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**METHOD FOR DISPOSAL OF CRUDE OIL
 RESIDUES**

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No Drawing. Continuation-in-part of application Ser. No. 546,547, May 2, 1966, now Patent No. 3,364,893. This application Nov. 22, 1967, Ser. No. 685,337
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6 Claims 10

ABSTRACT OF THE DISCLOSURE

Crude oil residues remaining in marine tanker cargo tanks are disposed of by washing the tanks with water and settling the resulting water-oil mixture to effect separation into water and oil layers. The clean water from the water layer is pumped overboard and the oil layer plus a small amount of water is then given additional chemical or mechanical treatment to separate additional clean water therefrom and to reduce the salt content thereof, if necessary. The oil, still containing small amounts of water, is then introduced into a secondary settling zone having a relatively small cross-sectional area as compared with its height and a relatively small volume as compared with the volume of the first settling tank. From the secondary settling zone, oil is recovered and used as fuel in the propulsion system of the tanker.

This application is a continuation-in-part of my copending application, Ser. No. 546,547, filed May 2, 1966, for Method for Disposal of Crude Oil Residues Contained in Marine Tanker Cargo Compartments, now Patent No. 3,364,893.

This invention relates to a method for disposing of crude oil residues remaining in marine tanker cargo compartments after the bulk of the crude has been discharged therefrom.

Since the end of World War II, pollution of the seas by crude oil has become an increasingly serious problem. One cause of pollution has been the practice of washing the crude oil vessel's tanks at sea and discharging the washings or "slops" overboard. More particularly, in the operation of a tanker it is usually necessary to clean from about 1/4 to about 1/2 of the cargo tanks on the return voyage to the loading port and refill these tanks with sea water as ballast to enable the tanker to be safely handled during the berthing operation, after which the clean ballast water is pumped overboard to make room for fresh crude oil cargo. For many years it was the practice of the industry to pump the slops recovered from the tank cleaning operation overboard in non-prohibited areas on the ballast voyage to the loading port. However, even though carried out at a considerable distance from land, the discharge of slops has added to the pollution of the seas and the concomitant killing of marine, plant and bird life as well as great damage to coasts and beaches.

More recently, a method known as "load-on-top" has been proposed to restrict pollution of the seas due to the pumping of slops overboard. In accordance with this method, the tank washings are collected in one or more of the ship's cargo tanks, commonly called "slop tanks." The slops are permitted to settle in the slop tanks to effect separation into an oil phase floating on top of a water phase. The water is then slowly withdrawn from the bottom of the tank and discharged to the sea until an oil slick is observed in the discharge. At this point, there is left in the bottom of the slop tank a small amount of free water on top of which is a layer of oil residue which

contains some water emulsified therewith. Fresh crude oil cargo is loaded on top of the retained oil residue when the vessel reaches the loading port, and the whole is discharged together at the discharge port, e.g. a refinery.

The "load-on-top" system has a number of serious disadvantages, among which is the fact that some refineries object to receiving cargo contaminated with the oily residues from tank washings. One reason for the refineries' position is that the salt water present with the oil recovered from the tank washing causes serious corrosion of the metal work in the refinery units.

Accordingly, it is one object of the present invention to provide a method for disposing of crude oil residues remaining in cargo tanks after the bulk of the crude has been discharged therefrom.

It is another object of the invention to provide a method for disposing of tanker crude oil residues without polluting the seas.

It is still another object of the invention to efficiently utilize the crude oil residues recovered from unloaded cargo tanks.

Various other objects and advantages of the invention will become apparent to those skilled in the art from the following detailed description thereof.

Briefly, the present invention contemplates washing one or more dirty crude oil tanks in the usual manner to form a mixture of oil and water, sometimes referred to hereinafter for simplicity as "slops," and passing the slops to a first settling zone to effect separation thereof into a lower water layer and an upper oil layer. A major portion of the water layer in the first settling zone is discharged, substantially free of oil, overboard from the tanker. A mixture of substantially all of the oil and a minor amount of water is recovered from the first settling zone and is further treated as by chemicals, mechanical separation or settling to remove additional water and, if necessary, salts therefrom. Oil of reduced water and salt content is then introduced into a secondary settling zone having a relatively small cross-sectional area as compared with its height and a relatively small volume as compared with the volume of the first settling zone. A lower layer of water and an upper layer of oil form in the secondary settling zone and oil from the secondary settling zone is recovered and preferably burned. Water from the secondary settling zone contains little or no oil and may be discharged overboard.

An important advantage of the invention is that the heat given off by burning the recovered oil may be efficiently utilized. Thus, in accordance with a preferred embodiment of the invention, the recovered oil may be utilized as a fuel for the propulsion system of the tanker. For example, the recovered crude oil may be supplied to one or more burners associated with steam generating machinery to generate steam for operating the vessel's propulsion system or may be supplied as fuel to diesel engines of a diesel propulsion system.

More particularly, the washing of the unloaded cargo tanks may be accomplished by employing conventional industry practices and equipment designed for this purpose. In most modern tankers, the tank cleaning operation is accomplished mechanically by the Butterworth System, in accordance with which water and steam under high pressure are sprayed into the unloaded tank by means of a revolving spray head lowered therein. Washing the tank by the Butterworth System effectively removes crude oil residues from the interior walls and bottoms of the tank.

As was noted above, it is common practice on the ballast voyage of a tanker to thoroughly clean from about 1/4 to about 1/2 of the cargo tanks. The slops from each tank cleaned are, in accordance with the invention, consoli-

dated in a lesser number of slop tanks than the cargo tanks washed, and are permitted to settle therein to effect separation of the slops into an oil phase and a water phase. Preferably, a single slop tank is used for this purpose. After the slops are transferred from the cleaned cargo tanks, the tanks may be filled with sea water as ballast to provide the tanker with sufficient stability and trim so that it can be safely handled during the berthing operation at the loading port. After berthing is complete, the clean sea water ballast is pumped overboard prior to loading crude oil cargo.

The consolidated slops from the tank cleaning operation are permitted to settle in the slops tank for a sufficient period of time to permit the formation of a lower water layer and an upper oil layer. If desired, conventional demulsification agents, which may, for example, be of the imidazoline type, or mechanical treatments may be utilized to effect a more rapid and complete breaking of the water-oil emulsion. In the case of certain crude oils, there will be a relatively sharp interface between the water and oil layers. However, in the case of other crude oils, for example, certain Venezuelan crudes, the water and oil layers will be separated by an intermediate water-oil emulsion layer.

As noted above, following settling of the slops, a major portion of the water is discharged overboard from the tanker substantially free of oil and a mixture of substantially all of the oil with a minor amount of water is recovered from the slops tank. Separation of the water and oil layers formed in the slop tank may be accomplished in a number of suitable ways. For example, a major portion of the water layer, e.g. 65% to 95% thereof, may be withdrawn from the bottom of the tank, leaving therein the oil layer, a small amount of free water and any oil-water emulsion not broken. In accordance with another suitable procedure, the oil layer and any oil-water emulsion layer which may be present, as well as a small amount of free water, e.g. up to about 35% of the total amount of water, may be skimmed off the top, for example, by means of a pump floating on the oil. The water remaining in the slop tank may then be discharged overboard.

Since the water discharged overboard from the slop tank is substantially oil-free, it does not cause any significant pollution of the seas. Desirably, the discharge water will contain less than about 500 parts of oil per million parts of water, preferably less than about 100 p.p.m. of oil.

The crude oil recovered from the slop tank will, of course, contain water as well as various inorganic salts which may be present in amounts up to about 60 pounds or more per thousand barrels of crude. Due to the salts and water mixed therewith, difficulties are experienced in burning the crude. These difficulties may be alleviated by substantially reducing the salt and water content of the crude oil subject to burning so that the crude oil contains less than about 20 lbs. of inorganic salts per thousand barrels of oil, preferably less than about 6 lbs. per thousand barrels of oil. Instruments such as the salt-itn-crude monitor manufactured by Precision Scientific Development Company are commercially available for use in determining the salt content of the crude oil. Furthermore, it is preferred that the water content of the crude oil subjected to burning be less than about 20 wt. percent and more desirably less than about 5 wt. percent.

Accordingly, the crude oil recovered from the slop tank is subjected to additional chemical and/or mechanical treatment prior to burning for the purpose of reducing the salt and water content to within the preferred ranges noted above and is then introduced into the secondary settling zone referred to above where additional settling permits further separation into an upper oil layer and a lower water layer. At least a portion of the oil layer is then recovered, as for example, by skimming off the top, and is in suitable condition for burning in the propulsion system of the tanker. The water is generally sufficiently clean so that it may be discarded by pumping overboard.

If especially complete separation of oil and water is desired, centrifuging may be used, either before or after the secondary settling zone.

Treatment of the mixture of oil, oil-water emulsion and water recovered from the slop tank may be in any suitable settling tank or mechanical water separator but is preferably in an oil-water separator in which the density difference of the oil and water is used in one or several stages to accomplish the separation of oil and water. Clean water recovered from the oil-water separator may, of course, be disposed of by pumping overboard. Suitable equipment for this purpose is commercially available as from Butterworth System, Inc. and is generally capable of processing relatively large amounts of oil and water economically and with relatively small sizes of equipment.

Treatment of the mixture of oil, oil-water emulsion and free water from the slop tank may also include chemical treatment if needed to break emulsion, to add anti-corrosion additives, etc. Chemicals and procedures for such treatments are well known in the industry and suitable additives are available from a number of commercial sources.

The secondary settling zone contemplated by the present invention usually takes the form of a settling tank which as mentioned above is of comparatively small cross-sectional area as compared with its height and has a smaller volume than the first settling zone. It is preferred that the volume of the secondary settling zone not exceed about one-tenth ($\frac{1}{10}$) that of the first settling zone.

While either batch or continuous operation of the various process steps of the present invention is contemplated, batch operation of the settling zones, especially of the secondary settling zone, is preferred. For such operations, the secondary settling zone preferably has a cross-sectional area which decreases from top to bottom over at least a substantial portion, e.g. about one-half ($\frac{1}{2}$) of its height. The cross-sectional area of the secondary settling zone at the bottom of the diminishing portion is preferably not more than about one-half ($\frac{1}{2}$) of the cross-sectional area at the top of such portion. By diminishing the cross-sectional area of the secondary settling zone in this manner, the interface between oil and water layers can be lowered by withdrawing water and its cross-sectional area simultaneously reduced. This has been found to substantially and unexpectedly increase the effectiveness of the secondary settling zone in obtaining a good separation of oil from water.

In the case of crude oil characterized by a flash point of below 150° F., the apparatus disclosed and claimed in the copending application of Robert C. Morrell, Ser. No. 542,641, filed Apr. 14, 1966, may be advantageously employed for safely burning the crude oil as fuel for a vessel's propulsion system. In accordance with this apparatus, all crude oil conduits and valves located in the power plant area of the tanker are arranged in such a manner that free-oil vapors and drippings are not permitted to come in contact with any source of ignition in the power plant. For this purpose, the various oil carrying conduits and valves required in the power plant area for supplying the crude oil to the power plant may be mounted on the front of the boiler or diesel engine and covered by a hood arrangement which is vented to the atmosphere. A drip pan covered by a flame screen of suitable mesh size which would permit oil to enter the drip pan but which would contain any fire developing therein is positioned below the hood to collect any crude oil drippings from the valves and piping mounted on the boiler or engine front. All crude oil carrying conduits extending through the power plant area and not protected by the hood are, in accordance with the Morrell application, enclosed in a vapor-tight duct.

However, when the crude oil recovered from the slops is characterized by a flash point above 150° F. there is no need to provide the burning system with the above-noted safety features contemplated by the copending Morrell

application. In this case, the recovered crude oil may be supplied to the burners or diesel engine of the tanker in a manner similar to that which is conventional with respect to Bunker C or other high flash point fuels.

While the invention has been described above in connection with certain preferred embodiments thereof, it will be understood by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention.

I claim:

1. Method for disposal of crude oil residues remaining in a plurality of tanks of a marine tanker which comprises:
 - (a) subjecting a plurality of tanks of the tanker, which tanks contain a residual quantity of crude oil, to thorough washing with water to form mixtures of water and crude oil;
 - (b) consolidating the water-oil mixtures obtained in step (a) in a first settling zone and therein effecting separation of such mixtures into a first upper oil layer and a first lower water layer;
 - (c) discharging between about 65 and about 95 vol. percent of said first lower water layer substantially free of oil from the tanker and recovering from the first settling zone a mixture of substantially all of said separated oil and between about 5 and about 35% of said water;
 - (d) subjecting at least a portion of the mixture of oil and water recovered from the first settling zone to further treatment to thereby remove additional water therefrom;
 - (e) recovering a mixture of oil and water of reduced water content from step (d) and introducing at least a portion of same into a secondary settling zone of smaller volume than said first settling zone and in said secondary settling zone effecting separation of oil and water into an upper oil layer and a lower water layer; and
 - (f) recovering oil from the oil layer of the secondary settling zone.
2. The method of claim 1 in which the further treatment called for in step (d) includes passing the mixture of oil and water through multiple stages of separation based upon density differential between oil and water.
3. The method of claim 1 in which the secondary settling zone has a volume less than about $\frac{1}{10}$ that of the first settling zone and a cross-sectional area which diminishes by at least about $\frac{1}{2}$ from top to bottom throughout at least about $\frac{1}{2}$ of the vertical height of the secondary settling zone.
4. Method for disposal of crude oil residues remaining in a plurality of tanks of a marine tanker which comprises:
 - (a) subjecting a plurality of tanks of the tanker, which tanks contain a residual quantity of crude oil, to thorough washing with water to form mixtures of

water and crude oil, which mixtures also contain inorganic salts;

- (b) consolidating the salt-containing water-oil mixture obtained from step (a) in a first settling zone and therein effecting separation thereof into a first upper oil layer and a first lower water layer containing less than about 100 parts per million oil;
 - (c) discharging between about 65 and about 95% of said first lower water layer from the tanker and recovering from said first settling zone a salt-containing mixture of substantially all of said first oil layer and between about 5 and about 35% of said water;
 - (d) treating at least a portion of the salt-containing, oil-water mixture recovered from the first settling zone to remove additional water and salt therefrom and recovering therefrom a salt-containing, oil-water mixture of reduced salt and water content;
 - (e) introducing at least a portion of the salt-containing mixture of reduced salt and water content obtained in step (d) in a batch operation into a secondary settling zone having a volume not more than $\frac{1}{10}$ the volume of the first settling zone, and in said secondary settling zone separating such mixture into an upper oil layer and a lower water layer;
 - (f) lowering the interface between the oil and water layers in the secondary separation zone and simultaneously reducing the cross-sectional area of such interface until it has been reduced by at least one-half; and
 - (g) recovering oil from the upper oil layer of the secondary separation zone.
5. The method of claim 4 in which the oil recovered from the secondary settling zone contains less than about six pounds of inorganic salts per thousand barrels of oil and less than about 5 wt. percent water and in which at least a portion of such oil is burned as fuel for the propulsion system of the tanker.
6. The method of claim 1 which includes operating the secondary settling zone as a batch operation and lowering the interface between the oil and water layers in the secondary settling zone, while simultaneously reducing the cross-sectional area of such interface by at least one-half, during separation of oil and water in the secondary settling zone.

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U.S. Cl. X.R.