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CLEANING AND INHIBITING CORROSION OF METAL TANKS OF SHIPS

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The present invention relates to a method of cleaning and inhibiting corrosion and more particularly to a method for cleaning and inhibiting corrosion of cargo tanks of aquatic vessels engaged in transporting liquid cargoes.

At the present time there is a tremendous problem present in that part of the shipping industry which concerns itself with the water transportation of liquid cargoes. Great expense is incurred annually for the upkeep and repair of metal bulkheads, structural members, etc., of ships (which bulkheads and members are usually made of a ferruginous metal, such as steel), which have been severely corroded, and much time and revenue are lost by the necessity for frequently taking ships out of service for overhaul and repair of damages due to such corrosion.

This corrosion may be due to various causes, and very often a combination of several causes. For instance, the liquid itself being transported may be corrosive to steel, or other ferruginous metals; or, as is usually the case, small amounts of water may be present dissolved or dispersed as an impurity within the liquid cargo, or as a distinct phase having separated from the cargo or atmosphere due to changes in temperature. This latter situation is particularly troublesome in the transportation of refined petroleum products, such as gasolines, kerosenes, various specialty products, and the like.

Another very cogent cause of corrosion stems from the requirement of shippers that cargo tanks be thoroughly cleansed of all previously carried cargo before taking on a new product. Many ships regularly operate on a schedule under which cargoes are carried only one way on a round trip, and these ships conserve time by carrying out the cleansing operations while under way without a cargo. In oil tankers, for instance, the cleansing is termed "butterworthing," and generally consists of spraying sea water at about 180° F. and 170 p. s. i. against the inner walls of the tanks for about 1½ hours in each tank. The combined rinsing and scouring effect of the high velocity hot liquid stream knocks any residual liquid products and loose scale from the bulkheads, etc. The mixture of salt water and residual product is pumped overboard, and men go into the tanks for the further removal by hand of rust and scale. Heating of the sea water has been considered necessary for proper cleansing action, and effective purging of the vapors resulting from the liquid cargo, the latter so that men may safely enter the space.

Thus, it can readily be seen that such tanks are

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repeatedly exposed to a highly corrosion-promoting cycle consisting of (1) exposure to a corrosive cargo (usually including water), (2) exposure to the atmosphere, (3) exposure to hot salt water solution, and (4) exposure to the atmosphere. It should be pointed out that because of the relatively high humidity of air over bodies of water the exposure to the atmosphere is itself an abnormally corrosive step. It should also be noted that whereas it has been well recognized that the use of sea water as a cleansing agent promoted considerable corrosion, it has been deemed necessary because of the scarcity and resulting high value of fresh water aboard ocean-going vessels.

Accordingly, it is an object of this invention to provide a method of increasing the life and efficiency of cargo carrying aquatic vessels by inhibiting and materially reducing the normal corrosion of the cargo tanks of such vessels. Another object is to reduce the number of man-hours required aboard liquid cargo carrying ships to clean tanks in preparation for future cargo. Further objects are to provide a non-corrosive method for cleansing such tanks, and one which markedly reduces the normal corrosion rates normally occurring in tanks aboard such vessels. Additional objects will become evident from the following description of the present invention.

In a copending application Serial No. 76,428, filed February 14, 1949, now U. S. 2,550,997, issued May 1, 1951, there is disclosed and claimed a method of attaining the above objects by treating the cargo tanks with an alkaline fresh water solution of an inorganic nitrite, such as sodium nitrite.

It has been found that despite the general beliefs set forth in the aforesaid copending application, substantially equivalent results may be obtained with the use of alkaline fresh water solutions, without the addition of sodium nitrite or any other corrosion inhibitor. The unexpectedness of this discovery is readily apparent when it is realized that sodium nitrite is a well-known and very effective corrosion inhibitor which would normally be expected to be entirely responsible for the protection achieved by the use of alkaline solutions thereof. Since nitrite salts are known to be relatively ineffective in acidic solutions, the alkaline agent in corrosion-inhibiting nitrite solutions is generally considered to be merely a means of controlling the pH of the solution. Thus, it is quite unexpected to find that under the peculiar conditions of corrosion in cargo compartments of sea-going vessels, the

nitrite salt may be eliminated, with considerable monetary savings, but with no appreciable change in protection from corrosion.

The alkaline fresh water solutions used according to the present invention may be obtained with any of the well-known alkaline metal oxides and hydroxides, including ammonia, such as CaO, KOH, NaOH, NH_4OH, and the like, or with salts of strong bases and weak acids, such as Na_2CO_3, K_3PO_4, $Na_2B_4O_7$, $NaC_2H_3O_2$, etc. In general, it is preferred to use those alkaline agents whose 0.01 molar solutions have a pH value greater than about 7.8, and preferably greater than about 8.0. The amount of the alkaline agent to be used in practicing the invention will vary with the particular alkaline agent utilized, but should be sufficient to give a solution having a pH of from about 8 to about 12 or more. A concentration of at least about ½% by weight will generally be desirable, between about 1% and about 10% by weight usually being used.

The precise mechanism by which this surprising inhibition takes place is not understood, but it has been found to be adversely affected by sea water. Consequently, best results are obtained by the use of fresh water solutions. The term "fresh water," as used herein, is intended to embrace that type of water (as distinguished from sea water or salt water) which is obtained from normal inland sources, such as springs, wells, rivers, lakes, etc., as well as rain water, and which contains a relatively low concentration of dissolved salts (as compared to the concentrations of said salts in sea water). It is also intended to include distilled water and water demineralized by ion-exchange material. By the term "alkaline fresh water solutions" and terms of similar import, are meant water solutions containing only the alkaline agent, the small amounts of minerals and other salts and impurities which may be normally associated with fresh water, and any additional material which does not adversely affect the corrosion-inhibiting action of the alkaline solution. By the term "alkaline agent" as used herein is meant a material whose water solution has a pH value greater than 7.0.

Because of the above-mentioned adverse effect of sea water, cargo tanks which are ballasted with seat water on return trips are not so effectively protected by the practice of this invention. The ballasted tanks may be protected by some other method of inhibition, as, for example, by the use of magnesium anodes as described in the British Patent No. 581,341, issued October 9, 1946.

In one respect, the simplest application of this invention would be to merely substitute the present solutions for the hot sea water now used in "butterworthing." However, (1) most vessels are not able to carry sufficient fresh water to discard the solution pumped from the cargo tanks, and (2) the cost of the alkaline agent would be excessively high. These disadvantages have been overcome by a preferred method of practicing this invention. According to this preferred embodiment, about a 5 weight percent solution of NaOH (in fresh water) is mixed in any tank, and suction is taken on the solution by a pump which delivers the solution to the butterworthing, or like, nozzles. After being sprayed on the inside of the cargo tanks the solution collects in the bottom of the tank along with any residual product which has been washed from the walls. Another pump takes suction on the used solution in the bottom of the cargo tank and, instead of pumping it overboard, returns it

to the original tank in which the solution was mixed. The solution and residual products separate by settling, the residual products are pumped overboard and the solution is re-used. Thus, it is readily seen that the total amount of fresh water required will be dependent upon the rate at which the solution is pumped and the time required for settling. Excellent results may be obtained with a total of as little as 200 barrels of fresh water, which can easily be taken aboard at the port of discharge of the cargo.

While it is a relatively simple matter to modify the piping of a vessel so that pumping may be done with permanently installed ship's pumps, the above recirculation or recovery may be accomplished by any other suitable means, such as by portable electric pumps and temporary flexible hose. Likewise, the application of the cleansing and corrosion-inhibiting solution to the tanks containing residual amounts of cargo may be by means other than spraying with butterworthing equipment, as for example, by directing a solid stream into the tank, or by installing stationary jets or spray heads. Also, if desired, the separation of solution and water-insoluble product may be accomplished by means other than settling, and in a place other than the original mixing tank. Such details are ones well-known to those versed in the art, and may be varied to fit the situation at hand. The important aspect is that the fresh water solution be recovered and reused, thus conserving fresh water and making the above-discovered fresh water treatment practical for sea-going vessels.

While this invention is especially valuable for use aboard ships such as oil tankers, normally used for transporting petroleum products, particularly refined products such as gasolines, fuel oils, etc., it may be used aboard other ships, barges and the like where severe problems of ferruginous metal corrosion exist. It may also be used for removing residual amounts of products other than petroleum products. If the solution is to be recovered and reused, the residual products should preferably be insoluble in the solution to facilitate a separation.

The following examples are presented as illustrative of the unexpected results which may be achieved by the practice of this invention.

From the above, it is readily seen that the practice of this invention results in all of the advantages of the earlier invention referred to above, plus the appreciable saving due to the elimination of the nitrite salt.

Example I

Tests simulating conditions in oil tanker compartments were carried out using various solutions for the cleansing and treating of the tanks. Specimens of uniformly pre-rusted low carbon steel (such as is found aboard oil tankers in actual use) were weighed before and after exposure in each test to determine the corrosion losses. The results are shown in Table I. Each value is an average figure obtained in three parallel tests, each of about 28 days' duration.

TABLE I

Treating Solution	Corrosion Rate (mils/yr.)
Tap water	12.7
5% NaOH in tap water	0.59
5% $NaNO_2$+2% NaOH in tap water	0.48

Example II

Tests carried on as above were repeated, except that the degree of pitting was measured instead of the weight loss. In measuring the degree of pitting, the average depth of the five deepest pits on each specimen was determined. As before, the values reported in Table II are average figures obtained in three parallel tests, each of about 28 days' duration.

TABLE II

Treating Solution	Pit Depth (in mils)
Tap Water	9
5% NaOH in tap water	1
5% $NaNO_2$ in tap water	28
5% $NaNO_2$+2% NaOH in tap water	2

From the foregoing results, it will be noted that the presence of $NaNO_2$ is not only unnecessary, but may even have a deleterious effect in that it accelerates pitting of the tanker cargo compartment bulkheads.

Example III

When tests were carried out using Na_2CO_3 instead of NaOH, it was found that the former was the substantial equivalent of the latter.

I claim as my invention:

1. A cleaning and corrosion-inhibiting process for a ferruginous metal cargo compartment of an oil tanker at sea which comprises spraying the inner bulkheads of said compartment, containing residual amounts of petroleum products, with an unheated solution consisting essentially of fresh water and sodium hydroxide, thereby forming a mixture of said solution and said products, withdrawing the mixture from said compartment, allowing said mixture to settle into two phases, separating the products from the solution, and returning said solution to the spraying operation.

2. A cleaning and corrosion-inhibiting process for a ferruginous metal cargo compartment of an oil tanker at sea which comprises spraying the inner bulkheads of said compartment, containing residual amounts of petrolelm products, with an unheated solution consisting essentially of fresh water and sodium carbonate, thereby forming a mixture of said solution and said products, withdrawing the mixture from said compartment, allowing said mixture to settle into two phases, separating the products from the solution, and returning said solution to the spraying operation.

3. A cleaning and corrosion-inhibiting process for a ferruginous metal cargo compartment of an oil tanker at sea which comprises spraying the inner bulkheads of said compartment, containing residual amounts of petroleum products, with an unheated solution consisting essentially of fresh water and an alkaline agent, said alkaline agent being one whose 0.01 molar solution has a pH of greater than about 7.8, thereby forming a mixture of said solution and said product, withdrawing the mixture from said compartment, allowing said mixture to settle into two phases, separating the products from the solution, and returning said solution to the spraying operation.

4. A cleaning and corrosion inhibiting method for ferruginous metal tanks of seagoing, cargo-carrying aquatic vessels at sea which comprises directing against the inner walls of said tanks, containing residual amounts of petroleum products, unheated fresh water having dissolved therein as the sole effective corrosion inhibitor an alkaline agent whose 0.01 molar solution has a pH of greater than about 7.8, thereby forming a mixture of said petroleum products and said solution, separating the solution from the removed products, and re-using said solution for further washing.

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