Paratene™ Sludge Fluidization and Recovery

Introduction

Woodrising develops and markets proprietary chemical products under its registered trade name Paratene™. Woodrising's primary focus is to provide chemical solutions to prevent or remove inorganic and organic deposits from equipment and facilities within the hydrocarbon production, refining, processing, storage, and transportation industry. Specific product applications include; paraffin dispersants, asphaltene dispersants, heavy oil viscosity reducers, degreasers, decontamination agents, control and removal of iron sulphides and polysulphides, nitric acid corrosion inhibitor, oxygen corrosion inhibitors.

For many years, crude oil terminal operators have utilized a number of methods to remove sludge formations from their crude oil storage tanks. Yet, many of the methods do not adequately satisfy current corporate concerns for safety, the environment, and lower operating costs. Today's modern, well managed terminals are in need of a sludge maintenance process that will minimize the requirement for a service worker to enter a tank, minimize the exposure of vapor released into the atmosphere, minimize the disposal volume of waste material, and maximize the recovery of entrapped hydrocarbons - all at a reasonable cost. Woodrising Resources has developed proprietary chemical formulations marketed under the tradename Paratene™ that provide a cost-effective solution to these concerns. Paratene™ was specifically developed to break-up sludge micelles, so that the valuable hydrocarbon, asphaltene, and paraffin components can be dispersed into the product stream as a crude oil.

Application

Paratene™ is applied using a closed-loop circulation system consisting of a centrifugal pump, and a high-energy mixing nozzle, which basically uses the tank as a mixing vessel. The suction fitting is connected on the external side of the tank from a water draw outlet (or other available location) and the discharge back into the tank is via a special nozzle assembly that is mounted onto an existing man-way flange. The suction and discharge connections can all be installed while the sludge or oil levels are above the level of the man-ways. Paratene™ is mixed with light oil (or other suitable fluid) that acts as a diluent, and assists with the dispersion of the sludge. The following represents a summary of steps involved with an application:

- A tank service questionnaire is completed by the customer and returned to Woodrising for review and assist with the creation of a proposal.
- A representative sludge sample is collected and sent to a Woodrising for analysis and for application recommendations.
- A proposal is created and submitted to the customer for review and approval.
- The project's resources are mobilized to the tank site.
- A circulation nozzle is either cold or hot tapped through a blind flange on a side man-way, and the pump and circulation piping are installed.
- The contents of the tank including the diluent are circulated through the system, and the Paratene™ is slipstreamed into the circulation loop using the circulation pump.
- Samples are tested to measure the concentrations of bottom solids and water, and viscosity.
- The level of the sludge can also be determined by dipping the level through inspection vents and leg posts located on the roof of the tank.
- When test results and dipping levels indicate that the treatment specifications have been met then the circulation is discontinued, and the tank contents are allowed to stand at rest or immediately shipped, depending on the Customer's requirements.

Sludge Testing

What is Sludge

Sludge is a general term used to describe the residual deposits found at the bottom of tanks and other storage vessels. Sludge found in crude oil storage tanks is typically made up of hydrocarbons, asphaltenes, paraffins, water, and inorganic solids such as sand, iron sulphides and iron oxides. An analysis of crude oil sludge shows that greater than 90% of the sludge material is composed of the valuable paraffin, asphaltene, and hydrocarbon. Sludge forms when a crude oil's properties are changed due to changes in external conditions. Cooling below the cloud point, evaporation of light ends, mixing with incompatible materials, and the introduction of water to form emulsions, make up the most common causes for sludge formation. The precipitate that forms is an agglomeration of micelles enriched in the second phase materials - waxes, water, solids, and asphaltenes. In the course of evaluating sludge from around the world, we have assembled a compositional profile for sludge originating from crude oil. The physical properties for this sludge profile are given in the table below:

Wax	**10 – 40%**
Asphaltenes	**1 - 10%**
Water	**0 – 10%**
Inorganic solids	**0 - 5%**
Light Hydrocarbons	**40 – 80%**
Viscosity	**60 – 5000 cP**
Cloud Point	**35 – 45°C**
Pour Point	**30 – 80°C**

Characterization of Sludge

An analysis to determine the composition of sludge is an important first step in determining the most efficient means to removing it. The analysis may consist of the following steps:

- Wax, asphaltene and residue determination
- Water content
- Viscosity profile (including cloud point and pour point)

Wax, Asphaltene and Residue Determination

This method of determining the composition of a deposit depends on the relative solubility differences of the components to be determined. The method uses boiling isopropanol to separate light hydrocarbons such as short chain hydrocarbons, cyclic hydrocarbons and aromatic hydrocarbons as well as the waxes from the high molecular weight asphaltenes and the other residues. Waxes are hydrocarbons with a chain length longer than C_{12}-C_{14} and potentially as long as C_{60}. Waxes are typically soluble in low surface tension solvents such as pentane or hexane but not in high surface tension solvents such as water or methanol. However, at higher temperatures waxes can be induced to form a solution with isopropanol, separating them from the asphaltenes and residues. Waxes are not soluble in isopropanol at lower temperatures and thus can be separated from the lighter materials by precipitation.

Asphaltenes are large complex aromatic molecules. Residues are those materials that are not soluble in most organic solvents and typically include inorganic solids (such as iron oxide, iron sulphides and sand), sulphur, coal and coke. The asphaltenes can be extracted from the residues using a solvent such as chloroform or toluene.

Water Content

The amount of water tied up in sludge is often not easy to determine by conventional means. The typical method – using a centrifuge to separate the water will often give inaccurate values due the hang up of the water in the extremely high viscosity of the sludge. Several methods can be used to overcome this problem. The first is analysis of the sludge using a Dean Stark extraction. The second uses a Karl Fischer titration, and finally, water can be determined by centrifuging a sample that has been diluted as much as ten to one with a suitable solvent such as xylene or toluene.

Viscosity Profile

The viscosity profile of sludge is a way of describing how the viscosity of the sludge varies with temperature. The viscosity of most liquids will increase with decreasing temperature. In the case of a pure substance the change of viscosity with temperature can be described by the empirical formula:

$\mu = Ae^{B/T}$ (Where A and B can be determined by plotting log of viscosity ($\log \mu$) versus 1/T).

Unfortunately, hydrocarbon sludge is not a pure substance. As the solution cools, a second solid phase will precipitate from the liquid. At this point, the rate of change of the viscosity with temperature ($\delta\mu/\delta T$) will change to reflect the presence of the solid phase.

When a second phase is present the viscosity of the solution is proportional to the volume fraction of the second phase. This reflects the growth of the wax crystals or the agglomeration of asphaltenes as the sample cools. Growing crystals will give an increasing viscosity as the volume occupied by the crystals increases.

The final component to sludge viscosity is the interaction of the particles in the sludge with each other. Waxes present in crude oil come in two varieties. The first is called macro-crystalline wax is composed of paraffinic hydrocarbons (C16-C36) and the second called microcrystalline wax is composed of naphthenic hydrocarbons (C30 – C60). Either type of wax molecule will form crystals on cooling that will interact with each other. This interaction leads to thixotropy. That is the solution's response to shear rate is non-Newtonian. A Newtonian fluid has a linear response to shear rate; the viscosity remains the same at all shear rates. A thixotropic fluid has a lower viscosity at higher shear rates, and a high viscosity at low shear rates. Thus, the fluid could be said to be shear thinning. Measurements using a variable shear rate viscometer are necessary to determine if sludge is sensitive to shear.

Wax Dispersants – Mechanisms of Action for Paratene™ S620

The viscosity of a mixture is often due to the presence of an internal phase. The interaction particles such as wax crystals or water droplets (in the case of an emulsion) are generally accepted to be the source of the viscosity of such systems. In the case where waxes form the internal phase, smaller particles will interact to form an interconnecting matrix, entrapping other materials such as water and inorganic solids. The combination of the matrix effect and the

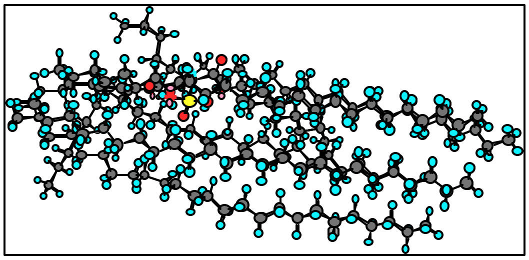


Figure 0 Wax Crystal with Dispersant molecule

interaction of the smaller particles leads this form of sludge to have a higher viscosity than could be explained by the presence of the second phase by itself.

The presence of the wax crystal matrix also makes the sludge thixotropic. That is, the sludge has a high viscosity when measured at a low shear rate and a much lower viscosity, when measured at a high shear rate. This type of sludge also exhibits a hysterisis; the properties of the material will change with its shear history.

This type of behavior results when mixing the sludge at a high shear rate breaks the weaker electrostatic-bonds that make up the matrix of crystals. The bulk viscosity of the fluid will be reduced and after the bonds have been broken the sludge may remain fluid (or having a lower measurable viscosity) at low shear rates. Given time, however, the network will reform and the low shear rate viscosity will reappear.

The fact that sludge with this kind of structure can be made pumpable at some arbitrarily high shear rate has been exploited by some to help remove sludge. When sludge is mixed at high shear with a sufficient volume of solvent two concerns must be considered. First, the volume and composition of the solvent must be adequate to prevent reforming of the sludge. Second, the entire sludge volume must be sheared at a high rate in order for mixing to occur. Dead spots or unprocessed sludge will still possess the original high viscosity properties. The result of both concerns is the re-deposition of sludge in the event that that re-suspended crude oil is not protected from the external conditions that allowed sludge to form initially.

Dispersants have a different effect on sludge. First the dispersant acts to change the electrostatic charge on the wax crystal particles. (This charge has the technical description as the zeta potential). By making the wax particles take on a new charge, the particles will repel each other making the formation and maintenance of the crystal matrix difficult (and hopefully, impossible). The dispersant in effect acts as an electrostatic wedge prying the agglomerated crystals apart.

Energy in the form of sheer is needed to disperse sludge. The amount of energy required is proportional to the Van der Waal forces that must be over come when the wax crystals in a sludge are torn apart. This energy is required in addition to the amount of energy required to move a static liquid. Paratene™ S620 acts in two ways. One of the surfactants in Paratene™ S620 acts as a wedge to initiate the opening of a “crack” or fracture between the wax crystal surfaces. The presence of the crack lowers the amount of energy required to create the new free wax crystal surface. By lowering the amount of energy required it becomes possible to easily disperse the waxes using lower pressures and flow velocities.

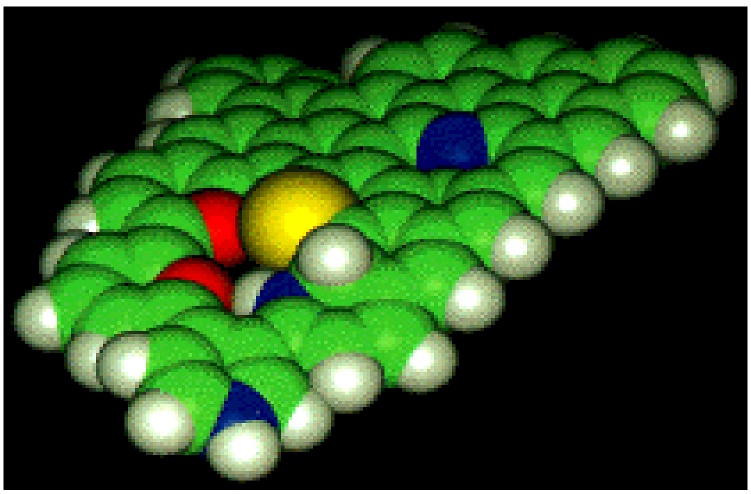
A second set of surfactants in Paratene™ S620 then act on the wax surfaces, modifying them to have a net negative charge. The wax crystals now repel each other. The repulsion between the crystals prevents their precipitation, keeping them suspended. This action can also significantly lower the pour point and viscosity of a mixture making it easier to pump and handle.

The net physical effect of the dispersant is to make the viscosity of the fluid at low shear rates resemble the viscosity of the fluid at high shear rates, eliminating the thixotropic properties of the fluid. In addition once sheared the fluid does not return to its old viscosity.

The second effect of dispersants is to make the particles more soluble in the bulk fluid. This is accomplished by using dispersant surfactants that when associated with the solids will make the surfaces of the solids more amenable to wetting by the solvent. This effect applies to all types of internal phases including asphaltenes, waxes, inorganic solids and water. By wetting the solids with the solvents, the solids disperse better, and do not interact with each other very well because they are farther apart.

Asphaltenes and Resins

Asphaltenes are the component of heavy oil responsible for much of the viscosity. By the classical definition, asphaltenes are the fraction of the crude oil that is precipitated by low surface tension solvents such as pentane or hexane. The actual chemical make up of asphaltenes is complex. Asphaltenes do not crystallize and cannot be separated into narrow fractions by composition. Thus, any evaluation of asphaltenes is a description of a range of structures and isomers. Postulated structures of asphaltenes generally illustrate asphaltene as a series of condensed aromatic rings incorporating sulphur, nitrogen and oxygen atoms. The actual structure of asphaltenes in a particular crude oil is undoubtedly a mixture of many molecules ranging in molecular weight from a few hundred grams per mole to several thousand.



Resins are the other group of compounds that are precipitated when low surface tension solvents are added to crude oil. Resins are thought to have structures much like asphaltenes, but have a lower molecular weight.

The actual physical chemistry of asphaltenes in solution is a matter of debate. Asphaltenes are thought to exist as colloidal particles surrounded by resins, which act to provide a transition between the non-polar oil and the polar asphaltenes. One suggestion is asphaltenes are associated in small clusters bound together by pi cloud interaction between the aromatic rings that make up the asphaltene molecules.

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    s s s
   s a a a s
  s a R R R a s
 s a R A A R a s
 s a R A A R a s
  s a R R R a s
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    s s s
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A = Asphaltenes (solute)
R = Resins (dispersant)
a = Small Ring Aromatics (solvent)
s = Saturates (nonsolvent)

A second hypothesis is that asphaltenes are associated with each other because of Van der Waals forces, and because of their relative insolubility in the bulk solution.

Effect of Asphaltenes on the Viscosity of Heavy Oil or Sludge

In either model the presence of resins in the asphaltene/oil system is critical to the maintenance of asphaltenes as independent small particles. Asphaltenes contribute to the viscosity of heavy oil in two ways.

First, asphaltene micelles act as a second internal phase dispersed in the oil. This second phase increases the viscosity of the system proportionally to the volume occupied by the phase. Shear (that is flow), changes in temperature and pressure, as well as changes to the chemistry of the oil due to release of light ends can act to further increase the size of asphaltene micelles – increasing the viscosity of the oil as it is produced.

Second, asphaltenes and resins are highly polar molecules having a higher affinity for the water phase of oil field emulsions than the oil. This tends to cause the accumulation of asphaltenes at the oil water interface of the emulsion droplets – stabilizing the emulsions, and making them difficult to break. The emulsified oil is even more viscous than the heavy oil itself.

Asphaltene Dispersants - Mechanism of Action for Paratene™ S627

Paratene™ S627 is a large organic molecule, with a charged hydrophilic aromatic end, balanced by a long chained aliphatic hydrophobic end. The molecule is designed to resemble the resin portion of heavy oil.

Paratene™ S627 acts to improve the stabilization of asphaltenes and maintain their dispersion in solution. It does this by providing increased stability to the resin layer of asphaltene micelles. The S627 molecule is incorporated into the resin layer and improves the asphaltene micelle’s dispersability in the oil.

Two effects of S-627 have been observed. The first is a lowering of viscosity. The viscosity effect usually requires the addition of another solvent such as aromatic naphtha or diesel fuel. Several possible reasons for this effect can be postulated. Paratene™ S627 may act to stabilize asphaltene micelles and prevent them from forming aggregates. Paratene S627 may improve the size of the solvation sphere surrounding asphaltene micelles, lowering interaction between the micelles, and preventing further agglomeration. Another possible effect is that Paratene S627 may partially neutralize the effect of electrostatic condensation.

Effects of Paratene™ Products on Refinery Operations

The Paratene™ products used for sludge removal from oil storage facilities have all been examined for their potential effects on refinery operations. The elemental composition of Paratene™ S620 and S627 are given below for an application at concentrations of 1000 ppm to the volume of sludge in a tank where the sludge to diluent ratio is 1:3

Paratene™ S627 (Asphaltenic Sludge Dispersant)

Element	Drum	Applied	Element	Drum	Applied

Carbon	82.01%	205 ppm	Sulfur	1.61%	4.0 ppm
Hydrogen	10.12%	25.3 ppm	Nitrogen	1.92%	4.8 ppm
Oxygen	4.31%	10.8 ppm	Sodium	0.0%	0 ppm

Paratene™ S627 does not contain any halogenated or alkaline earth compounds. There are no silicon, magnesium, iron, zinc, vanadium, nickel or other heavy metals. Sulfur is present as a sulfonic acid, and nitrogen is present as a pyrol.

Paratene™ S620 (Paraffinic Sludge Dispersant)

Element	Drum	Applied	Element	Drum	Applied
Carbon	83.0%	208 ppm	Sulfur	1.60%	4 ppm
Hydrogen	9.70%	24 ppm	Nitrogen	0.50%	1.25 ppm
Oxygen	5.0%	12.5 ppm	Sodium	0.20%	0.5 ppm

Paratene™ S620 does not contain any ring sulfur or ring nitrogen compounds. Nitrogen is present as water-soluble tertiary amine, and sodium is present in a readily hydrolyzed salt form. There are no chlorinated or halogenated materials, and there are no silicon, magnesium, iron, zinc, vanadium, nickel or other heavy metals. Organic acids are less than 1.0%

Equipment Requirements

A fundamental requirement for using Paratene™ is that it needs to be mixed with the sludge and with the diluent. Any efficient mixing system that can provide effective shearing and mixing can be utilized for application purposes. Woodrising can recommend a system that includes a centrifugal pump capable of producing 900-usgpm at a discharge pressure of 150 psi, and a fairly inexpensive nozzle and tank-mounting assembly. In circumstances where the sludge level is below the bottom of the man-way, the nozzle can be mounted by simply replacing the existing man-way with a nozzle that has been fitted to a plate having the identical size as the original man-way.

In situations where the sludge level is above the man-way, a special man-way adapter plate and valve is mounted over the existing man-way. The mounting plate allows a tap to be cut through the existing tank man-way while the tank is live. Once the access through the tank has been tapped, a specially designed nozzle is attached to the valve on the man-way allowing the nozzle to be inserted to provide the mixing energy within the tank during circulation.

The number of nozzles required on a tank is based on the amount of sludge, the size and geometry of the tank, and the amount of time available for fluidizing the sludge within the tank. Tanks up to 25 meters (80-feet) in diameter would require a single-nozzle system, tanks 25-46 meters (60-150 feet) in diameter would require two nozzle units, and tanks from 46-76 meters (150 to 250 feet) would require three nozzle units.

Project Application Comparison Paratene™ vs. Manual

If we look at a 45.7 meter (150-foot) diameter tank having a depth of sludge averaging 1-meter and compare removing the bulk volume of sludge from the tank using Paratene™ against manual methods. We will also assume that the sludge has a solids and water content of 5% with the remaining 95% being attributed to hydrocarbon, paraffin, and asphaltene. The manual method does not require any diluent, and the Paratene will require anywhere from a ratio of 1:1 to 1:3 in terms of sludge to diluent (oil). The diluent/oil is completely recovered. The manual method utilizes an 8-man crew, sludge bucket/scoop, and vacuum trucks, while the Paratene™ method utilizes a 4-man crew and an equipment spread involving two nozzles. Both are operating in accordance with Canadian safety regulations and standards.

The removal rate duration is 328 project hours manual, versus 141 project hours Paratene™, and if you consider that the manual method is probably allowed to work a single 12-hour shift per day basis for safety reasons, vs. the ability to circulate the tank on a 24-hour per day basis, then the Paratene™ method significantly reduces the time involved to remove the sludge from the tank. This example shows a project schedule comparison of 28-days for manual, vs. 6-days using Paratene™.

The manual method would not use any Paratene™ chemical, and we have assumed an amount equal to an application rate of 1,000 ppm of the sludge volume for the Paratene™ method. At the end of the bulk sludge removal, the manual method will either require a secondary treatment of 1,478 m3 of sludge outside the tank, or will require the sludge to be hauled to a disposal facility. The Paratene™ method recovers 90% of the sludge as marketable crude oil, which is pumped directly from the tank to the refinery, pipeline or ship. There will remain approximately 148 m3 of oil-wet solids and water for removal by the residual bottoms cleaning contractor and disposed offsite in accordance with local regulations.

Item	Paratene™	Manual
Sludge Volume	1,640 m3	1,640 m3
Diluent Volume	3280 m3	0
Removal Rate	35 m3/hr	5 m3/hr
Removal Duration	141 hrs	328 hrs
Crew Size	4 men	8 men
Man Hours	564 hrs	2,624 hrs
Paratene™ Chemical	1.64 m3	0
Recovered Oil	1,476 m3	0
Residual Bottoms - Disposal	164 m3	1,640 m3

Conclusion

When we set out to design our solution for sludge remediation, we focused our attention to concerns for safety, the environment and economics. We believe that we have satisfied those concerns, and that adapting Paratene™ to your sludge maintenance programs will offer the following benefits.

- Eliminates the requirement for workers to enter a confined space environment.
- Minimizes the time required by workers to enter a dangerous confined space.
- Paratene™ chemicals are relatively safe to handle and are concentrated to minimize the volumes required on a project.
- Paratene™ chemicals will contain no appreciable levels of materials that will have an effect on refinery process and systems.
- Minimizes the release of atmospheric emissions due to a closed loop application process.
- Minimizes the volume of both fluid and solid hazardous waste materials.
- Does not use water avoiding the creation of an additional waste fluid stream.
- Minimize the time a tank is taken out of service.
- Unlike manual methods, the tank is always available for an unscheduled use by the customer.

- Reduces the cost for final cleaning, removal and disposal of residual bottoms.
- Recovers a majority of hydrocarbons as marketable crude oil.

Woodrising Resources Ltd is able to adapt the provision of its technology to suit local business requirements, customs and regulations. Arrangements can be considered ranging from transferring the technology to the Customer's internal maintenance departments or to their designated local contractor, to supplying Paratene™ chemicals and equipment, or to providing the fluidization service using one of Woodrising's international service company partners.