Technical Service Bulletin

March 2015 TSB110.12

Biocides for Disinfection and Storage of Hydranautics Membrane Elements

This bulletin provides general information about biocides that may be used with Hydranautics membrane elements for disinfection and/or storage. Before storage or disinfection of Hydranautics elements, one should become familiar with Technical Service Bulletins 108 and 118 which describe the general storage and flushing procedures for all Composite Polyamide, and PVD membrane elements. Also, one should confirm which type of membrane elements are actually in the system. Since elements may be composed of either composite polyamide membrane or polyvinyl derivative, it is imperative to be certain of the type to be disinfected.

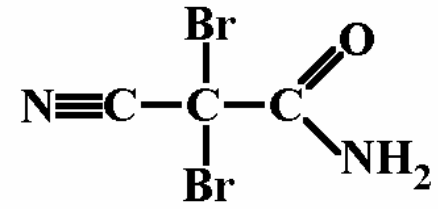
If any uncertainty exists regarding the type of elements in use, please contact Hydranautics for confirmation of compatibility of specific procedures with membrane types.

Warning: **Some of the biocides listed in this procedure are toxic in some degree to humans. Allow ample time for system flushing to remove the presence of the biocides before commencing normal operation. Hydranautics assumes no liability for the misuse of any chemical listed herein, and all safety issues are the responsibility of the end user. Consult manufacturers' material safety data sheets (MSDS's) for proper handling and disposal of any of the listed chemicals.**

Biocides which can be used with Composite Polyamide (ESPA, ESNA, Nano, CPA, LFC, SWC) and Polyvinyl Derivative (PVD) Membrane Elements

DBNPA

It is understood in the membrane industry that thin film composite polyamide membranes have limited resistance to chlorine based oxidants. Therefore, operators have relatively few options regarding chemicals which can be safely used to disinfect RO/NF systems and prevent biogrowth/biofouling. One option is the chemical, 2,2-Dibromo-3-nitrilopropionamide (DBNPA), which is a fast-acting, non-oxidizing biocide which is very effective at low concentrations in controlling the growth of aerobic bacteria, anaerobic bacteria, fungi and algae. The chemical formula of DBNPA is:



DBNPA is an advantageous disinfectant since it also quickly degrades to carbon dioxide, ammonia and bromide ion when in an aqueous environment. This allows the effluent to be safely discharged even in sensitive water bodies. It is degraded by reactions with water, nucleophiles, and UV light (rate is dependent on pH and temperature). The approximate half-life is 24 hr @ pH 7, 2 hr @ pH 8, 15 min @ pH 9. The vast majority of microorganisms that come into contact with it are killed within 5 to 10 minutes.

Product Forms

Most RO/NF chemical suppliers have a premixed private label version with varying solution concentrations of 5% to 20% or available as a white crystalline solid.

Recommended Usage for RO/NF Systems

For slug dosing, the supplier recommends 10 – 30 ppm of active ingredient for 30 minutes to 3 hours every 5 days (for waters less prone to biological fouling).

Slug dosing can be performed during service operation, during a low pressure flush mode, or by a batch CIP (Clean-In-Place) system. RO/NF permeate may need to be diverted to drain as operations dictate, though it is estimated that greater than 98% of the DBNPA is rejected by brackish water membranes and greater than 99.5% by seawater membranes. For waters containing > 100 CFU/ml (or if you already have biofilm within the RO/NF system), suppliers recommend 30 ppm active ingredient for a full 3 hours. During slug dosing, the permeate should be dumped to drain if product water is for a potable use. If a biofilm is present, sanitization should be preceded by an alkaline cleaning.

For continuous dosing during service operation, between 0.5 to 2 ppm of active ingredient is recommended to maintain a biostatic environment. RO/NF permeate may need to be diverted to drain as operations dictate. Continuous dosing can be significantly more expensive in terms of operating costs so the site situation will dictate if this is instituted.

DBNPA is deactivated by reducing agents, so a higher concentration of DBNPA will be required if residual reducing agents are present in the feed water. For example, Sodium Bisulfite (SBS) will deactivate DBNPA. If SBS is dosed during service or flushing operations, additional DBNPA will be required at a suggested dose rate of 1.0 to 1.3 ppm DBNPA per 1 ppm of SBS to account for deactivation. Excess SBS can also be used to accelerate the deactivation of DBNPA in discharged waters.

Although DBNPA is non-oxidizing, it will give an ORP reading of about 400 mv when in the range of 0.5 – 3 ppm (for comparison, 1 ppm chlorine typically gives an ORP reading of about 700 mv).

For CIP use, 30 - 50 ppm of active ingredient for 1 hour would be recommended. For heavy biofilms, it should be followed by an alkaline cleaning.

Test kits are available from the chemical suppliers to verify that DBNPA is at the desired concentration or has been completely rinsed from the system.

Warnings

- DBNPA is corrosive to metals, so plastics are preferred for storage and metering pumps. This is not as much of a concern at the very low concentrations used in RO/NF systems.

- DBNPA has minimal toxicology concerns, but the supplier recommends that for potable water systems the permeate be dumped during slug-dosing. Only off-line use of DBNPA is recommended for potable water systems.

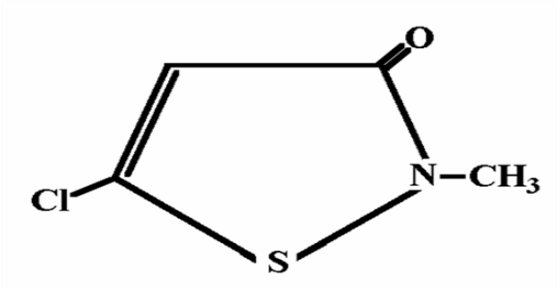
- DBNPA is classified as a “weak sensitizer.” As when handling any chemical, reference the Material Data Safety Sheet (MSDS) for precautions and proper handling and storage.

- Although DBNPA is useful as a disinfectant, it should not be used for storage since it is not long-acting

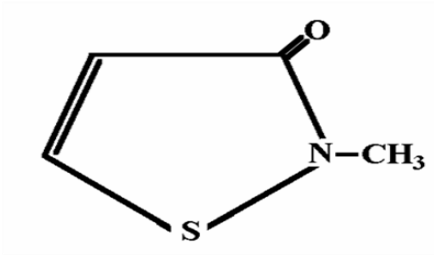
IMPORTANT: Users should review all technical product documents and talk to their supplier to ensure that they have the most recent and accurate information regarding precautions associated with the use of DBNPA.

Isothiazolin

Isothiazolin is another broad spectrum, non-oxidizing biocide. It is used to target aerobic and anaerobic bacteria, fungi and algae. Common forms of Isothiazolin are:



5-chloro-2-methyl-4-isothiazolin-3-one



2-methyl-4-isothiazolin-3-one

Isothiazolin has a much less rapid kill rate than DBNPA, therefore, DBNPA may be the initially preferred biocidal product to try. Slug dose rate for isothiazolin is typically in the range of 50 – 100 ppm, with a contact time of about 4 hours. Isothiazolin is more effective than DBNPA in waters with high organic content, and can be used at low dose rates on a continuous basis (10 – 20ppm). It should be used in a pH range of 6 - 9. It is recommended to clean the RO/NF of foulants, particularly organic in nature, prior to the use of isothiazolin.

Continuous dosing of active isothiazolin can be instituted to inhibit microbial growth, and it should be injected as far upstream in the process as possible to limit microbial growth over the entire system.

Isothiazolin is highly effective for train preservation for controlling biological growth in off-line trains for extended periods. The recommended long term preservation dose is 500-1000 ppm. The maximum period is six months.

Warnings

- The supplier recommends that for potable water systems the permeate be dumped during slug-dosing. Only off-line use of Isothiazolin is recommended for potable water systems.

- Isothiazolin is classified as a "sensitizer." As when handling any chemical, reference the Material Data Safety Sheet (MSDS) for precautions and proper handling and storage.

IMPORTANT: Users should review all technical product documents and talk to their supplier to ensure that they have the most recent and accurate information regarding precautions associated with the use of Isothiazolin

Sodium Bisulfite

Sodium bisulfite (SBS) can be used as a non-oxidizing inhibitor of biological growth at higher doses, particularly for aerobic bacteria. SBS at higher doses may be considered to have biostatic properties that inhibit biological growth, in part by removing available oxygen to aerobic bacteria, which in turns creates a hostile environment for bacteria, algae, and fungi to grow. To control biological growth with sodium bisulfite, it is applied at a dosing rate of 500 ppm for 30 to 60 minutes daily.

Sodium bisulfite at a 1% concentration can also be used as a preservative during long term storage of the membrane elements. Membranes preserved in a 1% SBS solution in a pressure vessel should be checked on a monthly basis to assure proper preservation. If the pH of the preservation solution drops below 3.0 due to oxidation by air, the solution must be replaced to prevent membrane damage.

Formaldehyde

A formaldehyde solution of 0.1 to 1.0% concentration may be used for system disinfection and as a preservative for long term storage. The membrane elements should be operated for at least 24 hours before being exposed to formaldehyde. *(See NOTE below.)*

Glutaraldehyde

A glutaraldehyde solution of 0.1 to 1.0% concentration may be used for system disinfection and as a preservative for long term storage. The membrane elements should be operated for at least 24 hours before being exposed to glutaraldehyde. *(See NOTE below.)*

NOTE: Addition of formaldehyde and/or gluteraldehyde to new elements may cause flux reduction of 10-50% depending on specific membrane chemistry. To minimize the chances of flux reduction, membrane elements should be run for a minimum of 24-hours prior to exposure to formaldehyde and or gluteraldehyde. Regardless, first time exposure to formaldehyde and/or gluteraldehyde may result in permanent flux loss. Subsequent exposure to formaldehyde and/or gluteraldehyde will result in additional temporary flux loss and will require significant flushing to return to pre-exposure flux rates.

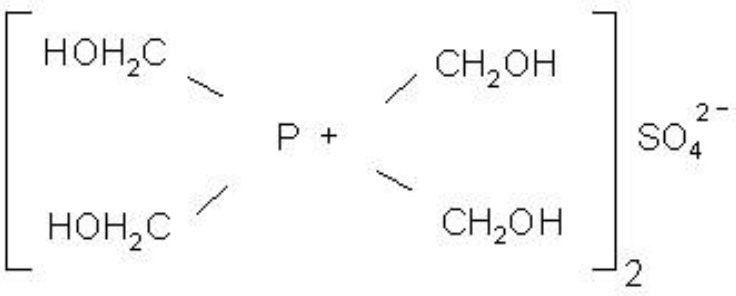
Hydrogen Peroxide

If the feed water contains any hydrogen sulfide or dissolved iron or manganese, the oxidating disinfectant (hydrogen peroxide) should not be used. Please contact Hydranautics for alternative methods of disinfection.

Hydrogen peroxide or a solution of hydrogen peroxide with paracetic acid can be used for disinfection. Special care must be taken that transition metals (Fe, Mn) are not present in the feed water, since in the presence of transition metals oxidation of the membrane surface may occur resulting in membrane degradation. The concentration of hydrogen peroxide in the disinfecting solution should not exceed 0.2%. Hydrogen peroxide should not be used as a preservative for long term storage of membrane elements. During application of hydrogen peroxide the water temperature should not exceed 25°C.

THPS

Tetrakish(hydroxymethyl) phosphonium sulfate (THPS) is used on oil production offshore platforms for sulfate-reducing bacteria (SRB) control. It is reported to be an environmental friendly biocide that is proved to be useful against SRB.



THPS is stable and persistent under abiotic conditions at acid pHs. When pH is above 8, it degrades within a week. The degradation products are trishydroxymethyl phosphine (THP) and trishydroxymethyl phosphine oxide (THPO). Slug dosing rate may be used at 50-100 ppm. The continuous dosing rate may be used at 10-20 ppm. The recommended long term preservation concentration is 600 ppm to 1000 ppm for RO and NF treatment system for SRB control on offshore oil production application. **This can lead to 25-30% flux reduction right after the chemical dosing.** Studies have shown that this flux loss can be recovered by caustic or certain surfactant cleaning.

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