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NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

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NAVAL SHIP RESEARCH AND DEVELOPMENT LABORATORY
Annapolis, Maryland 21402

SHIPBOARD OIL-POLLUTION CONTROL SYSTEMS FOR BALLAST AND BILGE WATERS A STATE-OF-THE-ART-SEARCH

By
T. S. Yu and D. R. Ventriglio

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Oil-Pollution Control Systems for Ballast and Bilge Waters - A State-of-the-Art Search

MATLAB 244

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Naval Ship Research and Development Center
Washington, D.C. 20007

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⑥ SHIPBOARD OIL-POLLUTION CONTROL SYSTEMS
FOR BALLAST AND BILGE WATERS.
A STATE-OF-THE-ART SEARCH.

By

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⑨ Research and development rept.

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ABSTRACT

An investigation was undertaken to provide U.S. naval combatant ships with the capability of avoiding oil pollution in excess of 100 parts of oil per million parts of seawater in their discharges of ballast and bilge waters. Examination of the open literature and patents as well as discussion with Government and industrial specialists revealed that:

- No available technology, alone, is practicable for shipboard reduction of the oil content to points below the required limit.

- A combination of two or more operations along with reprocessing might be suitable for the purpose.

- Reliable devices for measuring oil content in water are needed for satisfactory solutions to the problem.

Since no single means has been found, however, the development of a process has begun. The first goal is to solve the bilge-water, oil-pollution problem, which appears simpler, and then to extend this solution to the ballast-water, oil-pollution problem.

ADMINISTRATIVE INFORMATION

This report summarizes the current state of the art on oil water separation as applied to ballast and bilge waters aboard ships. It is Part A of Phase I "Defining the Problem and Setting Goals" in Task Area SF 35 433 006, Task 13216, "Shipboard Ballast and Bilge Water Oil Pollution Control System." It has been performed under Work Unit 1-821-156-A at the Naval Ship Research and Development Laboratory, Annapolis, Maryland.

The task was originally under Sub-project SF 013 08 18, Task 10183 (reference (a)). The inclusion of bilge-water, oil-pollution control was a result of a meeting with the sponsor in October 1968.

ADMINISTRATIVE REFERENCE

(a) ANNADIV NAVSHIPRANCEN Program Summary of 1 May 1967

ACKNOWLEDGMENT

This work was conducted under the sponsorship of the Naval Ship Systems Command. The program manager is Mr. R. R. Peterson (Ships 03413). Technical management was provided by the Naval Ship Engineering Center. Mr. A. Constant (SEC 6154H) is the project engineer.

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SHIPBOARD OIL-POLLUTION CONTROL SYSTEMS
FOR BALLAST AND BILGE WATERS

By
T.S. Yu and
D.R. Ventriglio

INTRODUCTION

One of the causes of oil pollution in navigable water is ship discharge of oily water. Other causes can be incidents like the Torrey Canyon disaster, oil well seepage such as that off Santa Barbara, California, and discharges of oily water from land-based facilities. This task concerns the abatement of oil pollution attributable to discharges of oily ballast and bilge water from naval ships. Its objectives are to develop a practical shipboard system for reducing oil content in the discharging water and to establish principles and operating procedures for that system.

This report constitutes Part A; "State-of-the-Art Determination of Phase I, Defining the Problem and Setting Goals." It will be followed by Part B, "Magnitude of the Problem Determination" and Part C, "Proposing Technical Approaches." Later phases will be prototype development and engineering transformation of the prototype into shipboard installation.

It is to be noted that when the work was first initiated, the main fuel oil for the Navy's surface ships was Navy Special Fuel Oil (NSFO). It has been announced that a distillate-type fuel is to be the Navy's main fuel for ship propulsion.⁽¹⁾ This change in fuel has not been overlooked in this survey of the state of the art.

BACKGROUND

SOURCES OF OIL POLLUTION

Oil pollution is usually the result of the presence of persistent types of oil on water. Such oils are not volatile and resist oxidation, while the nonpersistent type oils can either be vaporized or oxidized. Residual fuel oils, lubricating oils, and heavy tar oils have been classified as the persistent types of oil.⁽²⁾

The main sources⁽³⁾ of the persistent type of oil pollutant are:

- Natural seepage such as that found in the coastal waters resulting from leaks through cracks in the earth.

⁽¹⁾Superscripts in parentheses refers to similarly numbered entries in Appendix B.

• Land drainage resulting from careless discharges of oily wastes from industrial operations.

- Marine discharges due to:
 - . Sunken ships.
 - . Ship accidents.
 - . Tanker washings.
 - . Ballast and bilge discharges.

This report is concerned mainly with ballast and bilge discharges.

LAWS

Although the United States has been interested in pollution control for a long time, the earliest recorded oil pollution in navigable water occurred in the Caspian Sea in 1754. The Rivers and Harbors Act of 1899,⁽⁴⁾ the Oil Pollution Act of 1924,⁽⁵⁾ the Water Quality Act of 1965,⁽⁶⁾ the Federal Water Pollution Control Act (amended 1965),⁽⁷⁾ and the Clean Water Restoration Act of 1966⁽⁸⁾ are all aimed at assuring clean waterways. Internationally, a conference for abating oil pollution of the sea was first called by the British in 1954 after the issuance of the Faulkner Report.⁽⁹⁾ Later, the responsibility of coordinating the efforts of various governments was undertaken by the United Nations⁽¹⁰⁾ which in turn assigned the Intergovernmental Maritime Consultative Organization (IMCO) the responsibility of dealing with oil-pollution problems.

It was in the 1962 International Conference on Oil Pollution on the Sea attended by representatives from 41 countries and observers from 14 other countries that a limit of 100 ppm* (0.01% or one one-hundredth of a percent) of oil in ship's discharging water and a prohibited zone of 50/100 miles from shorelines, as set by the previous 1954 conference, were agreed to. The Third International Conference in 1965 resolved that naval ships of the signatory countries be asked to observe all the resolutions insofar as practical. U.S. Navy Regulations,⁽¹¹⁾ Article 1272, as amended in 1961, already had restricted the discharge of oily water in navigable waterways and coastal waters.

The Federal Water Pollution Control Act, as amended 2 October 1965, and the Executive Order 11258,⁽¹²⁾ "Prevention, Control and Abatement of Water Pollution by Federal Activities," of 17 November 1965 illustrate the desire of the United States Government for the maintenance of cleaner water.

Executive Order 11288⁽¹³⁾ of 13 May 1966 further establishes the purpose and policy of the Federal Water Pollution Control Act.

Department of Defense Directive 5100.50,⁽¹⁴⁾ "Environmental Pollution Control," of 4 January 1966 has a policy for its components to demonstrate leadership in pollution abatement and to cooperate in the development of pollution abatement programs with local communities. It also charges the Director of Defense Research and Engineering and his designee with the responsibility of undertaking such research as necessary to study environmental pollution problems.

*Abbreviations used in this text are from the GPO Style Manual, 1967, unless otherwise noted.

SECNAV Instruction 6240.6A(15) of 24 March 1967 set up the Navy Environmental Pollution Control Program and assigned the Naval Ship Systems Command the responsibility for implementing programs concerning naval ships.

COMPARISON OF COMMERCIAL SHIP AND NAVAL SHIP OPERATIONS

Oil pollution is not unique to naval vessels. Commercial ships have a similar pollution problem. However, because of different types of missions and therefore different requirements, the problems facing naval ships are different in some ways from those of commercial ships.

Ballast Water

Ballast water is the water a ship pumps into its empty fuel oil storage tanks or void spaces to keep the ship stable and in good trim. Because of the locations of the usual two suction outlets (one at 4-6 inches above the bottom for transferring the fuel oil to service tanks and another at 1½-2 inches from the bottom for stripping the tank) and of the viscosity of the oil (which causes it to adhere to the tank walls), there always will be some oil left inside the tank and the piping system. The motion of the ship will mix this oil with the water used for ballasting which often causes some emulsions to exist inside the tanks. When this water is pumped out in preparing the ship for refueling, there unavoidably will be some oil in the deballasting water which results in pollution.

Commercial ships can now avoid the oil contamination of their ballast water by having separate tanks for ballasting only. Naval combatant ships cannot afford the luxury of separate tanks because the effective use of available space aboard ship is of primary importance. Also, because of different emphasis in missions, naval ships often do not have time to deballast at a slow rate. Deballasting rates of 600-3000 gpm per pump can be expected.

Bilge Water

Bilge "water," on the other hand, is the result of collections of drains, drippings and leakages from water, lubricating oil, hydraulic oil, and fuel oil systems. Because of the presence of additives that may be found in the lubricating and hydraulic oils, the oily water mixture in the bilge is different from that in the ballasted tanks. This bilge water would have to be pumped out from the ship's bilge to keep from damaging the ship's machinery and flooding the ship. The amount of bilge-water accumulation varies with the ship's condition and maintenance. In general, the makeup rates of the ship's water, lubricating, and hydraulic oil systems can give some indication of the amount of bilge water to be expected. A bilge-water removal rate of at least 10 gpm is considered a target requirement for a combatant ship. Some commercial ships have been provided with bilge-water separators. At present these are not equipped with positive oil in water measuring and controlling devices. Without these devices, the effectiveness of such separators is not certain. However, they can at least reduce to some degree the amount of oil to be pumped out with the bilge water. Naval ships do not yet have such separators.

Tank Washings

The disposal of the water used for the on-board washing of the oil cargo tanks of commercial tankers or of the Navy's oilers is a problem similar

to that of ballast water. This water is often used as ballast water in the empty tanks on the ship's return voyage to permit good maneuvering capability. This oily water has to be discharged before new oil or other cargos are loaded again.

Commercial oil tankers have now adopted a "Load-on-Top" technique to handle their tank washings. In this technique, the oily part of the washing in any tank is consolidated by transfer to a "slop oil" tank after the settled water has been pumped overboard. The empty tanks are then filled with water to give the tanker its needed stability in maneuvering. This consolidated oily material is then allowed to be mixed with the new crude oil and delivered to the refinery for processing. The Navy's oilers may already practice consolidating the oily material from their tank washings, but they cannot mix this oily material with new fuel oil to be delivered to the ships at sea. The Navy's oilers cannot always unload this consolidated oily material from tank washings at the naval depots before taking on new cargos.

SUMMARY

Naval ships have a difficult problem in observing the oil-pollution requirement. Because of the space and weight requirements aboard naval ships, any process equipment installed to treat the ballast and bilge waters before their discharge has to be compact and of minimum weight. It was against these requirements that this search of the state of the art was carried out.

APPROACH

The search for the available oil-water separation methods was conducted through several avenues. These included examinations of patents (through NSRDC Patent Consul). Defense Documentation Center reports; open publications such as technical books, journals, and manufacturers' brochures; and reports published by other Governmental agencies and private organizations. The search included the collection of information by attending pertinent technical meetings and visiting pertinent Government agencies and private concerns. A few naval ships also were visited to develop information on operations and to obtain ideas of the space available. Ships' personnel were queried on their experiences in handling ballast and bilge waters. A Navy Fuel Reclamation Center was visited to learn of its operation.

The information collected on oil-water separation methods is presented in the section on Separation Techniques.

Recognizing that reliable measurement of oil content in water is an essential requirement for any proposed pollution-control process, the state-of-the-art determination also included the area of analytical instrumentation. The information collected is presented in the section on Measuring Methods.

Associated pertinent information collected with respect to the overall problem is reported in the section on Other Relevant Information.

SEPARATION TECHNIQUES

Separating two immiscible liquids, such as oil and water, in a ship's fuel oil tanks or bilges is not a simple process. The maintenance of two

separate liquid phases is confounded by the mixing of the phases caused by the ship's motion, by the action of pumps, and by surfactants, which may be present in oils (either as deliberately added performance-improving chemicals or as a result of oxidation). Thus, the oil and water inside a ballast tank or bilge can exist in forms ranging from well defined separate layers to mixtures (dispersions or emulsions) of varying degrees of stability. Although some dispersions or emulsions are very difficult to separate, the bulk of one or both liquids can generally be separated by either a single technique or a combination of several techniques.

The following sections cover possible separation techniques. Each of these techniques is discussed and then evaluated for its possible shipboard use within its section.

SETTLING

Separating oil from water by settling should be a natural first choice. Where it can be used, it requires comparatively little energy and inexpensive equipment. In general, oil-water mixtures will separate into two layers if they are allowed to stand for a sufficient period of time. Such technique has been used in many oil-producing fields and refineries, where large spaces are available and long settling times are of no great concern. This technique has been used in water works to separate suspended solid particles (oil-wet solids may be present in the form of rust in deep ballast and bilge waters) by allowing them to sink. The Navy's Fuel Reclamation Plant on Craney Island, near Norfolk, Virginia, is applying this technique in its settling ponds. There the oily water discharged by naval ships either through a piping system on the piers or brought back by barges and "doughnuts" is allowed to stand inside an open pond, and the oil that has floated to the top is skimmed off for the reclamation process. (A "doughnut" is an open-ended cylinder standing vertically in the water to confine oil and to prevent it from spreading.) The water that settles out in the pond is drained off to another trough for skimming off any oil still on its surface before it is discharged into the harbor.

The separation of a mixture of two immiscible liquids by settling depends on:

- The particle size of the inner, dispersed or discontinuous, phase in the outer or continuous phase.
- The difference in their densities.
- The viscosity of the outer or continuous phase.

Three laws (16) (17) have been suggested for the calculation of the rate of rising (separation) of a drop of the dispersed phase, for different ranges of a characteristic property, the Reynolds number ($Re = DV\rho/\mu$). Reynolds number is an indication of flow conditions. As Reynolds number increases, flow condition changes from laminar to turbulent. The three laws used for calculating the rising velocity of a drop of the dispersed phase are:

- Stokes Law (for Reynolds number below 2):

$$V_f = \frac{gD_f^2}{18\mu_h}(\rho_h - \rho_f);$$

- Intermediate Law (for Reynolds Number 2-500):

$$v_l = \frac{0.153 D l^{1.14}}{\rho_h \mu_h^{0.43}} \left[g \rho_h (\rho_h - \rho_l) \right]^{0.71};$$

- Newton's Law (for Reynolds Number 500-200,000):

$$v_l = 1.74 \left[\frac{g D l (\rho_h - \rho_l)}{\rho_h} \right]^{0.5};$$

where

v = velocity

g = gravitational force

D = diameter

ρ = density

μ = viscosity

and subscripts

h is for continuous phase

l is for dispersed phase.

These three laws indicate that the rising velocity or separation of an oil drop is favored by larger phase-density difference, larger drop size, and lower viscosity of the continuous medium. While the density and viscosity can be affected by temperature changes, the drop size is affected by degree of agitation. The change in density and viscosity with temperature is available for oils, water, and seawater. (18) (19) Table 1 serves as an example of the effect of density difference on rising velocity. In this table specific gravities of seawater, NSFO, and distillate-type fuel oil have been taken to be 1.03, 0.99, and 0.89, respectively.

Table 1

Effect of Density Difference on Rising Velocity of Oil in Seawater

	NSFO ($\rho_l=0.99$)	Distillate Fuel ($\rho_l=0.89$)	Increase in Rising velocity %
Stokes' Law $\rho_h - \rho_l$	0.04	0.14	350
Intermediate Law ($\rho_h - \rho_l$) ^{0.71}	0.101	0.248	245
Newton's Law ($\rho_h - \rho_l$) ^{0.5}	0.2	0.374	187

Note: ($\rho_h - \rho_l$) is density difference against seawater

Separation rate increases up to 350% can be obtained depending on the nature of the liquid. Figure 1 further illustrates the relationships of drop versus rising velocity and time required for an oil drop to rise a distance of one foot in calm water. The larger the drop size, the greater the ease of separation.

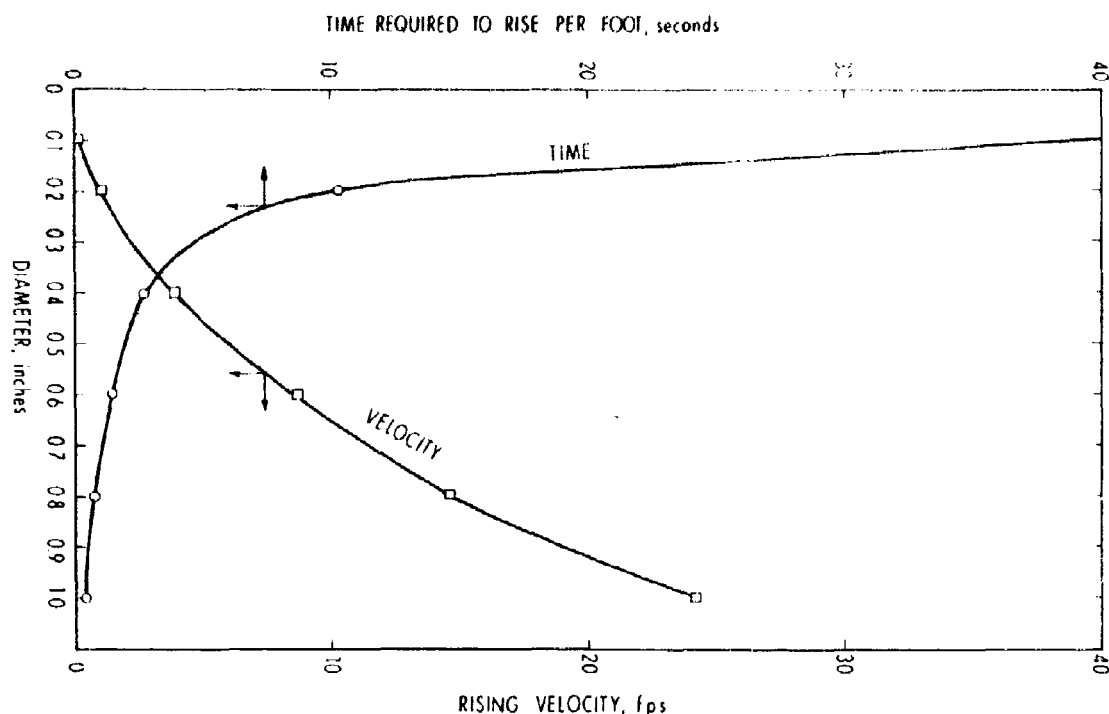


Figure 1
Rising Velocity and Time of Different Size Oil
(Specific Gravity 0.99) Globules

Several investigators⁽²⁰⁾⁻⁽²³⁾ have studied the effects of hydraulic behavior and turbulence on drop size in settling. They all agree that turbulence is not a favorable condition and that rising velocity or rate of separation changes with degree of turbulence. Separation also depends on the oil properties and residence time. The above investigators and some others^{(24),(25)} also looked into separation in a flowing stream. They came to the same conclusions as did the American Petroleum Institute (API) that the faster the flow, the less favorable are the conditions for separation. The API has made recommendations for separator design as a result of their supported investigation at the University of Wisconsin.⁽²⁶⁾ A depth width ratio of 0.3-0.5 is suggested. Figure 2 shows a relation based on depth/width ratio for drop size and length of separator needed for a flow rate of 3000 gpm. When sufficient time and a large area are available, continuous flow separation like that suggested⁽²⁷⁾⁻⁽²⁹⁾ is possible. Some refineries⁽³⁰⁾ have satisfactorily removed oil from their aqueous wastes with this type of separator. In view of renewed interest

in oil pollution, API has revitalized their support of investigations in this area. Further developments will be closely watched.

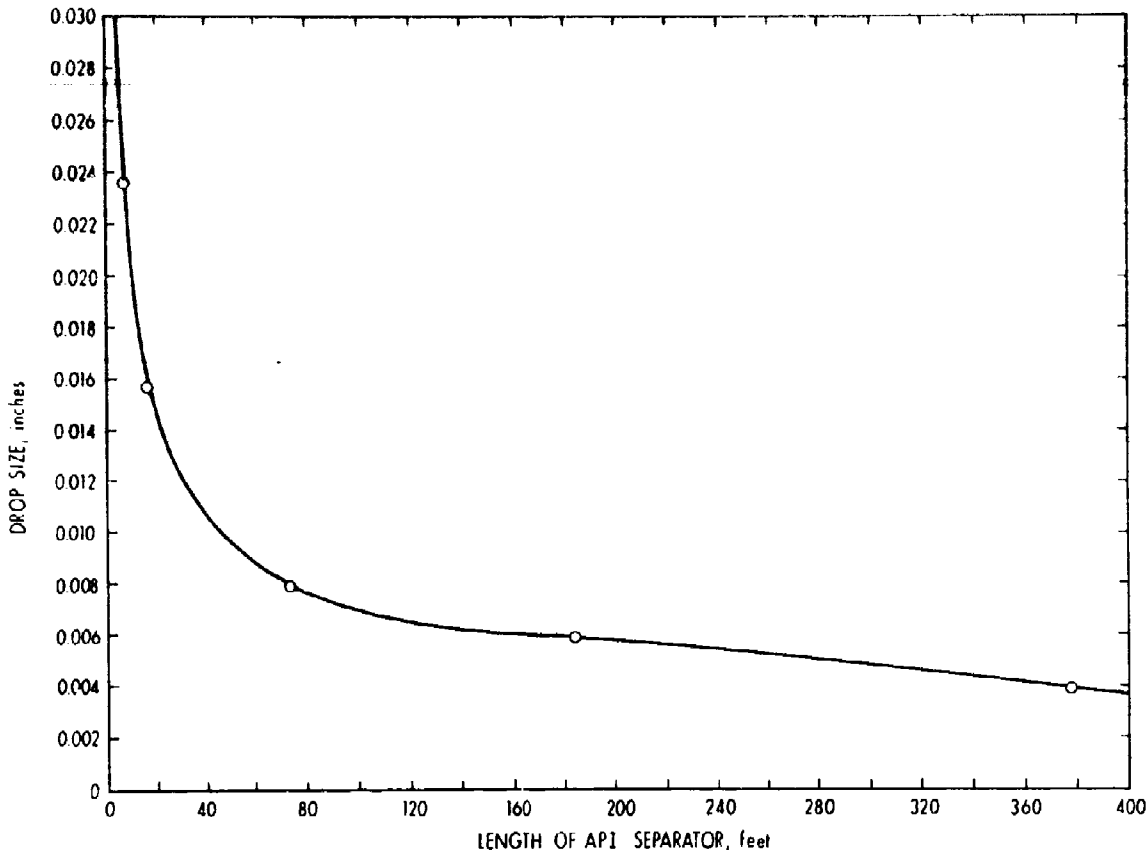


Figure 2
Diameter of Particle Which Will Rise to Surface of API Separator
(Cross Section 40 x 7.75 Feet)
Versus Length Necessary for Particle to Rise to Surface
(Specific Gravity 0.99, Flow Rate 3000 GPM)

Since the time required for a drop of a dispersed phase to rise to the interface for separation is dependent on the distance (depth) to be traversed, suggestions (31)-(34) have been made for reducing the depth by using several perforated conical plates a few inches above each other in a deep tank. This also is essence in reducing the settling length. A separator using a helical path (35) has also been suggested. This suggestion allows the mixture to have longer time for separation.

Settlers with perforated conical plates, or perforated plates of other geometry, have been built by various suppliers (Coded 1 thru 6) and used on ships for bilge water and/or ballast water. They are generally suitable for low flow rates (4-10 gpm). Recently built U. S. Coast Guard "cutters" have a similar type separator for their bilge water installed by Supplier 3. Unfortunately, no data on the quality of water purity before and after the separator are available at present. Suppliers 1 and 2 have not replied to inquiries.

and Supplier 4 has stopped building this kind of separator because of its inability to separate oil-water emulsion, which often exist especially when the mixture is being stirred by ship's rolling and pitching motion. The separator built by Supplier 1 requires that it be filled with liquid during separation. This indicates that a successful separation of oil and water could require a calm situation which may not always be available. However, if baffles to produce smaller compartments and thus reduce sloshing of the mixture can be added inside such separators, better separation could be achieved.

FLOTATION

Flotation is similar to settling in principle. It employs an essentially insoluble gas to surround and thus float suspended particles or drops by increasing the density difference between the suspended air-attached particle or drop and the continuous medium, thus facilitating the separation. The insoluble gas (usually air) may be added either in a dissolved or a dispersed form. Because of the low gas density, a drop of NSFO with an attached air bubble of the same size can rise 15.7 times faster. Even if the attached air bubble is only half its size, the NSFO drop can rise 10.8 times faster. Oil industries(36)-(39) and public water systems(40)-(42) have successfully applied this technique to separation problems in their settling ponds. However, the ponds are usually shallow (5-7 feet in depth) and long (30-110 feet).

Several patents (43)-(47) have been issued in the United States on this flotation technique with the aid of demulsifying agents and employing different means of distributing the insoluble gas.

A word of caution seems to be in order here. Under suitable conditions certain proportions of air oil (hydrocarbon) vapor form explosive mixtures.(48) Therefore, when such flotation technique is to be used, adequate ventilation and fire precautions must be carefully observed.

CENTRIFUGATION

Centrifuges have been used in removing solids from liquids or liquids from other mutually insoluble liquids. In general, when centrifuge is used for separating one liquid from another, a minimum difference of 3% between liquid densities is recommended. This is because smaller differences would require a very large centrifugal force for separation. In theory, the same Stokes' Law used for gravitational settling applies to centrifuging but with centrifugal force utilized instead of gravitational force. Under the same centrifugal force field, a mixture of liquids will behave as follows: The liquids of higher density will have a larger momentum and move toward the outer periphery of the centrifuge while the liquid of lower density will have less momentum and move toward the inner periphery of the centrifuge. The location of the boundary between the two liquids depends on the forces on both sides of the interface. Generally, the location along the radius is related to the density(49) as:

$$\frac{r_h^2 - r_i^2}{r_i^2 - r_l^2} = \frac{\rho_l}{\rho_h},$$

where

r_i = radial distance for the interface
 r_h = radial distance for the heavy phase

r_l = radial distance for the light phase
 ρ_h = density of the heavy phase
 ρ_l = density of the light phase.

There are two types of centrifuges used in liquid-liquid separation. Tubular-bowl centrifuges are usually of high force (in the range of 13000 g) and lower capacity (500 gallons per hour (gph)). Disk-bowl centrifuges usually can handle up to 5000 gph at a lower force (in the range of 7000 g). An equation⁽⁴⁷⁾ has been derived for calculating the critical drop size D'_l , which a given centrifuge can separate. It is:

$$D'_l = \left[\frac{9\mu Q}{(\rho_h - \rho_l)\omega^2 V} \frac{r_i - r_l}{r} \right]^{0.5},$$

where

Q = volumetric feed rate of centrifuge
 r = radius of the centrifuge
 μ = viscosity
 ω = angular velocity of centrifuge
 V = volume of centrifuge.

The critical drop size is the drop size smaller than that which will be in the light phase and larger than that which will be in the heavy phase. This relation indicates that the critical drop size varies inversely with the rotational speed of the centrifuge, and it varies with the square root of the feed rate. Since the centrifugal force is proportional to the square of rotational speed, a decrease of half the critical drop size would require twice the speed and four times the centrifugal force. Similarly, such decrease in critical drop size would reduce the centrifuge to one-fourth of its capacity. It is to be noted that when the rotational speed is increased, the wall thickness of the bowl and weight of the centrifuge will have to be increased.

A review of manufacturers' brochures reveals that a typical unit from Supplier 7 operating at a force of 6500 g with 500 gpm capacity would weigh 2 tons and require 75-150 horsepower. Major centrifuge manufacturers contacted did not express too much optimism in applying centrifugation to separate small amounts of oil from large volumes of water.

If centrifuging is elected to remove oil from ballast or bilge water where large percentage of the mixture is water, it would be inefficient and uneconomical when over 90% of the liquid centrifuged is to be discarded. This does not mean that centrifuge is not a good liquid-liquid separator. On the contrary, centrifuges have been satisfactorily used in removing water from lubricating oils aboard naval ships.

HYDROCYCLONE

The basic principle of separation by hydrocyclone is similar to that of the centrifuge. In a centrifuge the liquid is moved along a circular path by the circular motion of its core. In a hydrocyclone, the liquid is forced into circular motion due to tangential injection of the liquid against the circular configuration of the hydrocyclone. Usually a pump is the prime mover for the liquid. The vortex action leads to high centrifugal force which aids the phase separation. The advantage of a hydrocyclone over the centrifuge is that there are no moving parts. The initial cost is low, therefore, and maintenance

is easy. It also has the advantage of being relatively light in weight. These advantages make the use of this technique of separation potentially more favorable than centrifuges on ships. It would, however, require considerable amount of power to push the liquid mixture through at a fairly high rate in order to achieve a high-centrifugal force needed for separation.

Up to the present, the use of this technique in separating two immiscible liquids has not been very successful because the turbulence created by the high flow rate tends to shear and break the dispersed phase into a still finer dispersion. When the densities of the two fluid phases are close, a separation into two phases by this method may be difficult to achieve.

Experimental work⁽⁵⁰⁾ using kerosene (specific gravity 0.80) and white oil (specific gravity 0.84) with water in the ratios of 1/3 and 9/1 at a rate of 10 gpm has been able to reach efficiencies of 77%-91% with an underflow containing 1.5%-32.7% of kerosene or 0.5%-61.6% of white oil. These values are at least 50 times greater than the required 100 ppm limit, but the density differences in these cases were greater than what would be expected in the Navy's case. A recent presentation⁽⁵¹⁾ reveals that several hydrocyclone units in a battery used to recycle the underflow may achieve better separation results. This would require more pumps and a greater power supply. Unfortunately, not enough information on the effect of this cascade operation is available. This idea will be pursued in a continued follow-up.

Although it may not seem to be a feasible solution to ballast-water purification because of the large volume of liquid involved, it may be worth further investigation for bilge water.

COALESCER/FILTER

Coalescence is a much studied topic but not a very well understood phenomenon.⁽⁵²⁾⁻⁽⁵⁴⁾ The principal driving force is interfacial tension. Coalescence is promoted by lowering the interfacial tension by heat and/or demulsifying agent.⁽⁵⁵⁾⁻⁽⁵⁹⁾ It can also be promoted by physically uniting the interfacial boundary of similar particles.⁽¹⁶⁾

Coalescer/filter operation as applied to liquid-liquid separation essentially requires condensing smaller drops into bigger drops and then separating them according to gravity difference.

Physical interfacial film breakers used as means of coalescence have been mats, screens, and porous or fibrous woven meshes.^{(52),(60)} A criterion is that it have a large ratio of surface area to volume. Usually the two liquids to be separated have different surface properties. A selection of proper material to coat the coalescing element determines which of the two liquids is to be coalesced. Generally it is the dispersed phase that needs to be coalesced.

The Permutit Company⁽²⁴⁾ under contract (MA-2722) with U. S. Maritime Administration has used woven mesh to separate oil from water in their oil-water separation investigation. The presence of impurities (fish scale, scum, coagulated material, and the like) clogs up the coalescing screen and creates a large pressure-drop problem. A series of screens with slow flow rates of 10 gpm per sq ft was able to reduce the oil content in water from 1100 to 160 ppm. The clogging problem of the initial screen still exists. The U. S. Maritime Administration has now contracted with CUNO Division of AMF Company

(MA-4152) to make further investigations. The new investigation(61) uses "Auto Klean" in their disk-type filters to remove the clogging material between disks. The initial report indicates that acceptable effluent concentrations were obtained with 25 gpm seawater with up to 10% of No. 6 fuel oil in the influent. The U. S. Maritime Administration has extended the contract for further studies. Its development will be followed.

Other materials,(60)-(64) such as fuller's earth, diatomaceous earth, clay, granular polymer, glass, or wool fibers in singular or compound forms have been suggested. Not all of these materials can be satisfactorily used for all types of liquids (oils). When hydrophobic materials are used for the coalescer/filter, small water droplets can be coalesced and separated. This has been applied in the removing of water from light fuels, such as JP-4 and JP-5. Conversely when hydrophilic material (53) is used as coalescer, small oil drops may be coalesced and separated. However, the heavier fuel oil for Navy's use can have different origins and contain various kinds of impurities to coat the coalescer and render it inoperable in a short time. Three filter manufacturers (Suppliers 8, 9, and 10) consulted have not been able to find a material satisfactory for this kind of application. When a light distillate type of fuel is to be used, perhaps a suitable coalescer/filter material may be found.

One manufacturer (Supplier 11) has demonstrated the separation of an oil lighter and less viscous than NSFO from water in a coalescer after the mixture had been heated.

The use of coalescer/filter to remove both NSFO and distillate-type fuel from ballast water and various mixtures of lubricating and hydraulic oils from bilge water will be followed.

EVAPORATION/DISTILLATION

Separation of two immiscible liquids by alternate evaporation and condensation techniques is based on vapor pressure differences whether they are operated under normal or reduced pressures. Because of the large volume of mixture and small available space aboard a ship, these techniques are viewed as impractical. Besides, a large amount of energy in the form of steam or electricity for heating, pumping, and/or providing a reduced pressure is needed in vaporizing the water (over 90% of the mixture) before the persistent type of oil can be removed. Although evaporation of seawater is used to provide potable water for a ship's use, persistent types of oil would still remain with the concentrated brine solution as it is discharged into the sea.

FREEZING

Separation based on this technique utilizes the difference in the freezing points of the two immiscible liquids. This method of separation is not deemed practical for the same reasons discussed above in the case of evaporation/distillation.

SELECTIVE ADSORPTION

Adsorption suggests that one of the two immiscible fluids (preferably the one of lesser quantity) is selectively adsorbed on the surface of a suitable material. This technique was used in the 1967 Torrey Canyon incident. The adsorbent material used to sink with the oil is found to have released oil

later and is further reported to have affected marine life on the ocean bottom. Unless the oil adsorbed can be recovered or separated, ships would not only have to carry adsorbent but also the used oil-containing adsorbent. As well, this would create a storage problem on Navy vessels. Of course, another approach is to dispose the adsorbed oil and the adsorbent together. Until such disposal technique can be satisfactorily developed, separation by this method will have to wait for further development.

A very recent patent(65) suggests the use of gas bubbles with a selected surfactant film to hold one liquid inside and the other outside. These bubbles are to go through another layer of solvent to remove the adsorbed liquid and then another solvent layer for transferring surfactant back into the aqueous layer for reuse. Such a technology can only apply to a small quantity of mixture at very slow rate and is not suitable for ship's use at this time.

UNUSUAL PHYSICAL SEPARATION TECHNIQUES

Because of the need to produce pure and fine chemicals for industrial and biomedical use, several unusual separation techniques(66) have been developed in various laboratories. They will be very briefly mentioned.

- Chromatography: Continuous gas, liquid, and gel chromatographic techniques have been successfully operated in purifying some fine chemicals. Columns of several inches to several feet in diameter and up to 20-25 feet in height have been made and operated. Not only is the cost high but also column material selections have not yet been broad enough to include ordinary fuel oil.

- Sonic Separation: This technique is being tested on brewery and dairy products. A proper selection of wave frequency is required. Use of this technique to separate oil and water emulsions may be worth investigating.

- Membrane Separation: It requires the right membrane for the right material; also the volume and rate are limited.

- Electric and Magnetic Separations: Until a better understanding of these physical properties of the liquids to be separated is available, these techniques will have to wait for future development. Dialysis, electrodialysis, electrophoresis and magnetic-electrophoresis can be classified under this category of separation.

CHEMICAL SEPARATION TECHNIQUES

Certain chemicals can react with one component of a mixture and then be removed. In the case of separating oil from ballast and bilge waters, the general use of chemicals is not considered for the following reasons:

- Chemicals used for separation will be in the discharged water. Over a period of time they would also become pollutants to contend with.

- Experience has shown that chemicals used as demulsifying agents are very specific in their actions. No universal demulsifying agent is known.

- The use of chemicals would require special materials for tanks and piping systems.

• Since the amount of oil and water may vary over a wide range, trained operators or fully automated sensing and metering devices to administer the correct amount of chemicals may not be available.

Although the routine use of chemical, as a means of separating oil from water, is not recommended, occasional use of a limited amount of demulsifying agent is not totally objected to when stabilized emulsions are encountered. Such use should be minimized and avoided if possible. A report⁽⁶⁷⁾ on an oil spill which occurred at San Juan, Puerto Rico, by the ship OCEAN EAGLE on 3 March 1968 reveals that some of the detergent chemicals used even in the ranges of 0.1 ppm are harmful to many marine life forms. Conversely, the Navy Fuel Reclamation Plant at Craney Island, Virginia, uses demulsifying agents to assist in the separation of stable emulsions. In this application the oily mixture has to be held at 180° F for 20 hours for effective separation.

BIOLOGICAL SEPARATION TECHNIQUES

Biological treatment for removing oil from ballast water inside a fuel oil storage tank is not favored at present. The variable conditions to be encountered in ships would make biological activity and its control difficult to maintain. Furthermore, after its use in ballasted fuel oil tanks, the tanks would need to be thoroughly cleaned to ensure that there would be no microbes left to act upon new fuel oil charged to the tanks later. If applied to bilge water, a careful selection would have to be made for some microbes may emanate a disagreeable odor which could affect the personnel manning the nearby ship's machinery. Therefore, until better knowledge of such agents and their control is available, their use on naval ships has to be avoided.

SUMMARY OF SEPARATION TECHNIQUES

Having discussed various possible separation techniques, Table 2 summarizes their possible adoption for ship's use.

Table 2
Summary of Possible Separation Techniques for Ship's
Bilge and Ballast-water Oil-pollution Control

Techniques	Potential Use ¹		Comment
	Primary ²	Secondary ³	
Settling	Yes	Yes	Slow process
Flotation	Yes	Yes	Auxiliary process only; possibly hazardous
Centrifugation	No	Yes	Also suitable for removing water in oil
Hydrocyclone	No	Yes	Needs further development
Coalescer/Filter	Yes	Yes	A completely satisfactory element yet to be found
Evaporation/ Distillation	No	Possible	High cost
Freezing	No	Possible	High cost
Selective adsorption	No	Possible	Slow process; disposal of adsorbents need to be con- sidered
Chromatography	No	Possible	High cost & low rates
Sonic	No	Possible	May break emulsions or cause emulsion shattering of coalesced globules
Membrane	No	Yes	No satisfactory membrane yet; slow process
Electric/Magnetic	No	Possible	Needs development
Chemical	No	Occasional limited use of demulsi- fying agent	Requires new system equip- ment & trained operator; may produce another pollu- tant
Biological	No	No	May act on new fuel charged unless thoroughly cleaned out from tank; may present problems for personnel

¹Potential use = useful or not in a practical separation process. Yes in this column does not imply that complete separation is achievable using technique by itself.

²Primary = for removal of bulk oil contamination.

³Secondary = for polishing step removal of lesser amounts of contamination.

This table indicates that settling with or without the assistance of secondary processes such as flotation could be a good choice to separate the bulk of water from the oily mixture. It is to be understood that no single operation in the present state of its art can separate the oily aqueous mixture completely. Reprocessing of the mixture that contains more than the allowable amount of oil in the water can employ other separation techniques such as centrifugation or the coalescer/filter. Development of all these techniques is still required to make them less affected by the ship's motion. In the case of coalescer/filter techniques, a suitable coalescer element that can be used for all types of fuels may not be readily available at the present. Other secondary separation techniques listed in Table 2 could also be used when restrictions of low rates and high cost can be overcome.

MEASURING METHODS

Unless the characteristics and reliability of a process are fully known, means must be available to monitor and control its performance. In the present case of reducing the oil content in water to below 100 ppm (0.01%) limit, it is not known whether processes which will accomplish this objective and would not require sensing and control for their effective use can be obtained. Thus, it is necessary to inquire into the availability of methods and devices for sensing and determining the oil content in water at least to the level of 100 ppm. It is an additional requirement that the measuring methods and devices be able to function properly in shipboard environment. A survey of measurement methods was made and is reported in the following sections according to the sensing principles involved.

ELECTRICAL

Since water has a dielectric constant of 80 and petroleum oils have a dielectric constant of about 2 (2.5 for NSFO),⁽⁶⁸⁾ a mixture of oil and water should have readings in between these two values. When a fluid of a certain dielectric constant passes the electrodes of a capacitor, an impedance of a certain magnitude can be noticed on the circuit coupled to an oscillator. A change in the dielectric constant can alter the impedance; thus, the output signal can be used to indicate both the magnitude and the direction of change in the dielectric constant of the fluid passing through the capacitor. A continuous electronic sensor based on this principle^{(69),(70)} has been developed to detect suspended water in aviation gasoline fuel. When this technique was applied to NSFO with frequencies of 10 kc to 75 mc, it was found that for 19 different samples used, a wide variation in their dielectric constant values was noticed. It was believed that the difference in characteristics of the NSFO samples, because of different origins and different constituents, caused the wide variation. An increase in the dielectric constant values with seawater content was noticed, but they were still functions of the characteristics of the original fuels. With respect to measuring small amounts of oil in water, the method would be inconclusive unless the definite origin of the oil in question is known. Such information is often not available, and the problem

becomes complex when the oil to be encountered could be a mixture of oils from different origins.

Utilizing the same property of dielectric constant but under different conditions of detecting oil in water, the Permutit Company has used a capacitance probe of 3 picafarads to measure various amounts of oil in seawater.⁽²⁴⁾ It was concluded that the reproducibility of capacitance readings for a given concentration could be affected by changes in:

- Salinity of the water phase.
- Water temperature.
- The physical surroundings of the capacitance probe.

It also was reported that the capacitance probe could become coated with the NSFO used in the test and give content reading a higher than that of the actual oil in the sample.

The changeover from NSFO to a distillate-type fuel oil for ship's propulsion may make the use of this capacitance approach possible. Although the effect of slight change of oil concentration in seawater on capacitance may not be distinctly noticeable, a study of whether there is any marked change in the capacitance of seawater containing oil above and below the 100 ppm limit should be determined.

OPTICAL

The oil content in water may be detected on the basis of:

- Light absorption.
- Optical density.
- Luminescence and colorimetry.
- Light scattering.

Light Absorption

Three ranges of light spectrum— (1) visible, (2) infrared, and (3) ultra-violet - have been used to measure the degree of contamination in a transparent or semitransparent fluid.

• Visible spectrum. The Warren Spring Laboratory⁽⁷¹⁾ of England and the Mitsubishi Heavy Industries⁽⁷²⁾,⁽⁷³⁾ of Japan have both developed optical instruments that pass light through the oily water and measure the oil concentration by the use of photocells. The reduction of the light intensity is used as a measure of oil content. The systems are said to be accurate within $\pm 20\%$ for 100 ppm of oil in water. As the wavelength of the light used approaches the size of the contamination, the absorption coefficient increases. Any secondary contamination capable of absorbing light can cause errors in reporting oil content in water.

• Infrared spectrum. This method also is based on light adsorption. Wavelengths in the infrared range are used. Using spectrophotometers, refineries(74),(75) have successfully used this technique ($2.84 - 3.50 \mu$) to measure oil in their effluent water to 0.1 ppm. This technique involves the extraction of oil from the water with carbon tetrachloride first, and the infrared absorption of the extract is then measured.

Infrared in the wavelengths of 8-14(76) has been used to survey organic pollution by aerial photography. It was reported that at the shorter wavelengths, thermal effects are not noticed.

Currently an ongoing development for shipboard use employing infrared at wavelengths of 3.42(77) as an indirect method (requires an extraction step) for monitoring oil contamination in water is being carried out by the IIT Research Institute under contract (MA-3854) with the U. S. Maritime Administration. Its development has been reported as promising.

• Ultraviolet. Absorption of ultraviolet light(78) in the $210\mu - 300\mu$ range has been reported to be used as an organic matter pollution index of seawater arising from inland drainage or ship wastes. A continuous monitoring method(79) of aromatic compounds in water has been reported. It uses a differential photometric system in its analyzer. Empirical calibrations are often required.

Another device based on ultraviolet absorption claims to be able to detect 10-200 ppm of oil and other contaminants in boiler water. An inquiry has been made to Supplier 12 concerning its ability to detect oil or mixtures of fuel, lubricant, and hydraulic oil in seawater.

Optical Density

Optical density or refractive index might be useful in cases where the nature of the constituents does not change. In the case of fuel oil and seawater, both the oil compositions and the seawater concentrations could vary widely and therefore affect the readings. It is thus considered unsuitable for ship's application in oil-pollution control.

Luminescence and Colorimetry

These techniques are not favored as means of measuring oil content on the basis of fluorescence or color in the ballast and bilge waters on ships. This is because luminescence and color change with the composition of the oily materials. In the case of oils encountered on naval ships, their origins as well as constituents could vary so much that successful application of these techniques appears doubtful.

Light Scattering

The use of the principle of scattering an incident light beam when it passes through a medium containing particles as a means of measuring oil concentration in seawater presents difficulties. Other particulate contamination present including air bubbles could produce an erroneous signal. The nonhomogeneity of expected particle sizes of oil in water could also given inaccurate readings. Developments in overcoming these difficulties are under way.

OTHER MEASURING METHODS

Two other methods that have been successfully used to determine oil in water are chemical methods and gas-liquid chromatography.

Chemical Methods

Methods of determining oil in oily waters from boiler and boiler feed water,⁽⁸⁰⁾ industrial waste water,⁽⁸¹⁾ and oil-filled waste water⁽⁸²⁾ by chemical methods have been reported. However, they are not deemed practical for shipboard use because of their complexity and the time required for execution.

Gas-Liquid Chromatography

Use of gas-liquid chromatography⁽⁸³⁾ has been reported for traces of organic matter in water. Whether its use would be confounded by the variety of oils to be encountered in ships is yet to be established. In view of the complexity of the expected signal which would require skilled interpreters, the use utility of this technique aboard ship is dubious.

SUMMARY OF MEASURING METHODS

Table 3 summarizes the survey of the measuring methods.

Table 3
Summary of Measuring Methods

Methods	Potential Use	Comment
Electrical Capacitance using Dielectric Constant	Possible	Affected by salinity and other contaminants
Optical Light Absorption		
Visible	Possible	Secondary contaminants interfere
Infrared (2.8-3.5 μ)	Possible	Secondary contaminants interfere
Ultraviolet (210 μ -300 μ)	Possible	Secondary contaminants interfere
Optical density	Doubtful	Changes with salinity, dissolved matter, composition of oils
Luminescence and colorimetry	No	Changes with nature of oil
Light scattering	No	Non-homogeneity of particles & contaminants interfere
Gas-Liquid Chromatography	Doubtful	Too intricate for ship's use

Four methods are deemed to have possibilities in detecting small amounts of oil in large volume of water. These are capacitance using dielectric constant and light absorption in the visible, infrared, and ultraviolet spectrum ranges. These methods have been used or are actively being considered for ship's use.

OTHER RELEVANT INFORMATION

In the course of collecting information for this survey of the state of the art, some particularly relevant facts bearing on the problem were obtained. They are presented below.

- In general combatant ships do not ballast for fear of sea-water contamination of the fuel oil. If a reliable fuel oil purifier were installed between the storage and service tanks, probably more of the ships would ballast.

- The liquid gages on three combatant ships visited were noticed to be in various stages of inoperable condition. A survey⁽⁸⁴⁾ of liquid level indicators on ships reveals that 90% of them do not work. As a result, ship's operating personnel have to rely on a scaled-off stick to measure fuel oil levels through sounding tubes on the storage tanks. This is slow and often not able to stop the fast refueling rate in time to avoid spills due to tank overfilling. An ultrasonic device has been successfully used in a laboratory carbon dioxide scrubber as a liquid level detector.⁽⁸⁵⁾ Preliminary tests indicates that it also could be successfully used when the liquid level to be detected is an oil-water mixture.

- The reclaimed oil from the Navy's Craney Island Fuel Reclamation Plant has been reissued for ship's use under boilers.

- A commercial oil tanker has been reported⁽⁸⁶⁾ as having no problems in the disposal by burning of reclaimed slop oil directly from tank washings.

- At the API Division of Transportation 13th Annual Tanker Conference, Williamsburg, Virginia, May 1968, a film "Load-on-Top" was shown. The film shows how the tank washings aboard many commercial tankers are being handled. On the return voyage of an oil tanker, its tank washings in various tanks are first allowed to settle and the heavier water layer is pumped overboard. The oil layer and the liquid at the interface region are then consolidated into designated tanks for further separation of water and oil by settling. In the meantime clean tanks are ballasted to give the ship its needed stability. This ballasted water is pumped overboard before new oil is loaded to the ship's tanks. The oil in the consolidated oil layers from tank washings is now allowed to be mixed with the new cargo of crude oil and to be delivered to the refinery, provided its water content is within acceptable limits. The captains of the oil tankers of an oil company (Supplier 13) are also given the choice of discharging the consolidated oil layers to shore facilities when they are available, for separating the oil from any water still present. The "Load-on-Top" principle appears applicable to some aspects of the Navy's ballast-water oil-pollution problems. Two other items shown in the film are of note:

- To prevent the oil layer in the tank washings from being pumped overboard with the water layer, a crew member was seen hanging over the

side to watch the discharging water for color change. This was shown not to be very effective as there probably was much more oil than the allowable 100 ppm present when the color change due to oil in the discharging water became noticeable.

• Before the start of pumping water overboard, the oil interface above the water layer in the tank washings was determined approximately by an "interface meter;" from this determination the pumping process is slowed down when the interface reaches about 5 feet above the liquid discharging point inside the tank. It appears that further development of such interface detectors is needed.

• A batch interface detector system for refined hydrocarbon fuels in pipelines has been developed and evaluated.(86) The detector is not designed for hydrocarbon fuels whose API gravities are less than 25 (specific gravity 0.9). With the future main fuel for propulsion on Navy ships changing to distillate-type fuels whose specific gravity is likely to be in the neighborhood of 0.86-0.88 range, further interest in such an interface detector is indicated.

CONCLUSIONS

This state-of-the-art survey indicates that, with respect to early achievement of reducing the oil content in the ships' discharging of bilge and ballast waters below the 100 ppm level:

• A settling technique either alone or assisted by flotation, centrifugation, or coalescence/filtration techniques offers the earliest possible solution.

• No single technique in its present state of the art is capable of completely separating the oil-water mixtures to the desired level by a single operation.

• Satisfactory measuring devices for field use still need development. Those based on capacitance or light absorption in the visible or infrared spectrum ranges are in the most advanced stages of development for shipboard use.

• The "Load-on-Top" principle could be adopted in consolidating slop fuel into one tank for disposal.

RECOMMENDATIONS

In view of the state of the art for controlling oil pollution in ship discharging of bilge and ballast water, it is recommended that:

• Steps be taken by the laboratory to implement the development of a settling separation procedure suitable first for removing or controlling oil pollution arising from the discharge of bilge water, followed by the necessary scale-up to permit the treating of ballast-water discharges. A scheme for such a procedure is given in Appendix A. This can begin at once without waiting for the total problem definition, in terms of actual shipboard conditions, which is being developed through a Fleet questionnaire and discussions

with ship's operators. This information is in hand and is being processed for a report. It will establish the magnitude of nature of the pollution abatement problem ships can be expected to control.

- The practice of "Load-on-Top" technique be carried out to consolidate the slop oil from various water-ballasted fuel oil tanks for disposal later.

- As a total solution to the problem, consideration be given to finding means of disposing the recovered slop oil such as burning under the boiler after it has been purified to an acceptable level or proceeding sufficient shore facilities capable of accepting and processing such material.

- To ensure better management of fuel oil tank usage, development of tank liquid level gages, interphase meters, and oil concentration measuring devices be encouraged.

- Emphasizing those separation techniques and measuring methods and related ship operating techniques that appear promising for further development, the laboratory continues to follow the progress of the art.

Appendix A

Proposed Scheme for Shipboard Oil-Pollution Control Process

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It is apparent that no single process can separate a mixture completely into its constituents without complicated and lengthy operations. This proposed scheme intends the separation of the oily water mixture into two bulk streams: one, water and the other, oil. Each stream will permit its disposal until the contamination level reaches the allowed limits; the streams are then to be reprocessed. A schematic diagram is shown as Figure 1-A.

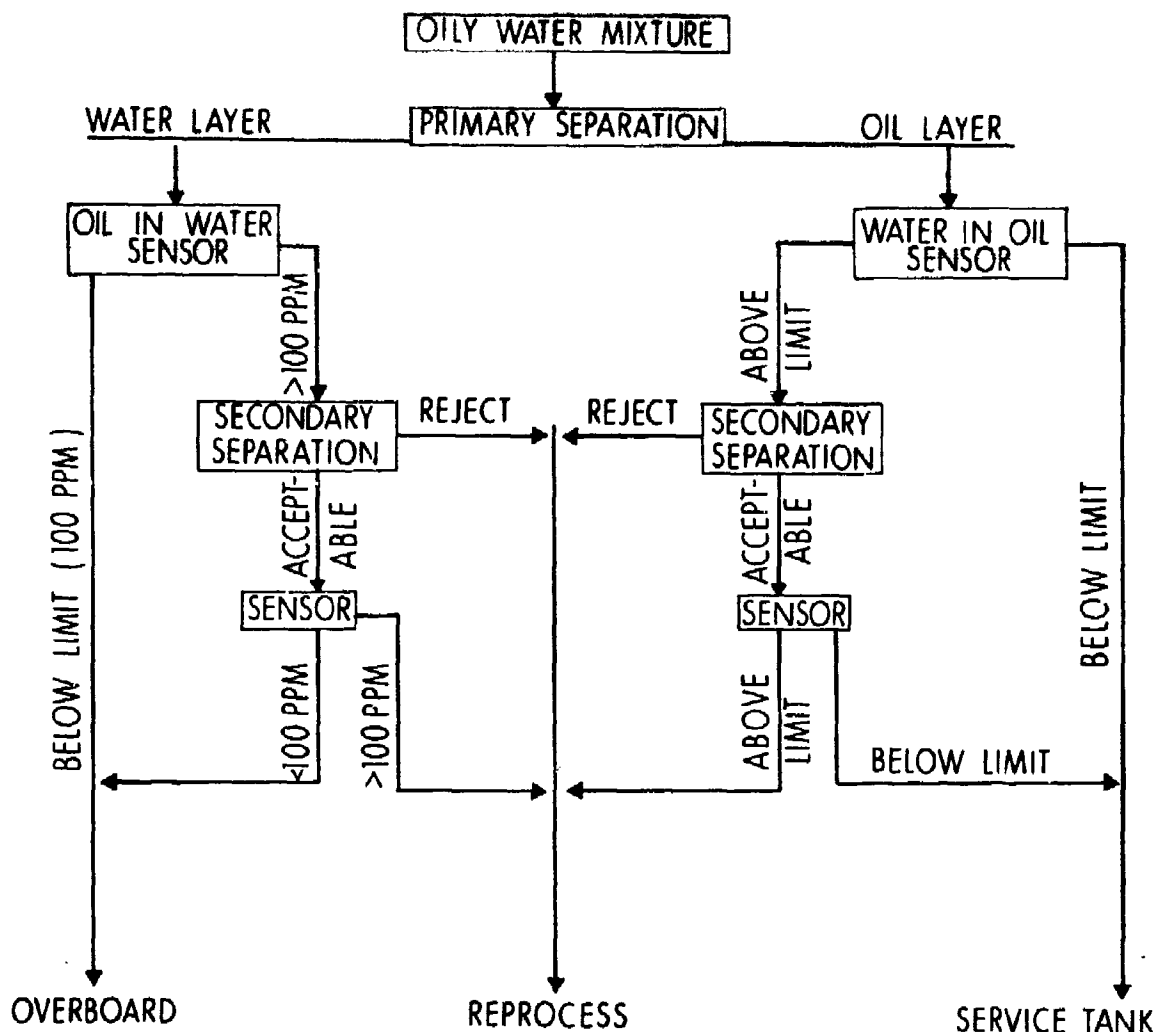


Figure 1-A

Proposed Scheme of Separation

This scheme has included the treatment of purifying the fuel oil as well. Ballasting empty fuel oil storage tanks is essential for a ship to have the needed stability and ease of maneuverability. Many naval ships have tried to

avoid such operation for the fear of contaminating the fuel oil. If a ship is to be ballasted and to have control of oil pollution from its discharging water, the ship should have a satisfactory fuel purification system so that the operator may not have the worry of a contaminated oil damaging the ship's propulsion system. A total success, therefore, requires both the water and oil purification systems to operate satisfactorily.

The above scheme requires the use of sensing and measuring devices for both oil-in-water and water-in-oil. For sensing oil-in-water, devices discussed in the section of Measuring Methods are to be followed to their successful development. For sensing water-in-oil, devices (references (a), (b), and (c)) reported would require investigation for their adaptability for use on the different oils that may be encountered.

Appendix B

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