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Factors affecting bilge water properties and oily water separator system performance

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SYNOPSIS

As of January 1, 2005 all new ship construction is required to be equipped with MEPC 107/49 Bilge OWS (Oily Water Separator) and OCM (Oil Content Monitor) so as to assure discharge of no greater than 15 ppm oil from the bilge. This new regulation was promulgated because it was determined that OWS built to the previous MEPC 60(33) standard were not capable of reducing concentrations of emulsified and otherwise dispersed organic materials to the 15 ppm level. This paper addresses the composition and properties of emulsified and non-emulsified systems and relates these to performance of 60(33) and 107(49) type OWS units. Technologies available for emulsion polishing are discussed and evaluated.

INTRODUCTION

Overpopulation has eliminated the ability of industry to view water as an infinite resource. Many industry sectors worldwide have been compelled to reuse water or treat to acceptable levels before discharge. Existing systems have been pushed beyond their limits of performance by stricter environmental standards. This is the case in the marine industry as regards oily bilge discharge. The bilge is the lowest part of the ship and the point of accumulation of a complex cocktail of compounds including soaps, detergents, solvents, soot and other particulate matter and sometimes microbial contamination. Ships have utilized MEPC 60(33) OWS to separate oil and other materials from the bilge before discharge. These units are generally gravity separation devices such as parallel plate coalescers or centrifuges. The principle of operation exploits the difference in buoyancy of two or more immiscible liquids or materials which may or may not be dispersed in each other. Dispersed oily droplets and suspended materials of between 0.1 – 10 micron tend to be neutrally buoyant and are impervious to gravity separation. For our purposes compositions of water containing suspended particulate matter or oil which will not separate from the water under the influence of gravity will be referred to as emulsions. This paper will address composition and factors affecting emulsion formation and measures which can be taken to minimize these effects. Technologies for removing emulsified components will be discussed and evaluated.

Author's biography

The author is a member of *Society of Naval Architects and Marine Engineers* (SNAME), *American Society of Naval Engineers* (ASNE), *National Defense Industrial Association* (NDIA), *American Filtration and Separation Society* (AFS) and serves on the editorial technical advisory board of *Environmental Protection* magazine.
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"*Practical Guide in Regard to Marine Bilge Water Properties and Treatment Technologies*", Society of Marine Port Engineers of New York, 2004, NY
"*Evaluation of IMO and Naval Type Bilge Cocktails*", SNAME 2004, Washington, DC
"*Regulatory and Technological Developments in Treatment of Oily Bilge Water*" – ICMES 2003, Finland
"*Filtration of Airborne, Chemical and Biological Agents in Military Applications: State of the Art and Emerging Technologies*", ASNE 2003, Arlington, VA
"*Removal of Organic pollutants and Warfare agents utilizing Surface Modified filtration devices*", NDIA 2003, CA

1. EMULSIONS

Measures must be taken to minimize the formation and presence of emulsified oils. Once oils have become emulsified they are not susceptible to removal by conventional OWS's due to the negligible difference in buoyancy between emulsified droplets and water. Emulsions are formed when one immiscible liquid is dispersed in another (oil in water / water in oil). This occurs when the interfacial tension between the liquids is reduced sufficiently to allow droplets of one liquid to disperse in another. Reduction of interfacial tension between immiscible phases is undesirable because it can lead to dispersion or emulsification of one phase in to the other. Mechanical agitation and shearing forces, solvents, surfactants and the presence of particulate matter can all cause reduction of interfacial tension and result in dispersion. Stable bilge emulsions are usually the result of one or more of these factors acting simultaneously. Salient points are as follows:

1. A Mechanical agitation:

Sufficient mechanical agitation can cause droplets from one immiscible phase to disperse into another. If shearing is sufficient to produce small enough droplets, surface repulsive charges will inhibit coalescence. Mechanical shear and impingement is commonly used in cosmetics & pharmaceuticals to achieve stable emulsions. Pump shear and others transfer operations on ships can result in similar effects.

1. A. 1 Effect of discharge head on the dispersability of oil in water:

Figure 1 and table 1 illustrate the effect of pump shear on oil dispersion in water. The evaluations were performed by recirculating a 10/ 90 (v/v) oil in water mixture through two recirculating pumps operating at the same flow rate of 50 gpm at variable heads of 1 bar and 3 bar. The resultant samples were collected at the discharge of the recirculating tank. All other factors such as temperature and composition were kept constant. The samples were allowed to stabilize and settle for 24 hrs until no further separator occurred between the aqueous and oil phases. This assures that the dispersed droplets in the aqueous phase are stable and will not separate out further due to gravity. Visual examinations of the samples in figure 1 show that sample A (50 gpm@ 3 bar) has a more opaque aqueous phase and less separated oil than sample B (50 gpm @ 1 bar). Analysis of the fractions as shown in table 1 demonstrates that sample A has 350 more dispersed oil in the aqueous phase and 50 % lower droplet size than sample B. The smaller average droplet size in sample A results in higher oil loading and greater emulsion stability in the aqueous phase. The result is that more oil must be removed by the OWS while at the same time the efficiency of the OWS is reduced due to a smaller buoyancy difference between the suspended droplets and the water. Transfer operations which minimize shearing effects will reduce the total load and increase the efficiency of downstream treatment technologies. Proper selection of pump operating conditions can reduce the load and increase the efficiency of downstream treatment technologies.

Pump capacity	Volume of oil dispersed in the sample	Droplet size of the emulsion
50 gpm @ 3 bar (A)	7 % v/v	< 20 micron
50 gpm @ 1 bar (B)	2 % v/v	< 10 micron

Table 1

Figure 1 illustrates two emulsions with identical composition prepared as above.. One notes that the emulsion on the right has a much larger gravity separatable phase. The opaque part of the emulsion on the left is stable and will not separate indefinitely due to gravity alone. Liquid transfer with minimum shearing will reduce emulsion formation and stability..

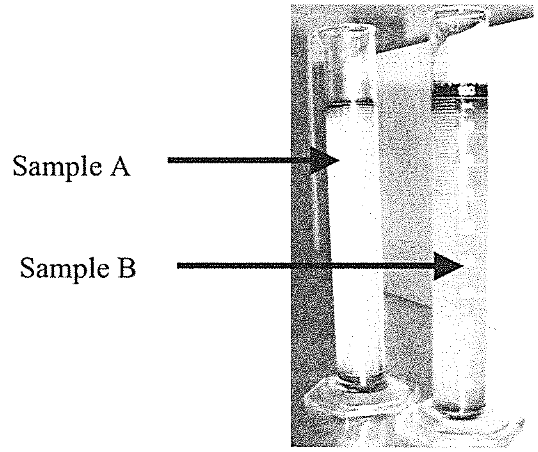


Figure 1

The selection of proper pump is important because it affects the shearing or emulsification of oily droplets in water

1. A. 2 Effect of pump type on emulsification characteristics of Oil/Water mixture:

The following evaluation was performed by recirculation of oily water mixture through different types of pumps at a constant rate and back pressure. The resultant mixture was evaluated for dispersion stability.

Pump	Results
Centrifugal	Oil completely emulsified after 15 minutes of recirculation. Emulsified fraction – significant and stable
Diaphragm	Oil dispersed in to small islands in water but not emulsified. Disperses fraction separates out by gravity over time.
Lobe Pump	Completely emulsified after 30 min. Emulsified fraction - stable.
Progressive Cavity	Oil droplets emulsified after 30 minutes. Emulsified fraction - unstable
Disc	No emulsification after 30 minutes. Dispersed fraction – significant and gravity separable.

Table 2

As can be seen in table 2 all pump types generate some degree of dispersion. The most critical factor is the percentage of dispersed droplets which are small enough to stay suspended in water indefinitely. Centrifugal and Lobe pump produce significant amounts of emulsion droplets in the aqueous phase. Positive displacement pumps also cause dispersion but the dispersed phase is not stable and the droplets eventually separate from aqueous phase over time. Pump selection and operating conditions can have a direct effect on the Oily Water Separator performance by affecting the degree of emulsification of oily components in the bilge water. Pumps with lower rpm and lower head will cause less emulsification of the bilge. Even though the pump may operate at lower efficiency, the emulsification of the oils will be reduced dramatically, which will allow gravity separation devices like OWS to be more effective.

1. B Solvents

For our purposes, solvents are organic compounds which exhibit the ability to dissolve oil. Examples include naptha, methylene chloride, alcohols and diesel fuel. Solvents have the ability to produce stable emulsions in conjunction with detergents, particulate matter and mechanical agitation by reducing interfacial tension. Isolation and segregation of solvents before they can get to the bilge can be an important factor in controlling bilge water emulsification.

1.C Particulate matter (Soot and rust)

Fine particulate matter in the form of soot, rust or microbial contamination can act as an extremely effective emulsifying agent. Washing operations can generate large amounts of soot on ships. In the case where a settling tank is employed, most of the soot will undergo gravity separation from the water. Fine soot of 1 micron or less will give the remaining water a grayish appearance. Once in the bilge, this fine soot will behave as an emulsifying agent and a film former. If not removed, this fine particulate matter on its own can also cause 107(49) OCM's to give inaccurate readings. In the case of direct discharge of soot to the bilge, a secondary problem can occur due to sludging and fouling of the coalescer plates by the accumulated separable phase of the soot. This condition can cause OWS to not operate properly. Entrainment of this captured soot can burn downstream treatment technology and affect the accuracy of downstream OCM readings.

1.D Temperature

Temperature is often a factor in the resilience of an emulsion. In general, increases in temperature result in greater coalescence of dispersed droplets. Lower temperatures usually result in more stable emulsions. Centrifuges will often employ a preheating step in order to enhance coalescence during centrifugation. Table 3 and Figure 2 illustrates the relative contribution of surfactant concentration and temperature to droplet size. As can be seen each 10 degree increase in temperature has and order of magnitude larger contribution to droplet size as compared to a 100% increase in surfactant concentration. This generally will hold true at all surfactant concentrations above the CMC (Critical Micelle Concentration). CMC is the concentration of the surfactant which is sufficient to reduce interfacial tension in order for dispersion to occur. Usually small amounts are required to reach the CMC. In many cases, excess surfactant above CMC does not enhance emulsification. When surfactant concentration is tripled in the IMO emulsion, droplet size is minimally impacted. When temperature is reduced even at lower surfactant loading, droplet size is decreased to a much greater degree than the contribution by using additional surfactant. This is significant because smaller droplets have higher surface tensions and tend to be more neutrally buoyant. It should be noted that temperature is not specified in the IMO 107(49) test procedure. The author feels that this factor can inhibit rigorous evaluation of equipment for specification. Table 3 and Figure graphically illustrates the relationship between temperature, surfactant loading and droplet size and indicates that the same test conducted at two different temperatures on the same equipment can result in drastically disparate results.

IMO Bilge Emulsion	Dh/Dt Cm/s	Mean Diameter Micron
SDS (200 ppm)		
Temp: 70F	0.000416	1.045074
Temp: 40F	0.000177	0.682650
SDS (700 ppm)		
Temp: 70F	0.00033	0.934743
Temp: 40F	0.00008	0.457929

Table 3

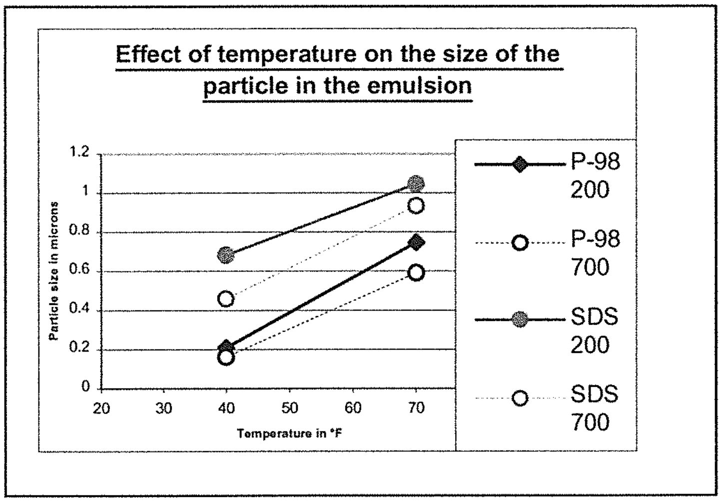


Figure 2

1.E Surfactants (Surface active agents)

Surfactants are long chain organic compounds which have the ability to reduce interfacial tension due to their partial solubility in each phase of two immiscible liquids. As the name implies, surfactant operates at the interface between the liquids with the result that relatively little surfactant is required to achieve a high degree of emulsification. Detergents contain surfactants as do most formulated lubricants. Generally, the phase in which the soap or detergent is most soluble becomes the external phase of the emulsion. (Bancrofts'rule). Since water-soluble detergents are used on ships, shipboard emulsions tend to be oil in water emulsions. The degree of emulsification will decrease as the water solubility of the cleaner decreases. Selection of cleaners which utilize less water soluble surfactants will increase the amount of surfactants which can reside in the bilge before emulsification occurs.

2. BEHAVIOR AND EVALUATION OF EMULSIONS

For our purposes we will consider emulsions to be composed of a gravity separatable phase and a non-gravity separatable phase. As an example let's consider the IMO MEPC 107(49) C emulsion. All the components discussed above (surfactants, solvents, particulate matter, etc.) are present and the mechanical agitation is specified in the test procedure of the MEPC specifications. .

Type C Emulsion

- Marine lube oil - OIL
- Marine distillate fuel oil - SOLVENT
- Sodium dodecyl benzene sulfonate (SDS) – DETERGENT/SURFACTANT
- Iron oxides – PARTICULATE MATTER
- Water

When emulsion C is prepared and mean droplet diameters and loading ratios are compared, the results are as in Table 4.

Type	Influent Average Droplet size	Influent Concentration
IMO emulsion As made	20 micron	6000-6500

Table 4

Recirculation of this emulsion through a gravity separation device such as a simple underflow weir results in a separable phase and a non- separable phase (emulsified phase). The characteristics of this phase are shown in table 5

Separation between phases was achieved through employment of a simple underflow wier.The influent concentration and droplet size was 6000 ppm and approximately 20 microns. After separation a stable emulsion resulted in a concentration of 1000 ppm at approximately 1 micron mean droplet size. This fraction of the IMO 107(49) emulsion is impervious to gravity separation and requires some sort of post gravity polishing for removal from the effluent stream. Figure 3 illustrates the difference between clean water and the stable part of the IMO emulsion.

Type	Mean Droplet Diameter In Microns	Post OWS Concentration
IMO emulsion Post gravity	1	1000 ppm

Table 5

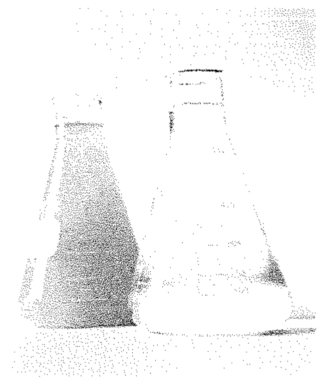


Figure 3

As can be seen the emulsified portion of the IMO C emulsion is approximately 1 micron mean droplet diameter and about 1000 ppm in concentration. This is the fraction which cannot be separated from the water by gravity alone and which downstream polishing devices must be concerned with. Figure 4 shows the difference between clean water and this emulsified component. An efficient upstream coalescer should be able to remove most of the separable phase so that the polishing unit can be dedicated to removal of the 1000 ppm emulsified component. It appears that one of the problems in regard to day to day operations is that most upstream coalescer units are not able to remove a large part of the separable phase thereby overburdening the downstream polishing devices. Polishing devices such as Ultrafiltration membranes and other polishing technologies are often fouled by the separable phase resulting in downtime and maintenance.

3. EMULSIONS AND OILY WATER SEPARATOR PERFORMANCE

Means other than gravity separation must be employed to remove the non-separable phase of the IMO C emulsion. Technologies available for this sort of polishing include adsorbents, flocculents, ultrafilters, chemical addition with temperature enhanced centrifugation devices and polymeric surface modified filtration devices. All these types of devices can be effective when operated and maintained properly and protected form high loading of the separatable phase of the emulsion. Performance is dependent on 60(33) units operating robustly enough to protect polishing apparatus from high loading. Following is a list of available polishing technologies with relative merits and demerits. Table 6 illustrates possible points of application.

3. A Gravity separation devices -- Oily Water Separator, Centrifuge

- Best and most economical for non emulsified systems
- Can treat large volumes economically
- Relatively low maintenance Unable to handle emulsions
- Do not work effectively in rough weather conditions

3. B Adsorbents – Clay, Carbon

- Low Cost
- Most effective in low volume, low fouling applications
- Susceptible to plugging up due to oil slugs.
- Very effective in removal of solvents and light emulsions
- Can support microbial growth if not maintained causing loss of effectiveness
- Maintenance required.
- Consummables.
- Does not bind captured pollutants permanently

3. C Flocculation – Chemical Addition

- Usually zeolites and polyelectrolytes
- Low cost on land
- High cost at sea due to high degree of automation required
- Requires maintenance
- Requires chemicals
- Can be effective if operated by experienced technician
- Fouling is an issue.

3. D Cross Flow Membrane Filtration

- Reverse osmosis, ultra filtration
- Utilize pressure to force water through membranes with pore size small enough to exclude pollutants
- High cost
- Ceramic membrane replacement rate ~ 40% as compared to predicted 6%
- Membranes foul when exposed to slugs of oil when OWS is out of nominal operating conditions i.e., choppy seas.
- Can be effective but requires maintenance and protection from fouling .

3.E Polymeric Filter Technology

- Low cost
- Highly effective in primary treatment – low volume
- Polish high volume emulsified streams
- No delta P
- Not fouled or plugged by slugs
- Self activating
- Ultimate protection for ship owners against accidental discharge

4. SUMMARY OF TREATMENT OPTIONS

	OWS	GAC	Membrane Filtration	Flocculation	Centrifuge	Polymeric Filtration
High Flow Primary Treatment	x				X	
High Flow polishing Treatment		x	x	x		x
Low Flow Primary Treatment	x			x		X
Low Flow Polishing Treatment		x				X

Table 6 Summary of treatment options of different technologies

The separable and non-separable parts of the IMO emulsion amount approximately to 6000 ppm. This loading is generally too high to achieve bulk removal and polishing sensitivity. Proper operation of 60(33)component is essential for the robust and sensitive performance of 107(49) OWS. Put another way what is robust is not sensitive and what is sensitive is not robust enough. These factors must be balanced and evaluated in regard to the bilge emulsion in order to make informed decisions. Degree and type of technology required can be gauged in an approximate way through the Table 7

Behavior in Water	HLB Range	Treatment Technologies
No dispersability	1 - 4	Gravity Separation-OWS
Poor dispersion	3 - 6	Gravity Separation, Centrifugation, Heating
Milky dispersion after vigorous agitation	6 - 8	Polymeric Filtration, Clay, Membranes, Carbon
Stable milk dispersion (upper end almost translucent)	8 -10	Polymeric Filtration , Membranes
From translucent to clear	10 -13	Polymeric Filtration Performer Media
Clear solution	13 +	Polymeric Filtration Performer Media

Table 7

The HLB is a measure of the water solvency of a surfactant or emulsion system. Lower HLB indicates lower solubility. The resilience of bilge emulsions can be estimated by noting the degree and time duration of dispersion

Poor dispersion and separation after agitation is usually amenable to gravity separation devices. Milky or dark dispersions after agitation which do not separate require polishing. Both conditions can exist at different times on a ship. The employment of modular polishing unit to enhance 60(33) performance may be an alternative to replace them with 107(49) in many cases for existing vessels. Some of the factors which should be considered are as follows

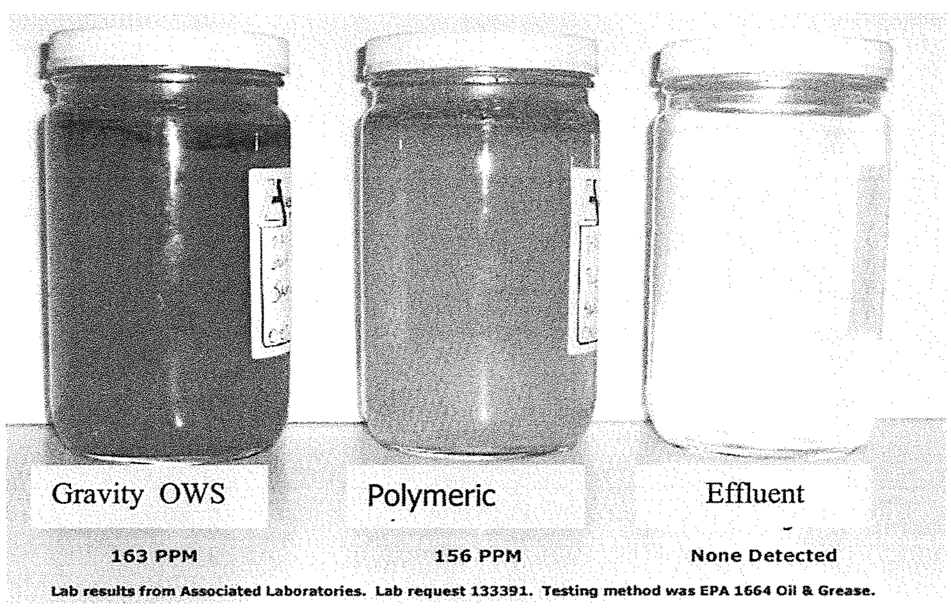
- Volume to be treated
- Amount of oil loading
- Degree of emulsification
- Crew size
- Operating conditions and climate
- Ambient water temperature
- Presence of existing equipments

Note: As an interesting aside we have noticed that degree of bilge emulsification is often directly related to the number of crew members and passengers on the ship. This is probably because more people need more services causing ship system to operate for longer periods of time and also greater the number of people greater the chance of incidental contamination by individual by introduction of soaps into the bilge.

5. CASE STUDY

Crew members of a commercial vessel were having persistent problem with emulsified bilge water. The parallel plate OWS installed in the bilge system was not able to meet the discharge standard of 15 ppm. The effluent of the OWS contained a sizeable fraction of separable phase along with the emulsion. It was evident that the OWS was not effectively removing the separable phase. The crew were urgently in need of a treatment system to be able to discharge the water overboard. UF and a Clay/ Carbon systems were tested . The systems were ineffective due to fouling by the non-emulsified component. A system was required to be robust enough to handle the slugs of non emulsified components without fouling while at the same time being able to remove the emulsified components to meet the discharge standard. Polymeric surfactant modified polishing filter system was installed post OWS and the results can be seen as in Figure 5 .The discharge standard was met immediately and the ship was able to discharge directly overboard..

Figure 4



The above samples were taken from a 6 month old OWS onboard an oil tanker that has emulsified oil problems.

It was ultimately determined that the problem was caused due to improper control and segregation of emulsifying agents. The crew of the vessel thus instituted proper house keeping measures and utilized demulsifying solvents cleaners in the bilge system. As a result the emulsification of the bilge water was reduced drastically. The bilge water treatment system was reconfigured with the polymeric filter system as in Figure 5:

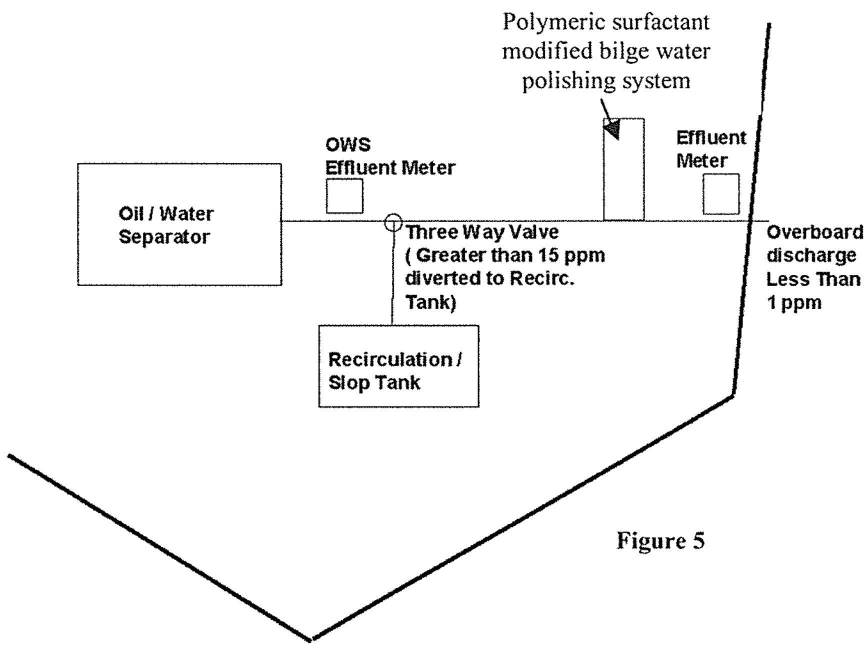


Figure 5

The Polymeric surfactant modified polishing filter system was engaged only when the discharge from the OWS went over 15 ppm. By proper maintenance and smart house keeping, the vessel has always been able to operate the bilge water treatment system effectively without much maintenance.

5. DISCUSSION

Oily bilge water has two distinct components comprised of a gravity separable phase and an emulsified phase. Both must be recognized and addressed in order to produce clean bilge water. Control of the separable phase should include provisions to minimize generating activities, control of transfer operations in order to minimize shearing and to prevent conversion of the separable phase in to an emulsion. Use of tanks which facilitate gravity separation (High aspect ratio tanks ,generally tanks with high length to diameter ratios) and the ability to decant oil which has separated in the tanks before it gets to the OWS. Once emulsification has occurred polishing devices must be employed which rely on gravity to achieve separation. Control of the emulsified phase should include incorporation of higher temperatures whenever possible , reduction of solvent, surfactant and particulate loading and protecting of polishing devices from separable or non-emulsified phase fouling .

Units capable of removing the emulsified portion of IMO 107(49)- C tend not to be robust enough to handle high, viscous or particulate laden oil loading. This results in problematic operation and high maintenance. Fouling of these components can cause 107(49) OCM's to malfunction. Conversely gravity separation devices which are robust are not able to remove oily droplets between 1-10 micron in diameter. The key to produce clean bilge effluent depends equally on the performance of the coalescer component of the 107(49) unit as well as the performance of polisher. The author does not believe that there is currently a single device which can fulfill these demands under all conditions. Maintaining maximum flexibility by incorporating modular polishing units and by maintaining proper house-keeping and proper segregation procedures can go long way in reducing the scope and expense of the problem in addition to protecting owner of unintentional discharges.

6. CONCLUSION

- Gravity separation devices are incapable in removing emulsified droplets or other neutrally buoyant materials
- Emulsions are complex and can be formed in multiple ways
- Polishing devices cannot generally operate under high oil loading conditions.
- Coalescer performance must be evaluated and made more consistent in order to assure consistent polishing treatment system performance.
- Degree of emulsification can be reduced by proper selection of cleaners, segregration of solvents and by following good house keeping procedures.
- There is no single 107(49) certified device which can handle all ship board contingencies
- Often problems are seen at OWS but created upstream.
- Polishing system performance depends on effective pre-polishing coalescers or OWS.

The following factors should be addressed to establish a consistent base line before selection of a bilge water treatment technology.

- Use of minimally emulsifiable or soluble cleaners
- Segregation of oily wastes and solvents
- Heating of bilge water before processing whenever possible
- Using decanting tanks to allow oil separation followed by polishing
- Utilizing high aspect ratio tanks to enhance separation
- Utilizing minimally shearing liquid transfer operations

7. REFERENCES

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