also lists sulfur/sodium (S/Na) atomic ratios. If all the sulfur and sodium came from NaSO_3 , this ratio should be 1.0. Due to differences in sampling depths related to the kinetic energies of the Na 1s and S 2p core photoelectrons, this ratio is dependent on the thickness of the adsorbed foulant film. Specifically, the S 2p photoelectrons can originate from the top 5 nm of the film whereas the Na 1s photoelectrons can only come from the top 1.5 to 2.0 nm of the film. As the film thickness exceeds 2.0 nm, we expect the S/Na atomic ratio to increase, since we cannot measure Na photoelectrons that reside at deeper film depths. Thus, this ratio can be used in conjunction with the oxygen/sulfur (O/S) ratio to obtain relative film thicknesses. This can be seen in the case of the 13-FT substrate where we

know from UV-VIS results and the O/S ratio that the adsorbed film is extremely thin. The S/Na ratio measured for this substrate is very close to the theoretical value of 1.0 as opposed to HMDS (S/Na = 7.0) where we know from UV-VIS and the O/S ratio that the adsorbed film is much thicker than 5 nm.

Table 2 — Adhesion to Substrates as Measured by ESCA

Surface	O/S	S/Na	S/C
Fused Silica	-	-	-
OTS	-	-	-
13-FT	31	1.5	-
HMDS	4.4	7.0	0.012
EDA	4.9	3.7	0.015
Phenyl-11	5.7	1.7	0.012
Benzyl Cl	5.1	2.2	0.011

Also, used in conjunction with UV-VIS and the O/S ratio, the S/Na ratio can be used to indicate segregation of the detergent from the hydrocarbon component of the foulant. For example, Table 2 lists O/S ratios as 4.9 for the EDA substrate and 4.4 for the HMDS substrate. UV-VIS also shows that these two substrates have comparable adsorbed film thicknesses. The S/Na ratios for these two substrates, however, differ significantly, i.e., 7.0 for HMDS and 3.7 for EDA. Therefore, these results indicate that the sulfonate-containing component of the foulant film is spread more homogeneously throughout the film adsorbed onto the HMDS than onto the EDA, whose S/Na ratio indicates that the sulfonate is segregated more towards the surface of the adsorbed film.

Fluorescence Results and the Relation of Suspended Oil to Detergent Concentration

The bilge oil obtained from NSWCCDC consists of a mixture of 2190 steam turbine oil (MIL-L-1733I), 9259 lubricating oil (MIL-L-9000 G), and DFM Shell Oil. This oil blend is intrinsically fluorescent (Fig. 4) and this fluorescence can be used to estimate the amount of oil in suspension. The oil fluorescence is normally quenched until the oil has been diluted approximately 100 fold, or to approximately 8900 ppm (Fig. 5), at which point the oil solution-concentration can be calibrated. The oil-mixture fluorescence maximum ($\lambda_{\max}$) ranged between 389 and 404 nm. In fact, its spectrum is similar to that of compounds such as prodan (6-propionyl-2-dimethylamino naphthalene), a PAH fluorophore sold commercially as a fluorescence probe. The similarity likely means that there is a significant amount of PAH in naval ships' engine oils.

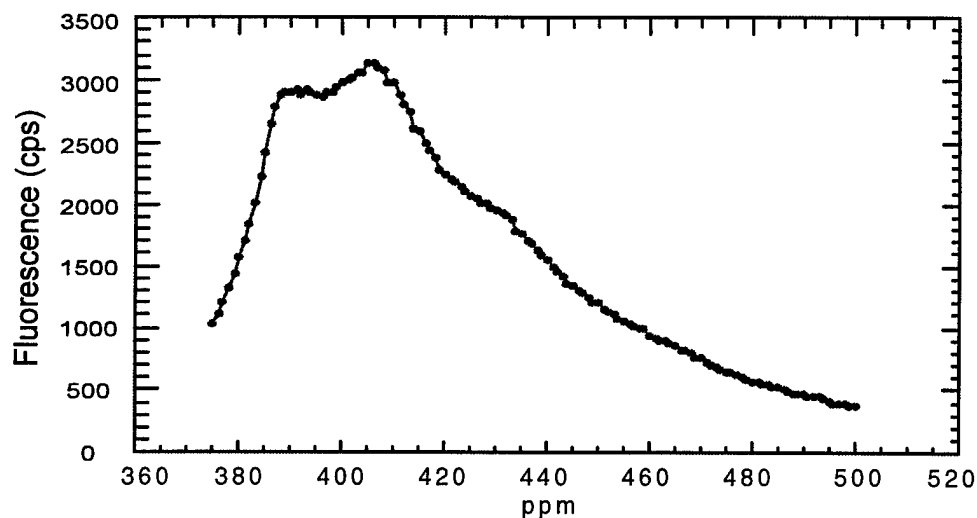


Fig. 4 — Bilge oil fluorescence (excitation is 360 nm)

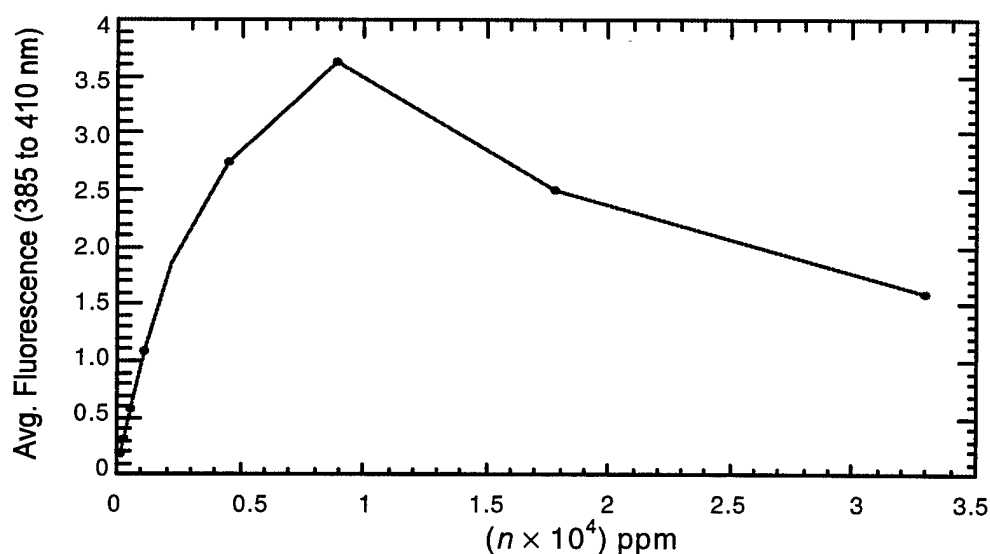


Fig. 5 — Dilution curve for bilge water

The question of how much oil is brought into the water phase by the presence of detergent was addressed by measuring the amount of oil in the aqueous phase as a function of detergent concentration. The “detergent” blend is made up of nonylphenoxypolyethoxyethanol (M. ID 16791), liquid Tide™ (without bleach), and stoddard solvent, a dry cleaning solvent. Seven samples of 1000 ppm oil and 0, 50, 100, 200, 300, 400, and 500 ppm detergent, respectively, were measured, and the amount of oil in the water-rich subphase was tracked by using the intrinsic oil fluorescence signature. When there is no detergent in the oil-water mixture, no suspended oil can be detected, fluorometrically, in the bulk phase of water. The amount of oil increases monotonically with added detergent up to 100 ppm detergent, at which point a plateau of oil-in-water is reached. Between 300 and 400 ppm detergent, the amount of oil increases again. At about 500 ppm detergent, or an oil:detergent ratio of 2:1, the oil concentration drops dramatically—to a concentration similar to that obtained with the addition of only 50 ppm detergent or less (Fig. 6).

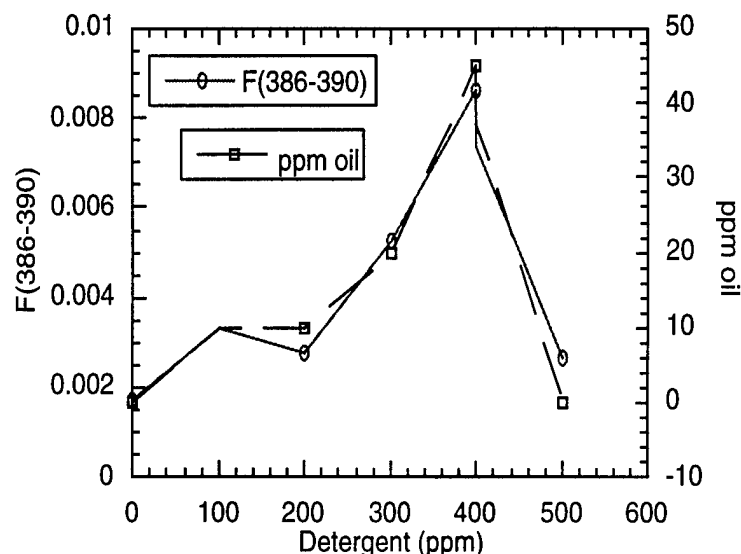


Fig. 6 — Fluorescence and amount of oil in subphase vs detergent concentration

The same information is also given in the figure, but in terms of the oil concentration corresponding to that fluorescence intensity. This reversal in trend for the dispersion of oil into the watery phase is surprising but is consistent with the observation that the subphase becomes much clearer at 500 ppm detergent. One possible explanation is that the oil/detergent structures are so big at this concentration that the natural buoyancy of the hydrocarbon chains will cause the droplets to rise. The buoyancy effect is thought to be significant when the droplet size is around 10 μm .

Light-Scattering Results

The total scattered light at 90°, given as counts per second (cps), follows the behavior monitored by the fluorescence measurements (data not shown) with a drop occurring in the cps at 500 ppm (oil:detergent of 2:1). It is not usually a surprise to observe a decrease in scattered light at very high (500 ppm) detergent concentrations. At high detergent levels, the size of the emulsified particles should be decreasing, resulting in an accompanying drop in light scattering, provided that the total number of particles (or, equivalently, the amount of oil solubilized into the bulk water) is fairly constant. However, when coupled with the fluorescence data, which show that less oil is in the water, the intensity drop can be attributed to a decrease in the total amount of material (i.e., oil) in the water.

Measurements of the size distribution of the oily droplets in the bilge water show a definite bimodal trend. For vortexed suspensions, the larger population was in the tens of microns range with the two populations differing by a factor of approximately 16 for the lower oil concentrations, while the two populations differed by a factor of about 6 for the more concentrated oil suspensions (Fig. 7).

When sonicated for 10 minutes (to simulate turbulence), both size populations decrease by one order of magnitude and the ratio of small-to-large particle sizes generally rose by a factor of 30 (Fig. 8). The large size separation between the two populations suggests that filters of differential pore sizes can be used in a multistage system to filter out first the larger then the smaller particles. A pore size of about 10 nm or smaller would be the minimum necessary for effective removal of most of the smallest oily droplets. The distribution displayed in Fig. 9 shows that most of the population is concentrated in the larger mode.

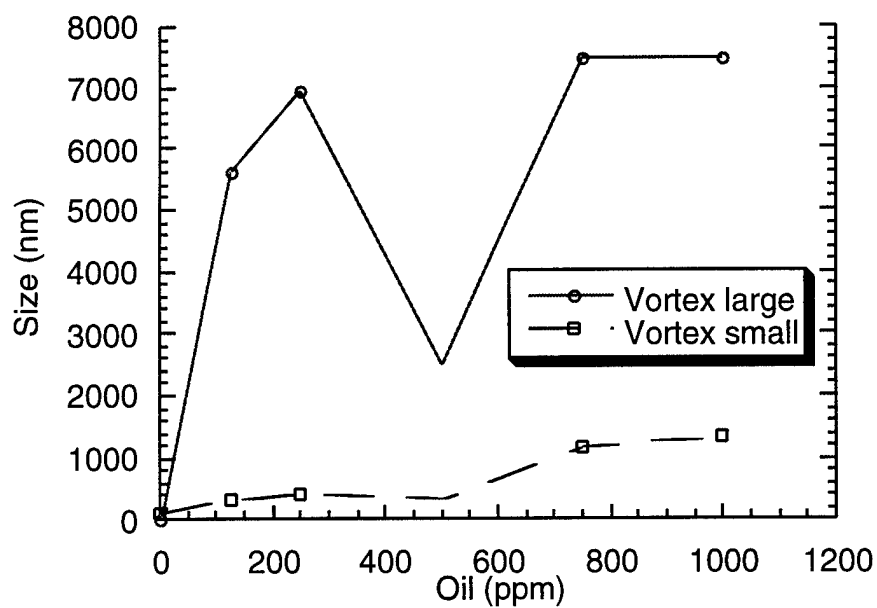


Fig. 7 — Bimodal size population for vortexed oil droplets

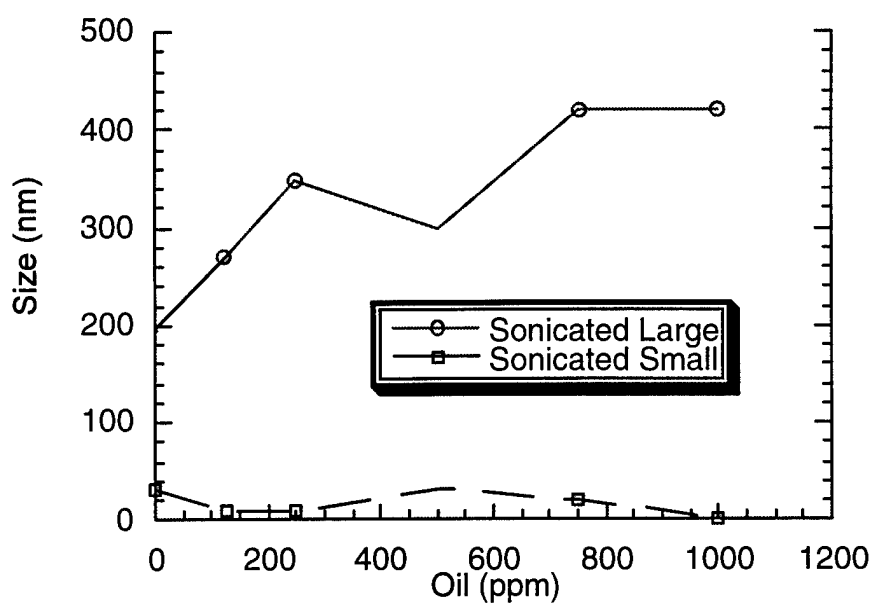
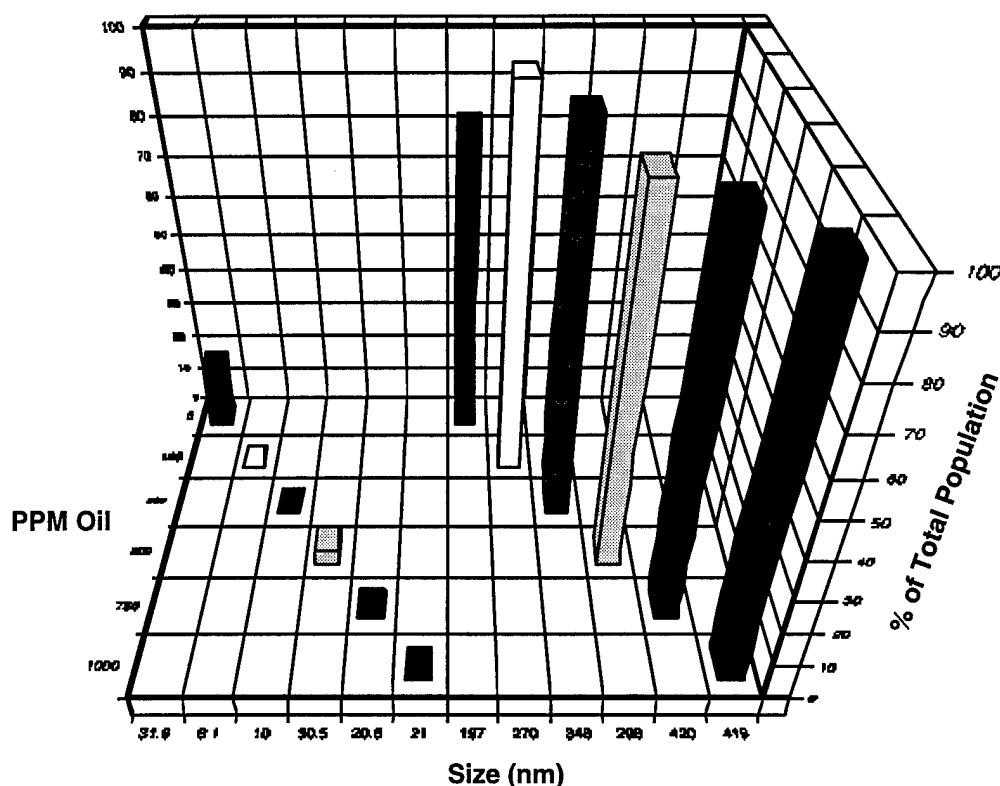


Fig. 8 — Bimodal size population for sonicated oil droplets



nonfouling as the other three. One possibility is that the fused silica has a very smooth surface that may physically limit the ability of foulants to stick.

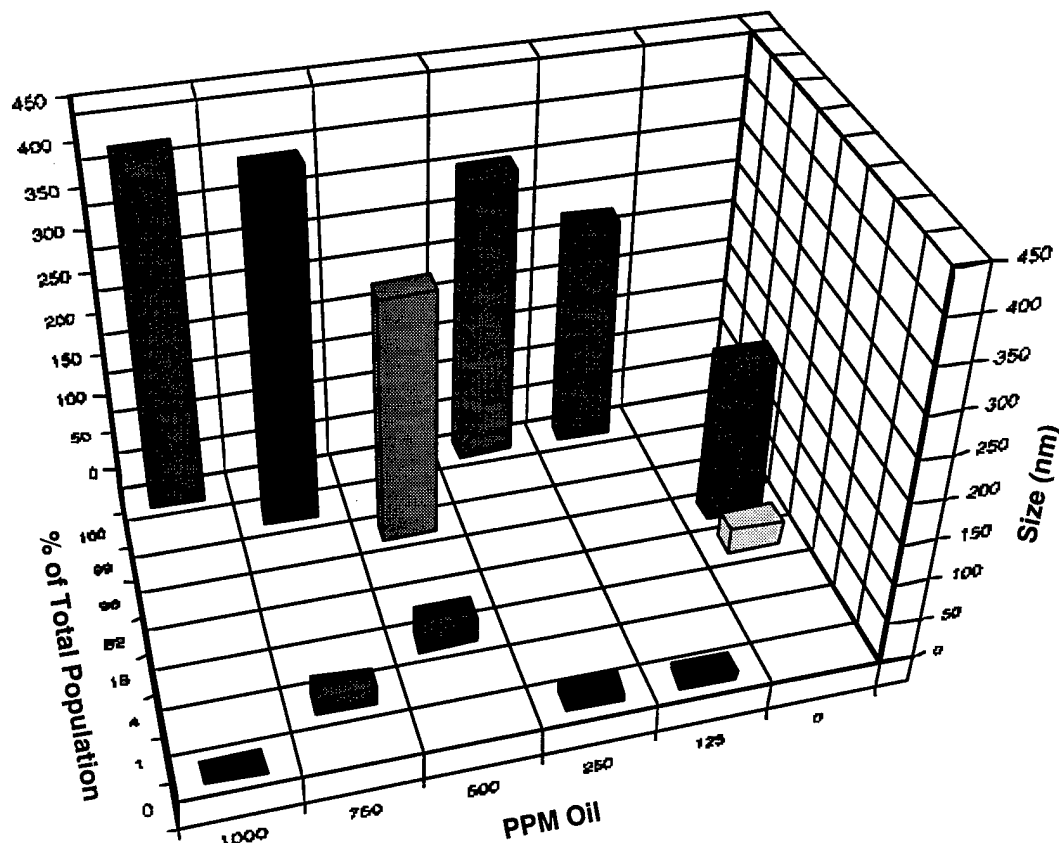


Fig. 10 — Size change as a function of oil concentration (det = 250)

The scattered light intensity and fluorescence measurements examined the effects of increasing detergent concentrations on the amount of oil in suspension. We found that very little oil could be found in the bulk of the suspension in the absence of detergent. The oil concentration in suspension increases with added detergent. Of most interest, however, is the observation that incorporation of oil into bulk water decreased abruptly when the detergent concentration reached 500 ppm in the presence of 1000 ppm oil (Fig. 6). The decrease was equivalent to creating a condition where the amount of oil in suspension was less than 50 ppm detergent. This oil decrease in the bulk phase is also accompanied by a concomitant decrease of total "solute" in the bulk region, as borne out by the scattered light intensity which shows that there is less total material in suspension at the same oil:detergent ratio of 2:1.

A correlation between the fluorescence and the particle-size measurements can also be observed from the light-scattering size distribution data. These data show a decrease in size of the sonicated (larger) population at 500 ppm oil and 250 ppm detergent. This decrease is counter to the general trend of increasing size with increasing oil and, what is of more interest, the ratio of oil to detergent is 2:1, the same ratio found in fluorescence measurements for different absolute values of oil and detergent concentrations. It appears that something unique is occurring at the 2:1 concentration that both decreases the amount of oil and the oily particle sizes in water. The question of where the oil has gone is readily seen by the increased amount of oil "slick" on the water surface within the sample flask and the sudden clarification of the bulk of the suspension.

SUMMARY AND CONCLUSION

In summary, we have made some initial measurements of the physical characteristics of the synthetic bilge water mixture, looked at the surfaces of the fouled filters for evidence of fouling mechanisms, and found several surface modifications that, under laboratory conditions, work well to prevent adhesion. These findings and conclusions are outlined below.

- Four surfaces were found to have superior nonadsorption surface properties: 13-FT, OTS, sulfonate, and cleaned silica. The results show that either an extremely hydrophobic or a negatively charged surface could help with antifouling. Cleaning off-the-shelf filters with our procedure may also provide a salutary effect, without a need for additional modifications.
- If one takes as a hypothesis that fouling occurs only when the oily phase is brought in contact with a surface, then detergent—by its emulsifying properties—will allow more interaction between filter surface and oily waste, leading to an intensification of the fouling problem. We have found, however, that when oil and detergent reach a 2:1 ratio, the mixture appears to coalesce in visible oil film on the water surface. That is, the oil becomes significantly separated from the water. This observation points to dynamic adjustment of the oil:detergent ratio as a possible way to alleviate fouling of filter membranes. This remedy would also obviate any need for prior surface modification of the filters.
- The bimodal size distribution data suggest that for a multistaged filtration system, it may make sense to have the pore size of the initial filter be between the two population sizes. The second, or latter, stages can then be designed to specifically rid the system of the smallest particles.
- We have found that resistance to fouling in the presence of bilge water does not depend on just one parameter. Either a highly hydrophobic surface or a negatively charged surface may function well. Furthermore, it may be possible to enhance the performance of the commercially available filters by precleaning them using our procedures.

Future Work

The size distribution and oil concentration results are very intriguing and point to possible ways to improve ceramic filter performance in addition to, or in place of, filter surface modification. Our major task for the coming year, however, will be to take the candidate coatings and modify whole filters for testing. Initially, we will try 3-in. coupons of the filters to test both our modification procedures and filter performance on a smaller level. However, given that ceramic filtration has to have custom end-fittings to perform, the 3-in. coupon tests may not be adequate to resolve which coating is a clear winner. Therefore, we will also be developing modification procedures for the whole (13-in.) filters. Due to their size, either special troughs will have to be built or otherwise obtained or fittings made to cap the ends during modification. Preliminary tests will be done on these filters to gauge their optimum test parameters. These preliminary tests will be followed by long-term testing.

ACKNOWLEDGMENT

The authors acknowledge the Office of Naval Research for their support of this project.

REFERENCES

1. J. Kraska, "The U.S. Navy and the Marine Pollution Convention," *Amer. Bar Assoc. Natl. Security Law Report* **15**(9), 1-2, 5-6 (1993).
2. R. R. Bhawe, *Inorganic Membranes Synthesis, Characteristics, and Applications* (Chapman and Hall, New York, 1991).