Clean Water Notebook

Issues and Answers Regarding Holding Tank Deodorants

Volume 5
June 30, 1995
Updated January, 2001

Controlling Holding Tank Odors

Growing awareness of the harmful impacts of sewage discharged from pleasure craft will lead to increased usage of holding tanks and related deodorizing or masking agents. The concern is that boaters may be creating a new environmental problem in their attempt to solve an existing one. This document will present information regarding types of agents used and their health and environmental impacts.

Controlling or minimizing waste-related odors is essential to being comfortable in the compact interior living spaces of a typical cruiser or sailboat. Deodorant additives are intended to suppress the malodors caused by the growth of bacteria while masking the unpleasant odors associated with other components of wastewater.

The sewage holding tank is not the only source of malodor on a boat. Any space which is damp and warm can become a source of malodor. Boaters frequently misdiagnose malodors as coming from a waste holding tank when they actually originate from water standing in some remote space such as a refrigerator condensate tray or a shower sump.

It is estimated that there are more than 50 different gaseous substances associated with sewage. The major categories are listed in the following table.

Table 1: Major Categories of Offensive Odors in Holding Tanks[1]

Compound	Typical Formula	Odor Quality
Amines	CH_3NH_2, $(CH_3)_3N$	Fishy
Ammonia	NH_3	Ammoniacal
Diamines	$NH_2(CH_2)_4NH_2$, $NH_2(CH_2)_5NH_2$	Decayed Flesh
Hydrogen Sulfide	H_2S	Rotten Eggs
Mercaptans	CH_3SH, $Ch_3(CH_2)_3SH$	Skunk
Organic Sulfides	$(CH_3)_2S$, CH_3SSCH_3	Rotten Cabbage
Skatole	$C_8H_5NHCH_3$	Fecal

Controlling Holding Tank Odors (continued)

The major cause of malodors in an onboard holding tank is heavier-than-air gases such as hydrogen sulfide and organic sulfides. Contrary to the common belief, methane has no odor. Most of the time, a person is actually smelling a combination of some of the malodors listed above, but not methane.

Several of the compounds on Table 1 are byproducts of the decomposition or biodegradation of the organic waste deposited in the tank. Decomposition can take place in generally one of two different ways: aerobic (using free oxygen) or anaerobic (in the absence of oxygen). The byproducts of the two processes differ significantly. Under aerobic conditions, bacteria digest waste and produce CO_2, H_2O, nitrates, sulfates and phosphates. All these compounds are highly stable and do not give off offensive odors.

Anaerobic digestion, on the other hand, is performed by a completely different set of microorganisms to which oxygen is, in fact, toxic. The byproducts of this type of decomposition are less stable. Nitrogen compounds stabilize only to ammonia (NH_3) and sulfur ends up as foul smelling hydrogen sulfide (H_2S) or organic sulfide gases.

Because of the very small amount of flushwater used by typical marine toilets, the available oxygen is consumed rapidly and the holding tank becomes anaerobic within two days after the first flush. The primary uses of holding tank deodorants are either to inhibit the growth of anaerobic bacteria, thereby stopping the production of odoriferous gases, or to chemically lock onto the molecules of odoriferous gas and prevent them from escaping. In either case, the challenge is to effectively control odor in the holding tank but not allow the same compound to harm the proper operation of sewage treatment facilities, the marine environment, or the system users.

Deodorant agents also generally include surfactants and other detergents to help reduce scaling in the holding tank, and break down fats, greases and solids. A dye is usually added to mask the appearance of the waste when discharged. Finally, a perfume may be included. The perfume assists in masking the non-bacteriologically produced odors.

Types of Deodorants

There are basically four categories of deodorizing agents found in a typical marine accessory store or catalog (Table 2)[2]. These include: formaldehyde based; quaternary ammonium chloride (QAC) compounds; enzymes; and biocidal preservatives.

Formaldehyde-base compounds are most prevalent and are sold under a number of brand names. Formaldehyde controls bacteria growth by denaturing protein. Bacterial cells are made up of various proteins and are effectively penetrated by the comparatively small size of the formaldehyde molecule. Formaldehyde is a simple compound made up of one carbon, one oxygen and two hydrogen atoms. It is thought, however, that the main mechanism by which formaldehyde deodorizes is by directly reacting with mercaptans, hydrogen sulfide, amines and ammonia to form more complex, less odorous compounds.[3]

Formaldehyde's major advantages are that it is the most effective odor controlling agent available[4] and is effective over a wide range of temperatures and pH and in water containing dissolved minerals.[5] The major disadvantage is a strong pungent odor and the need for a little extra care in storage, as will be explained later. Formaldehyde is actually a colorless gas which is found in an aqueous solution with methanol (wood alcohol) referred to as formalin, or in dry form is known as paraformaldehyde.

Types of Deodorants
(continued)

Quaternary ammonium chloride or QAC's are very long, complex molecules. They are commonly found as the active ingredient in household detergents, cleaning agents and disinfectants. These compounds interfere with specific enzymatic processes associated with bacteria which ultimately cause the bacterial cell wall to rupture.[6] QAC's generally have a much higher manufacturing cost than formaldehyde-based formulations. QAC's are also effective at very low concentrations.

QAC's have the advantage of less special care in handling. They have the disadvantage of reduced effectiveness in hard or salt water. It is also thought that after repeated emptying of the holding tank without thorough cleaning after each service, QAC's lose their effectiveness. Unlike RV's, most marine holding tanks tend to not empty completely when discharged. This condition was noted during testing of a Type I flow-through treatment device which was a nine-gallon sewage holding tank. The bacteria were nearly completely treated on the first cycle with a clean tank and substituting a QAC for the usual treatment fluid. On the next cycle there was little effect on bacteria levels with the same QAC formula. The reason was thought to be the small residue of liquid in the tank rapidly depleted the QAC formula before the tank was used on the second cycle.[7]

Table 2: Marine Holding Tank Treatment Products[2]

Active Ingredient	Advantage	Disadvantage	Typical Brands	Supplier/ Distributor
Formaldehyde	Most effective odor control. Effective over wide range of temperatures and water conditions.	Pungent odor. Liquid will need some care in storage.*	SeaLand® Aqua-Kem® Liquid Gold®	SeaLand Technology, Inc. Thetford Corp. Sanitation Equip.
Quaternary Ammonia Chlorides (QAC)	Effective at very low concentrations. No special handling required.	Reduced effectiveness in hard or salt water and after repeated emptying of the holding tank without cleaning.	Liquid Gold Formaldehyde-Free Insta Fresh Marine Head and Holding Tank Treatment	Sanitation Equip. Starbrite West Marine
Enzymes	Non-toxic to humans and marine environment.	Narrow range of effectiveness. Not recommended for recirculating or portable toilets.	Aqua-Zyme Kills Odor Headzyme Head Zyme	Thetford Corp. Peal Products West Marine Marine Development & Research
Preservatives	Very low human or environmental toxicity. Effective over broad range of temperatures and water conditons.	Lower effectiveness than formaldehyde. Higher cost than other deodorant types.	Secure® Aqua-Kem Green (New)	SeaLand Technology, Inc. Thetford Corp.

Types of Deodorants
(continued)

Because QAC's are in such common use in various household products, bacteria in typical sewage treatment plants become acclimated to their presence and readily break them down.[8]

Enzymes are naturally formed in all cells as part of the cell's normal metabolism. There are approximately 2,000 known enzymes, all synthesized in the cell from 20 commonly occurring amino acids. Most enzymes are highly specific in their ability to combine or associate with certain compounds in order to break them down. Holding tank deodorants which utilize an enzyme or mixture of enzymes control odor indirectly by accelerating the digestion of the organic material present. Enzyme treatments have proven effective in applications where there are large volumes of lightly polluted wastewater, such as sewage lagoons. Enzymes, however, are generally only effective in a narrow range of temperatures and pH. Like QAC's, they also require a very clean tank to begin and all residuals of other deodorants must be removed.

The main advantage of an enzyme-based deodorant is that it is believed to be nontoxic to humans and the marine environment. The disadvantages are that they generally have a narrow range of effectiveness. (Although some enzymes have been designed to be effective at higher temperatures or pH levels, they generally do operate effectively above 100ºF, nor outside a pH range of 6.0-8.5.)[9] At least two major suppliers do not recommend them for recirculating toilets or portable toilets.

Preservatives. Two recent entries in the market are Secure® brand by SeaLand Technology, Inc. and Aqua-Kem® Green® by Thetford Corporation. Both utilize base ingredients used as preservatives in various consumer products.[10] Most preservatives have a limited range of organisms against which they are effective. Secure deodorant utilizes two other naturally occurring ingredients to broaden its range of effectiveness. In-house tests of Secure have shown it to be about 85% as effective as a comparable formaldehyde based product.[11] The effectiveness of Aqua-Kem Green is claimed by Thetford Corporation to be the same as their formaldehyde formulas.[12]

Preservative compounds, such as those in Secure or Aqua-Kem Green, have other advantages of very low human or environmental toxicity, the disadvantage of a higher cost, and possibly somewhat lower effectiveness than formaldehyde.

The above four categories cover the majority of products currently available. No manufacturer today supplies a zinc or zinc sulfate-based deodorant. Zinc sulfate was a common ingredient up to the early 1970s when it was found to be environmentally toxic and non-biodegradable.

Hazards to Human Beings

Everything that we are exposed to can be hazardous given the proper set of conditions. Even the air we breathe, compressed and improperly directed, can become very hazardous. Products such as holding tank additives have the potential to be respiratory, skin or eye irritants; or, toxic by ingestion, absorption or inhalation.

Since the early 1970s, manufacturers of consumer or commercial products have been required to provide their distributors and dealers of their products with information on the hazards associated with the product. This information must be distributed in the form of a Material Safety Data Sheet or MSDS. Section V of the MSDS is entitled Health Hazard Data. This is a good place to begin evaluating a product's hazards. Note that MSDSs are not intended for, nor available to, "ultimate users" (consumers).

Hazards to Human Beings
(continued)

Another source of information is the product label. The two lead Federal agencies involved are the Environmental Protection Agency (EPA) and the Consumer Products Safety Commission (CPSC). The EPA's jurisdiction is over products which are classified as pesticides (or more generally biocides). The CPSC specifically controls labeling for some hazardous solutions which are not EPA-registered pesticides.

Some confusion is caused by the way in which the two agencies approach warning labels. For instance, the EPA reserves the skull and crossbones symbol for the most lethal materials. The CPSC, on the other hand, requires the skull and crossbones on materials with a lower level of hazard. In the case of liquid formaldehyde, the CPSC requires a skull and crossbones symbol because of the methanol present (wood alcohol), not because of the formaldehyde in the solution (which is listed as a strong sensitizer). Methanol can cause blindness if ingested. Dry or paraformaldehyde formulations which do not have methanol present are not required to carry the skull and crossbones symbol.

Since enzymes are the natural byproduct of normal cell metabolism, they are non-toxic. QAC's and preservative-type chemicals also have low human toxicity, but many be very irritating if inadvertently splashed into the eyes.

This leads us to the central issue of this discussion: formaldehyde. Make no mistake, formaldehyde – whether as formalin solution or as dry paraformaldehyde – is a very powerful chemical which must be treated with respect. Unlike other odorless compounds such as carbon monoxide, formaldehyde does have good warning properties due to its pungent odor and strong irritating effect on the eyes and respiratory tract. Humans detect the presence of formaldehyde at less than hazardous levels.

As a matter of fact, airborne exposure has been the major focus of governmental regulation. Studies have shown that rats exposed to very high levels over a two year period developed nasal cancers. Some evidence also exists which links very high exposure in the workplace to increased risk of cancer[13] (see **Note** at the end of this section). As a result, Federal regulators have taken a very cautious approach in dealing with formaldehyde in the workplace. Current OSHA standards require very low exposure limits (0.75 parts per million in an eight-hour period and not more than 2.0 parts per million for any fifteen-minute period).[14] **SeaLand has calculated boatowner exposure during normal handling of formaldehyde-based deodorant to be well below these safe workplace limits.[15]**

One extra point of caution should be made in regard to the use of liquid formaldehyde deodorants onboard pleasure craft. Should a bottle stored in a remote locker be inadvertently damaged (someone carelessly tosses a heavy piece of gear into a storage space), the resulting leak could release sufficient formaldehyde gas to make the living space below decks very uncomfortable due to the irritating effect on eyes and respiratory tract. The solution is to either take extra care in storing the liquid product or switch to a dry paraformaldehyde formula.

> **Note:** The epidemiological data base, as of 1986, was approaching 56,000 formaldehyde-exposed individuals. Formaldehyde is the most studied chemical to date, yet its carcinogen status is still controversial. While the studies do not show an excess cancer risk with formaldehyde-exposed workers, one cannot exclude the possibility that formaldehyde is a carcinogen.[16]

Environmental Impact of Formaldehyde

Environmental impact of holding tank sewage treated with formaldehyde must be considered from two points of view: its impact on land-based sewage treatment systems when emptied at a pumpout station, and its impact on receiving waters when discharged directly overboard.

Impact on Sewage Treatment. The major benefits of formaldehyde deodorizing treatments are excellent odor control effectiveness and a high degree of treatability in conventional wastewater treatment systems. Various microorganisms isolated in sewage treatment plants have shown to be very efficient in fully degrading formaldehyde concentrations under 100 ppm.[17] Essentially, complete degradation is thought to be achieved in 48-72 hours, if proper temperature and nutrient levels are maintained.[18]

One recent study has shown laboratory-activated sludge and septic tank treatment units can withstand shock loadings amounting to 25% of the initial recommended dose for holding tanks without loss of efficiency. This study concludes:

> In general, most local wastewater treatment plants located at marinas can handle boat tank wastes without difficulty. The combined effects of dilution and the deterioration of the strength of the odor-control chemical in the boat holding tank probably eliminates the chance of serious deterioration of the performance of either the activated sludge or the septic systems.[19]

This is not to say that the highly concentrated nature of all holding tank sewage does not require special design considerations. **See SeaLand Clean Water Notebook, Volume 4, "Disposal of Sewage from Pump-out Stations," for further information.**

Impact on Receiving Waters. What then is the impact of formaldehyde discharged directly into the marine environment? Formaldehyde is present in the environment as a result of natural processes, as well as from man-made sources. It is the only known hydrocarbon thought to occur in outerspace.[20] Formaldehyde has even been found in meteor fragments which fell to earth.[21] In water, formaldehyde is rapidly biodegraded by several species of microbes in a matter of days, provided the concentration is not too high.[22] Based on tests performed by SeaLand on holding tank and portable toilet contents, residual levels of formaldehyde are very minimal after three days.[23]

Formaldehyde is also readily biodegradable in soil.[24] It breaks down readily into water (H_2O) and carbon dioxide (CO_2) and is not expected to bioaccumulate in aquatic organisms.[25]

A recent study prepared for the State of Maryland found the following values would protect 95% of aquatic species from acute toxic effects of various active ingredients found in holding tank deodorants. Enzymes were not included since they are thought to be non-toxic. Formaldehyde was estimated to be 95% safe at a concentration of 0.74 ppm. QAC's, on the other hand, actually require a lower concentration of 0.42 ppm to achieve the same level of safety. Based on this comparative data, formaldehyde was thought to be less toxic to marine species than QAC's. Finally, the study pointed out that chlorine (which is used as a disinfectant in some Type I and Type II marine sanitation devices) has a very low safe concentration level of 0.01 ppm which illustrates the powerful environmental impact of a common household product.

Table 3: Comparative Safe Levels for Aquatic Species[26]

Compound	Safe Concentration Level*
Formaldehyde	0.74 ppm
QAC	0.42 ppm
Chlorine	0.01 ppm

* for 95% of aquatic species

Specific data concerning preservative-based deodorants (Secure® and Aqua-Kem® Green) were not included in the same report. In the case of Secure brand deodorants, marine toxicity levels are similar to formaldehyde for fresh and saltwater species. Human hazard is very low.[27]

For the boatowner, marine dealer or anyone else involved in marine sanitation issues, the following guidelines based on this discussion will be helpful:

- **Formaldehyde is the most effective odor controllant, but liquid formulations require a little extra care in storage.**
- **QAC's may have limited odor control effectiveness and have higher marine toxicity than formaldehyde.**
- **Enzymes, although non-toxic, may have limited effectiveness in terms of odor control.**
- **Preservative-based deodorants offer reasonable odor control levels with minimal handling or environmental hazards.**

Appendix: Helpful Information on Controlling Onboard Odors

1. **Finding Malodor Sources:** Your nose can detect odor at very low concentrations (even in the parts per billion range). Begin by closing all exterior hatches or doors and turning off the air conditioning system. This procedure will concentrate the odoriferous gases near their source. Slowly walk through the entire boat, noting which compartments tend to have more apparent odor levels. Because your nose can easily become sensitized to a particular malodor in higher concentrations, stepping into the fresh air for three to five minutes will usually return its normal acuity. Here are some common sources of malodor:

   Air conditioning or refrigerator condensate drain pans: A clogged drain will cause water not to drain and become stagnant. Use a mild solution of hydrogen peroxide to clean.

   Fuel system leaks: A small leak in the top of a fuel tank can be very difficult to detect. Fuel spilled into a remote recess of the bilge will turn rancid if not removed.

   Vinyl adhesives: Sometimes the source is not microbial, but adhesive compounds used to apply vinyl wall or overhead coverings. These adhesives release gases as they set up. The permeated surface can be confirmed by a simple procedure. Use a clean cloth to wipe all suspected areas. Sniff the cloth at frequent intervals. Where molecules of the malodor have permeated the surface material, the malodor will be transferred to the cloth.

   Sewage hose permeation: This problem is caused by sewage standing in the hose for sufficient time to allow anaerobic decomposition to begin. Use the clean cloth technique described above to determine hose lengths which must be replaced. When replacing hose, avoid routing hose so liquid is left standing in it. Use rigid PVC pipe where this condition cannot be avoided.

   Shower or sink traps or sumps: These areas are frequent sources of malodor. SeaLand Secure (see label) will effectively control odors in these or other areas with standing water.

2. **Dealing with Spills and Leaks: In all cases before starting, ventilate the area with as much outside air as possible.**

   Formaldehyde-based deodorants: Immediately ventilate the area. Open windows, doors, hatches, etc. If possible, set up fans to move extra air into the space. Work in short periods (fifteen minutes or less). If needed, respirators are available with cartridge/filters for formaldehyde. Note that proper respirator use may require special training in their proper use. One source is Champion America, Inc. 1-800-521-7000 (8:00 a.m. to 6:30 p.m. ET).

   Cover the spill with a generous amount of dry absorbent material such as baking soda, cat litter or even earth. Allow the absorbent material to soak up as much as possible then sweep up. Dispose of the residue in a plastic bag.

   If the spill has traveled into an inaccessible area, mix a solution of one cup baking soda to one gallon warm water and flood the entire area. Repeat several times to dilute the residual. Later, follow the instructions which follow for removing stains if needed.

   Deodorant stains: A commonly available household product called Resolve® carpet cleaner has been used with effective results for cleaning spills of this type. If not available, use the following procedure: Mix 1/4 cup of color-safe laundry bleach to one gallon cool water. Apply generously to the stained area and let stand. Blot dry and repeat until the stain is removed.

   Holding tank contents: Wear protective gloves. Blot area of the spill with a paper towel. Disinfect the area with the same procedure as for deodorant stains. Residual urine odors can be removed by flooding the area with a solution of one cup vinegar to one gallon warm water. Let stand as long as possible and blot dry. When finished, wash hands with soap and hot water.

Appendix: Helpful Information on Controlling Onboard Odors (continued)

3. **Usage and Safety Information: Always read and follow product label instructions.**

   Higher temperatures: Bacterial activity doubles for every ten degrees of temperature increase. In climates with higher temperature, deodorant dosage has to be increased to allow the same level of odor control.

   Safe storage: Keep liquid deodorants in a separate plastic storage bin. In any case, do not store deodorant products in lockers with equipment, such as anchors or tools, that could shift and cause damage to bottles.

   Homemade concoctions: Never mix chemical compounds, even if they are commonly available household products. Never mix ammonia with chlorine bleach or holding tank deodorants with toilet bowl cleaners containing hydrochloric acid.

Endnotes

[1] R.W. Moncnieff, The Chemical Senses, 3rd ed., (London: Leonard Hill, 1967) quoted in George Tchobanoglous, Editor, Wastewater Engineering: Collection and Pumping of Wastewater (New York: Metcalf & Eddy, Inc., 1981), 262.

[2] This information was compiled from visits to marine accessory outlets and review of major marine mail order catalogs.

[3] Mary R. Burrows, Staff Engineer Chemical Development, Thetford Corporation, letter to Ed McKiernan, 24 April 1995 (On file at SeaLand Technology, Inc., Big Prairie, Ohio.)

[4] Buchart-Horn, Inc. and Versar, Inc., A Survey of the Quantity, Characteristics, and Potential Impacts of Boat Pumpout Waste Generated Within Chesapeake Bay Region of Maryland (Prepared for the State of Maryland, Department of the Environment, March 1992), 23.

[5] Based on proprietary testing of formaldehyde based deodorants by SeaLand Technology, Inc. over the last eight years.

[6] Buchart-Horn, 16.

[7] Results of unpublished test of TDX, Type I, Marine Sanitation Device, Trusdale Laboratories, 1979. (On file at SeaLand Technology, Inc., Big Prairie, Ohio.)

[8] Buchart-Horn, 16.

[9] Mary R. Burrows, Staff Engineer Chemical Development, Thetford Corporation, telephone interview by author, 4 April 1995.

[10] This information is listed on product label. Aqua-Kem Green lists bronopol as the main ingredient which is classified as a cosmetic preservative.

[11] Results of unpublished test results comparing odor control effectiveness between formula EXO13 (Secure) and standard SeaLand brand formaldehyde-based deodorant. (On file at SeaLand Technology, Inc., Big Prairie, Ohio.)

[12] Burrows, telephone interview.

[13] Ronald W. Hart, Angelo Terturro and Lorraine Neimeth, "Report on the Consensus Workshop on Formaldehyde," Environmental Health Perspectives, Vol. 58 (1984), 323-81.

Formaldehyde Institute, "Formaldehyde Epidemiology," unpublished monograph, October 1986. (On file at SeaLand Technology, inc., Big Prairie, Ohio.)

[14] ibid, 22307.

[15] Fred Morris, Technical Director for Consumable Products, SeaLand Technology, Inc., to Dr. Steven A. Book, State of California, Health and Welfare Agency; letter requesting safe use determination, 4 October 1988 (on file at SeaLand Technology, Inc., Big Prairie, Ohio).

[16] U.S. Department of Labor, Occupational Safety and Health Administration (OSHA), Occupational Exposure to Formaldehyde; Final Rule, 29 CFR Part 1910 (Washington, D.C.: Office of the Federal Register, National Archives and Record Service, 27 May 1992).

[17] International Program on Chemical Safety (ICPS), Environmental Health Criteria for Formaldehyde (Geneva, Switzerland: WHO, date unavailable), 38.

[18] ibid.

[19] John T. Novak, C. Russel McDaniel, and Samuel C. Howard, "The effect of boat holding tank chemicals on treatment plant performance," Reserarch Journal WPCF, Vol. 62, No. 3 (May/June 1990), 294-5.

Endnotes (continued)

[20] Gessner G. Hawley, Editor, The Condensed Chemical Dictionary, 8th ed., (New York: Van Nostrand Reinhold Co., 1971), 399.

[21] Yvonne J. Pendleton and Dale P. Cruikshank, "Life from the Stars?", Sky and Telescope (March 1994), 42.

[22] ICPS, 12.

[23] Fred Morris, "The Effects of RV and Marine Waste Discharge on Sanitary Treatment Systems," unpublished monograph. (Available from SeaLand Technology, Inc., Big Prairie, Ohio, 1990.)

[24] ibid.

[25] ibid.

[26] Buchart-Horn, 19.

[27] This conclusion is based on aquatic and human toxicity testing of the primary active ingredient in Secure. This formula is considered proprietary. Test results are available for evaluation by qualified parties. Contact: SeaLand Technology, Inc., Big Prairie, Ohio 44611.

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