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METHOD OF REDUCING VAPOR ZONE CORROSION

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This invention relates to a method of handling and storing liquid materials which release corrosive vapors. More particularly it relates to a method for inhibiting the corrosion of metallic surfaces which are exposed to corrosive vapors. In a still more specific aspect, this invention relates to a method for inhibiting vapor zone corrosion in metallic storage vessels which contain sour crude petroleum.

The domestic production of sour crude oil has rapidly increased during the past several years, and, as a result, many new problems in the storing of crude oils have arisen. One of the most troublesome problems which has arisen is the corrosion of storage vessels which are used in the storage and handling of these sour crude oils. The term "sour crude" as used in this specification and the appended claims denotes a crude oil containing dissolved hydrogen sulfide whereas "sweet crude" denotes a crude oil which is substantially free of hydrogen sulfide. Sour crude oils being produced in areas such as West Texas, Central Kansas, and other fields contain hydrogen sulfide in varying amounts. When these sour crudes are stored in metallic storage vessels the hydrogen sulfide is evolved, and when this vapor combines with condensed moisture and oxygen on the surfaces of the metallic vessels servere corrosion occurs. This type of corrosion is prevalent in the vapor space above the liquid in the vessel and is particularly noticeable on the metallic roof of the storage vessel. It has been found that the useful life of tanks used in storing sour crude oils is reduced to as much as one half or less than one half of the service life which could be expected if sweet crudes were stored in the same tank.

Many methods have been suggested to prevent or reduce the corrosion of metallic storage vessels which are used in sour crude oil service. For example, a large variety of protective coatings have been employed to prevent vapor zone corrosion in sour crude storage vessels. However, this type of corrosion prevention has been uniformly expensive and unsatisfactory. In most cases, such as the application of coal-tar-base coatings and Gunite coatings, the degree of protection afforded is largely dependent upon the preparation of the surface to be coated and upon the application of the coating material. Poor preparation of the metallic surface prior to application of the coating and poor coating practices have invariably resulted in little or no protection. Normally, the metal surface must be cleaned and prepared for application of the coating by sand blasting to remove scale and roughen the metal surface. This preparation of the surface prior to coating is in itself an expensive proposition, and the results to be obtained are seldom capable of accurate prediction. In addition, once the coating has been applied there is a resultant loss of investment if the storage vessel is to be changed from sour crude to sweet crude service.

Another method which has been considered for preventing vapor zone corrosion in sour crude storage vessels

is the use of specialized materials of construction for the tank itself and for the tank roof. This method is also extremely expensive and is generally unsound on this basis alone.

A third and more logical method of preventing vapor zone corrosion contemplates the use of vaporous or gaseous inhibitors. According to this method of corrosion control, a vaporous or gaseous material is injected into the vapor space of the storage vessel in amounts sufficient to mitigate the corrosive effects of acidic gases, such as hydrogen sulfide, on the metal surface. It is normally found that amounts of inhibitor less than the stoichiometric amounts required to completely neutralize the hydrogen sulfide present will afford almost complete protection. This phenomenon is probably due to the buffering action of salts formed by the reaction of the inhibitor with acidic materials rather than to general neutralization. Among the vaporous inhibitors which have been suggested is gaseous ammonia obtained from anhydrous liquefied ammonia. This inhibitor has been found to be quite effective in the prevention of vapor zone corrosion. However, there are certain drawbacks in the use of this material. In the first instance, since ammonia is a gaseous material at normal atmospheric temperature and pressure means for storing the ammonia in its liquid state and for subsequently metering out and injecting the desired amount of gaseous ammonia must be provided. This introduction of gaseous ammonia results in a comparatively expensive system of equipment and piping. The equipment normally includes a pressure vessel for storing liquefied ammonia, suitable expansion equipment for converting the liquefied ammonia to its gaseous state, and metering and gauging equipment for controlling the rate of flow of gasous ammonia to the crude oil storage vessel. Therefore, the use of anhydrous liquefied ammonia as an inhibitor for vapor zone corrosion is limited in its application to large storage vessels and to unified storage systems and is unsuitable for small or widely scattered storage vessels. In addition, if the storage vessels are to be changed from sour crude service to sweet crude service the initial investment in equipment and piping is lost in spite of the fact that the ammonia itself may be cut off from the vessel.

It is therefore desirable that a less expensive and easily handled source of ammonia inhibitor be found. One such source of ammonia vapor which has been suggested for use in vapor zone corrosion control is ammonium carbonate. Ammonium carbonate sublimes under ordinary conditions at temperature and pressure to emit carbon dioxide and ammonia. Therefore, by suspending a container of ammonium carbonate in the vapor zone of a storage vessel corrosion in the vapor zone may be prevented by the action of the ammonia evolved. However, ammonium carbonate is not entirely satisfactory as a corrosion inhibitor. This material is a bulky solid and, therefore, is difficult to handle. In addition, ammonium carbonate exhibits a dissociation pressure of approximately 61 millimeters of mercury at 20° C. and a partial pressure of ammonia of about 41 millimeters of mercury at the same temperature. Thus it may be seen that ammonia is given off at a rather slow rate by this material, and there is no way of controlling the rate of ammonia evolution.

It is, therefore, an object of this invention to provide a simple and inexpensive method of reducing the corrosion of metallic surfaces which are exposed to corrosive vapors. Another object of this invention is to provide a simple and inexpensive method of preventing vapor zone corrosion in metallic vessels used to store liquids which release corrosive vapors. A further object of this

invention is to provide a simple and inexpensive method of preventing vapor zone corrosion in metallic storage vessels which are used to store sour crude oils. Another and further object of this invention is to provide a simple and inexpensive method of preventing vapor zone corrosion in storage vessels which are used to store sour crude oils, which method is easily adapted to use in a large variety of storage vessels and to a large variety of storage conditions. Other and further objects of this invention will be apparent from the following description of my invention.

In accordance with the present invention, I have found that vapor zone corrosion in metallic storage vessels used in the storage of sour crude oils can be greatly reduced by maintaining in vapor communication with the vapors of the storage vessel a solution of an ammonium compound in liquid ammonia. The solutions of my invention are preferably saturated solutions of an ammonium compound in liquid ammonia. The ammonium compounds suitable for use in the practice of my invention are compounds which are sufficiently soluble in liquid ammonia to lower the vapor pressure of the liquid ammonia to a value below atmospheric pressure at the temperature existing within the vapor zone of the vessel. Examples of such ammonium compounds include: ammonium nitrate, ammonium thiocyanate, and mixtures of ammonium nitrate and ammonium thiocyanate.

One method which has been found useful for introducing these solutions into the vapor zone of storage vessels is to suspend a container of the inhibiting solution in the vapor space of the vessel near the thief hatch. In this manner the inhibitor container may be easily removed or replaced and the condition of the inhibitor within the vessel can be readily observed.

Solutions of ammonium nitrate and ammonium thiocyanate in liquid ammonia are well suited for use as sources of gaseous ammonia because of their desirable vapor pressures. For example, at a temperature of 20° C. a saturated solution of ammonium nitrate exhibits a vapor pressure of approximately 706 millimeters of mercury, a saturated solution of ammonium thiocyanate has a vapor pressure of about 235 millimeters of mercury, a saturated solution of a mixture of ammonium nitrate and ammonium thiocyanate in the molar ratio of 1:3 has a vapor pressure of about 173 millimeters of mercury, a saturated solution of a mixture of ammonium nitrate and ammonium thiocyanate in the molar ratio of 1:1 has a vapor pressure of about 384 millimeters of mercury, and a saturated solution of a mixture of ammonium nitrate and ammonium thiocyanate in the molar ratio of 3:1 has a vapor pressure of 546 millimeters of mercury. Therefore, these solutions will release ammonia to the atmosphere at relatively rapid rates but at rates far below the rate at which liquid ammonia itself would revert to its gaseous state under similar conditions of pressure and temperature. Thus it may be seen that no special equipment is needed to handle the inhibitors of my invention while a great deal of expensive equipment is necessary to handle liquefied ammonia. It is also to be observed that the vapor pressures of my inhibiting solutions are much more desirable than that of solid ammonium carbonate. Since ammonium carbonate has a dissociation pressure of about 61 millimeters of mercury at 20° C. and an ammonia partial pressure of about 41 millimeters of mercury at 20° C., this material will release ammonia at a much slower rate than my inhibiting solutions, and large amounts of ammonium carbonate would be required to obtain the same results which could be obtained with a small amount of my inhibiting solutions.

As pointed out above, the inhibiting solutions of my invention are preferably saturated solutions. The saturated inhibiting solutions of my invention contain approximately the following amounts of ammonium compounds per gram of liquid ammonia at 20° C.: 3.9 grams of ammonium nitrate for ammonium nitrate alone,

3.6 grams of ammonium thiocyanate for ammonium thiocyanate alone, 1.4 grams of ammonium nitrate and 4.0 grams of ammonium thiocyanate for a mixture of ammonium nitrate and ammonium thiocyanate in the molar ratio of 1:3, 1.9 grams of ammonium nitrate and 1.9 grams of ammonium thiocyanate for a mixture of ammonium nitrate and ammonium thiocyanate in the molar ratio of 1:1, and 2.8 grams of ammonium nitrate and 0.9 gram of ammonium thiocyanate for a mixture of ammonium nitrate and ammonium thiocyanate in the molar ratio of 3:1.

Another advantage of my inhibitor solutions is the ease with which they may be regenerated. In order to replenish the supply of liquid ammonia in the solution, all that is necessary is to release liquid ammonia from a portable cylinder to the residue present in the inhibitor container. The residue of ammonium nitrate, ammonium thiocyanate, or the mixture of ammonium nitrate and ammonium thiocyanate in the inhibitor container will rapidly dissolve ammonia. The regeneration may be further facilitated by providing suitable markings on the inhibitor container to show the height of inhibitor solution when a saturated solution is present.

My method of inhibiting vapor zone corrosion has the further advantage that the amount of ammonia released can be definitely controlled. In cases in which ammonium nitrate or ammonium thiocyanate alone are dissolved in liquid ammonia, the rate of ammonia evolution can be controlled by varying the cross-sectional area of the surface of the solution exposed to the atmosphere. If a mixture of ammonium nitrate and ammonium thiocyanate in liquid ammonia is used, the rate of ammonia evolution can be controlled by varying the ratio of ammonium nitrate to ammonium thiocyanate in the solution. From what has been said above, it may be seen that by increasing the molar ratio of ammonium nitrate to ammonium thiocyanate in the solution the vapor pressure and consequently the rate of ammonia evolution of the solution can be increased. Therefore, my method of corrosion prevention is capable of accurate control and is applicable to storage vessels of various sizes, to storage vessels containing crude oils having different hydrogen sulfide contents, and to storage vessels employed under a variety of atmospheric conditions. In spite of the adaptability of my method of corrosion prevention to a large variety of storage conditions, its greatest advantages will be evident when it is used in small or widely scattered vessels due to the portabiilty of the inhibitor container and the ease of removing or replacing the inhibitor container.

It may also be desirable to employ supersaturated solutions of ammonium compounds in liquid ammonia in situations in which wide variations of temperature are expected. If a solution which would be saturated at a low temperature is employed and the temperature of the surrounding atmosphere suddenly rises to a higher temperature, the solution would no longer be saturated at the increased temperature; and a variation in the rate of ammonia evolution would be experienced until sufficient ammonia is given off to adjust the relative amounts of liquid ammonia and ammonium compounds in the solution to their saturation proportions at the high temperature. This problem can be eliminated by employing a solution which will be saturated at the highest temperatures expected and which will accordingly be supersaturated at temperatures below this maximum.

In the practice of my invention, it has been found that a 600 barrel tank of sour crude having a vaporous atmosphere containing about 2% by volume of hydrogen sulfide can be protected by supplying approximately 10 grams per hour of ammonia to the atmosphere. It has also been found that a saturated solution of ammonium thiocyanate in liquid ammonia evolves gaseous ammonia at the rate of about 0.7 cubic foot per hour per square foot of surface area of solution at 20° C. Therefore, to

protect a tank of this size under the above conditions, a saturated solution of ammonium thiocyanate in liquid ammonia would be placed in a container having a cross-sectional area of about 0.65 square foot and the container suspended in the vapor zone of the tank to be protected.

It will be apparent that no attempt has been made to describe all the possible procedures by which my invention may be practiced, but that other variations of my invention will be readily apparent to those skilled in the art without departing from the scope of my invention.

The nature and objects of my invention having been described and illustrated above, what is claimed as new and useful and is desired to be secured by Letters Patent is:

1. A method of mitigating corrosion in the vapor zone of ferrous metal vessels containing sour crude oils comprising maintaining in vapor communication with the vapors in said vapor zone a solution of a mixture of ammonium nitrate and ammonium thiocyanate in liquid ammonia, and controlling the rate of evolution of ammonia by varying the concentration of one of said ammonium compounds in relation to the concentration of another ammonium compound.

2. The method in accordance with claim 1 in which the rate of evolution of ammonia from said solution is increased by increasing the ratio of ammonium nitrate to ammonium thiocyanate in said solution.

3. The method in accordance with claim 1 in which the rate of evolution of ammonia from said solution is decreased by increasing the ratio of ammonium thiocyanate to ammonium nitrate in said solution.

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