How Paratene® Vapour Phase Products Work

Tom McCartney
Clean Harbors Energy and Industrial Services
9/9/2022

How Paratene® Vapour Phase Products Work

Using Paratene D742 and 742 in Steam Applications

Contents

Introduction and History

Clean Harbors Energy and Industrial Services formulates and manufactures a variety of products for industrial cleaning applications. Paratene® D740 and Paratene® D742 are used in steam applications and have been successfully applied by a number of industrial cleaning contractors.

The idea of steam and vapour phase cleaning is not a new one. Steam of course, has been used to purge vessels and towers since the beginning of refining and chemical processing. Vapour phase systems were introduced in the late 1950's to improve on the ability to remove hydrocarbons and use a lower amount of chemicals and steam to achieve the desired goal.

The goal of traditional steam-outs or decontamination treatments was to render vessels and tanks free of hazardous components and safe to enter. Vapour phase cleaning as it was known in the earliest days was seen as a means to deliver a chemical cleaning solution using a vapour and remove the internal deposits.

Early vapour phase systems used solvents such as perchloroethylene, but other systems using surfactants and acids were considered [1]. The 1963 Dow patent essentially describes the systems used today. Chemicals are added to the steam and carried as a mist to the cooler metal surface where the condensing steam applies the chemistry to the metal.

Modern practices have expanded on this system employing a variety of chemistries. The principle intent of modern vapour phase cleaning is to remove the hazardous materials often present in industrial systems rendering them inert and safe to open.

The Hazards expected include:

- Hydrocarbon vapours
- BTEX (benzene, toluene, Ethyl benzene and Xylene)
- Hydrogen Sulphide (H_2S)
- Pyrophoric materials

These primary hazards combine with the presence of inorganic scale and deposits and organic deposits to make up the fouling present in most systems.

Recent developments in products for steam applications have been divided into two types. The first type is surfactant blends such as Zymeflo[2,3] and Paratene® D740 and the second type is solvent blends such as US 1600[4], Paratene® D742 or as described in US Patent 6893509[5].

In all cases the cleaning agent is added to the steam as a mist. The applied products should not vaporize. This would result in loss of the effective product in the escaping steam and possible separation of the product components resulting in ineffective application.

Steam

Steam is the original vapour phase cleaning solution. Steam is water vapour created by boiling water and the technology to generate steam is centuries old. Pressurized steam delivers heat and condensed water to the surfaces to be cleaned and aids in vaporising or mobilizing hydrocarbon deposits in process equipment.

When equipment – heat exchangers, towers, and vessels such as flash tanks and stripper towers are brought down for maintenance It is typical to use perform a "steam out" to remove the residual hydrocarbon and vaporize any volatile material. Steam is the ideal medium to do this as it has a high heat capacity and the vapour itself is relatively non-hazardous.

Other substances have been tried in place of steam, such as hot nitrogen, but steam retains the benefits of both availability and heat transfer. When steam is applied by itself surface wettability is a serious problem.

Water has a high cohesive surface tension. That is, it prefers to stick to itself rather than other surfaces. When water is applied to a metal surface it tends to form beads or droplets that don't adhere to the surface. Worse when hydrocarbons are present the hydrocarbon excludes the water from contacting the surface, so it is difficult to remove.

When heated the surface tension decreases linearly with temperature but the viscosity change is exponential, so liquids with viscosities in the range of 20000 cP can be reduced to much lower viscosity by applying heat. So, Substances that may have little or no flow can be induced to flow by increasing the temperature.

Unfortunately, the hydrocarbons' surface tensions are also reduced and the ability of hot water to displace it does not actually change much with temperature. As a result, the hydrocarbon continues to stick to the surface and is difficult to actually displace.

Finally, the steam causes the lighter hydrocarbons to boil and become vapour as it heats up the system, as a result the residue left behind by the steam has a decreased volatility, high viscosity and a high molecular weight.

In addition to the residue problem steam does not directly react with Hydrogen sulfide (H2S) or pyrophoric materials. The presence of water on the deposits may inhibit the formation of H2S gas or fires and explosions resulting from the presence of pyrophoric materials but it certainly doesn't remove them.

In order to improve the ability of steam to quickly remove hydrocarbons from process equipment a number of chemical additives have been created.

Chemical Additives

Chemical additives come in three classes:

- Surfactants
- Microemulsions
- Solvents

Each of these additives have limitations and advantages in achieving the goals for both removing hazards and cleaning the process systems.

Surfactants

Examples of surfactant cleaning solutions include:

- ❖ Paratene D740
- ❖ United Zymeflow UN657
- ❖ ROC 40
- ❖ FQE LEL-vapor

Only D740 is purely a surfactant. ROC40 also contains EDTA and ethanol, Zymeflo contains an enzyme. These other products contain ingredients that theoretically improve cleaning but may have issues of volatility and separation of the cleaning solution from the solvents.

Paratene® Products Mechanism – Paratene® D740 (Surfactants)

Paratene® D740 is a surfactant blend. It contains a mixture of several surfactants designed to maximize rapid water wetting of metal surfaces. The principle actions for D740 are removal of light hydrocarbons and neutralization of H_2S and pyrophoric materials.

The first type of surfactant used is amine oxides. These are typically biodegradable molecules that are made by reacting a tertiary amine with hydrogen peroxide.

```
             CH3
              |
CH3-(CH2)n-N=O
              |
             CH3
```

Reactions with Hydrogen sulphides

Amine oxide surfactants are a good choice for this application. They have very low surface tensions, are relatively non-toxic, and have good biodegradability. In addition to this amine oxides are made by reacting an amine with hydrogen peroxide and resulting product also have a small amount of free peroxide present. The free hydrogen peroxide will be volatile in the steam and will react with H_2S in the vapour space.

Work by Shulman and Link[6] show that the Amine oxide also can potentially take part in the reaction because it will deoxygenate at high temperature reverting to a tertiary amine and a peroxide or free oxygen. This allows the hot liquids in contact with the pyrophoric materials as well as Hydrogen sulphide trapped in the deposits to be neutralized and converted either to elemental sulphur or a sulphate.

If the amine oxides alone are considered, the capacity of the solutions for H_2S can be calculated. In the case of Paratene® D740 using a reaction of one mole of amine oxide reverting[7] to the ammonium peroxide as shown in the reaction below:

$$R_3N + H_2O_2 \leftrightarrow (R_3N.H_2O_2) \leftrightarrow R_3NO + H_2O$$

The intermediate form will react with H_2S:

$$8\ H_2S(g) + 8\ R_3N.H_2O_2(aq) = S_8(s) + 16\ H_2O(l) + R_3N$$

This reaction requires elevated temperatures for the ammonium peroxide to form.

Based on the activities of the surfactants used, 1 litre of Paratene® D740 will neutralize 18 g of Hydrogen sulphide or about 0.51 moles.

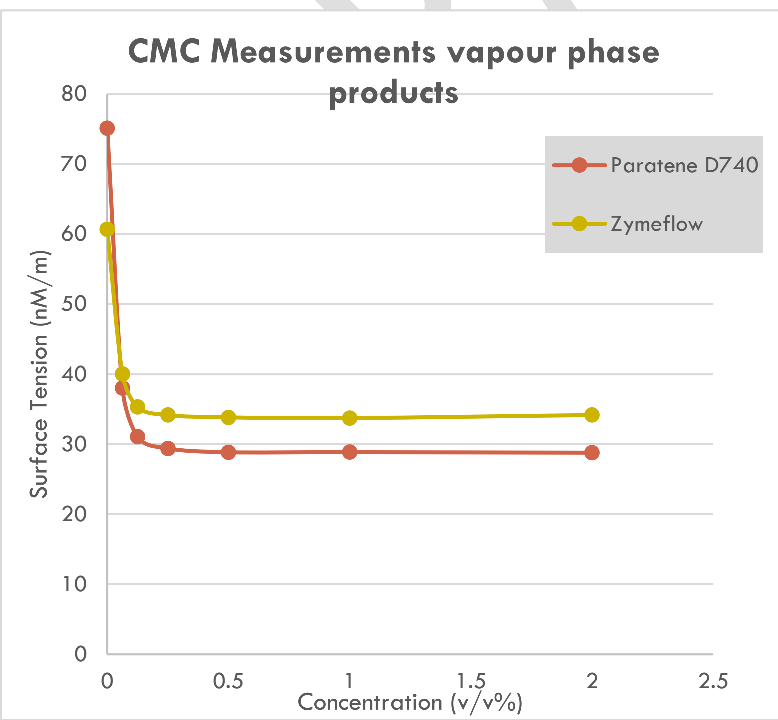
When the amine oxide reacts the resulting product is a tertiary amine. This means that in high H_2S environments or environments with high pyrophoric content the amine oxides' surfactancy will be depleted.

Products that only contain amine oxide as a surfactant would therefore require more surfactant to do the other functions of hydrocarbon control and surface wetting.

Removal of light hydrocarbons

Paratene® D740 is a blend of surfactants designed to water wet metal surfaces and displace and emulsify light hydrocarbons. Degreasing, cleaning and hydrocarbon control have three distinct aspects. First to remove light and even heavy hydrocarbons from a surface the hydrocarbon has to be displaced by the aqueous media. Then the oil or grease has to be suspended in some way in the water so it will not redeposit on the surface and finally in the case of hydrocarbon control the light hydrocarbons need to be sufficiently emulsified as to lower their apparent vapour pressure.

In the case of steam vapour cleaning, the two most important factors are the wetting of the metal surface and displacement of the hydrocarbon. The surfactant blend travels in the steam as an atomized droplet. When the steam containing the surfactant droplets reaches a cool surface the steam condenses and the combination of the water and the surfactant acts to displace the hydrocarbons. The resulting mixture of emulsified oil and water runs off the surface.



Wetting is controlled by the surface tension – the CMC or critical micelle concentration gives the minimum concentration of the surfactant that gives a constant surface tension. Solutions that have lower surface tension are better displacing hydrocarbons and spreading on lower surface energy solids.

The second effect is the speed that the solution reaches the minimum contact angle. The faster the cleaning solution wets the surface the more efficient the cleaner is at removing the coating.

If the surface is a mix of solids and oil, penetration of the solids to permit displacement of the hydrocarbon content by the water needs to be rapid. If no surfactant is present the water will form a bead on the surface of the oil covered material and not penetrate to the surface. The heat transferred by the steam will eventually cause the lighter hydrocarbons to vaporize and leave behind hydrocarbons that have a higher boiling point than the steam. When the system is water wet removal of H_2S and pyrophoric materials is also greatly improved.

Overall Paratene D740 provides more rapid wetting and lower surface tension on surfaces contacted by hydrocarbons. This has been shown to give quicker hydrocarbon removal when compared to other products.

Neutralization of Pyrophoric Materials

Pyrophoric materials can form in refineries, oil storage or gas production systems when H_2S reacts with iron oxides or directly with the base metal to form a variety of Iron sulfides. The exact sulfide or blend of sulfides formed is dependent on the reaction conditions, temperature, partial pressure of H_2S, presence of water and the initial source of iron[8].

Iron sulfides come in many varieties some of which are metastable as the result of various combinations and permutations of oxidation states available to the iron and sulphur system[9]

Mineral Name	Chemical composition	Structure and Properties
Mackinawite	FeS_n	Tetragon crystals, metastable
Cubic FeS	FeS_c	Cubic crystals, unstable
Trolite	FeS_i	Hexagonal
Pyrrhotite	$Fe_{1-x}S$	Non stoichiometric stable in monoclinic form

		Close to Fe_7S_8 hexagonal $Fe_{10}S_{11}$
Smythite	Fe_9S_{11}	Metastable – related to $Fe_{1-x}S$ group
Greigite	Fe_3S_4	Metastable Fe^{2+},Fe^{3+} thiospinel of Iron
Pyrite	FeS_2	Stable cubic crystal
Marcasite	FeS_2	Metastable orthorhombic crystal

According to Walker and Morgan the reaction path for deactivating pyrophoric iron sulfides depends on the initial form of the sulfide – Mackinawite having a different reaction path than Pyrite/Greigite mixtures. In the case of Mackinawite the sulfide undergoes a slow oxidation requiring a stoichiometric amount of oxygen. The Pyrite/Greigite case, when exposed to low concentrations of an oxidizing agent they found no substantial change in the chemical composition of the samples but SEM images show a substantial change to the morphology of the solid rendering them inert. This is consistent with the results we have seen in the field where the small amounts of oxidizing agent (relative to the amount of iron sulfide present) were capable of neutralizing the pyrophoric sulfides that had previously been a problem. The reaction is relatively quick. If the intention to actually remove the sulfides then we recommend using Paratene® SHP.

Microemulsion

A micro emulsion is a thermodynamical stable emulsion where the droplets are smaller than visible light, resulting in a clear mixture with no visible phases. The external phase is typically water and the internal phase is most often hydrocarbon. Microemulsion is a way to deliver solvents and carry hydrocarbons in the resulting solutions delivering results that are a bit of both water wetting and solvent suspension.

In addition to the cleaning capacity of microemulsion systems these products also reduce the effective vapour pressure of the suspended solutes making the resulting solution have higher apparent flash points and lower odor.

Examples of these products include

- Paratene D742
- Decon 88
- Phase Out
- Safeguard

Most of these EXCEPT Paratene D742 contain D 'Limonene. (D 'Limonene is present in D742 at 1% to provide an odor.)

Paratene® Products Mechanism – Paratene® D742 (microemulsions)

Emulsions are dispersions of one insoluble phase in another. The dispersed phase is called the internal phase and the continuous phase is the external phase. Typical emulsions come in two forms water external-oil internal and water internal-oil external. Microemulsions are a form of emulsion where the droplets forming the internal phase are small – between 1 and 100 nm and the resulting mixture is thermodynamically stable and won't separate.

Microemulsions are produced by mixing an insoluble oil or hydrocarbon phase, stabilizing surfactants and sometimes salts to form a clear liquid.

Paratene® D742 is a unique micro emulsion blend. It is intended to provide a stronger degreasing and encapsulation action then is available with a straight surfactant blend like Paratene® D740. It does not contain any oxidizing agents as are present in the surfactant blends. However it does contain a potent organic solvent.

The solvents used in Paratene® D742 are a blend of a small amount of a terpene solvent with a much larger amount of aromatic glycol ether. The glycol ether has a much higher boiling point and lower vapour pressure than the solvents typically used in these systems. There are two important factors in this.

When the droplets of the degreasing solution are exposed to the hot steam vapour the temperature of the steam will be sufficient to vaporize at least a fraction of the typical solvent being used. This depletes the droplets and either loses the solvent in the steam exhaust or separates it from the surfactant package in the condensing steam. The solvent may re-condense at the area of the system still below the boiling point but for the most part the solvents will be carried out of the vessel in the steam vent.

By comparison all components of Paratene® D742 have relatively low volatility and will remain together as a package when they arrive at the surface to be cleaned.

When the solvent in D742 is compared with commonly used solvents this can easily be seen:

Property	**D742 Glycol Ether**	**D-limonene**	**Aromatic naphtha**
Boiling Point (°C)	253	176	363
Vapour Pressure at 20°C mm Hg	0.01	2	1
Vapour Pressure at 120°C mm Hg		240	
Flash point °C	115	50	63
Henry's Law Coefficient (atm-m^3/mole)	$2.05x10^{-8}$	.38	0.5 -0.8

The solvent is coupled to the cleaning solution as a micro emulsion. This allows it to attack the heavier components of deposits found in most hydrocarbon processing systems and disperse them in the resulting liquid. The resulting liquid contains both dispersed hydrocarbons, suspended inorganic particles and encapsulated hydrocarbons. The capacity of the solution to encapsulate hydrocarbon is dependent on the amount of the D742 in the solution.

When a hydrocarbon is encapsulated as a micro emulsion, the apparent flash point and vapour pressure of the solute is lower than it would be if the system was a true solution. This is because the energy of the micelle holding the solute in the aqueous matrix is higher than the energy required for the vapour to escape.

Hydrocarbon – Emulsion Solvents

Solvent based products contain no water and use the solvation effect to dissolve the hydrocarbons present. Some use vaporizable solvents, all have surfactants to give emulsification of the resulting heavy hydrocarbons

There are several products in this category

- Paratene D731
- Quikturn

- Enterfast
- Kixsolv

Emulsion solvents – Paratene D731 and dispersed solvents

The other type of emulsion is the macroemulsion. In this case larger droplets of one liquid are disperse in a separate liquid. Unlike microemulsions these mixes are not thermodynamically stable and will separate given enough time.

This is true at temperatures below the boiling point of the solute. This is an important thing to note. Substances of interest such as Benzene have relatively low boiling points - (see table). When systems operate above the boiling point no amount of encapsulation will prevent the release of the vapour.

Chemical	Boiling Point (°C)
Benzene	81
Toluene	110
xylene	144
Ethyl benzene	136
Aromatic 150	176
Aromatic 100	161

Studies we have performed on a related product (Paratene® D728) have shown that the solution will hold approximately 6 – 8 vol. % benzene before any substantial amount of benzene can be measured in the vapour. (These tests were performed by measuring the air bubbling through a saturated D728 solution and analyzing for benzene using a gas chromatograph.) The actual capacity of Paratene® D742 applied is hard to determine. Lab studies of a 2% solution show that approximately 2000 ppm of benzene can be encapsulated.

Some of the products in the list use a volatile solvent – that has a low boiling point expecting the condensed vapour to wash or dissolve the existing hydrocarbons and then permits the water washing solution to water wet the residual hydrocarbon.

In the case of Quikturn the solvent used is a para menthane[5] with a boiling point of 170°C and a flash point of 43°C. this material will partially flash when heated to 110° but will not emulsify very well and is injected separately from the surfactant.

For Kixsolv the solvent is selected from the list of aromatic solvents. Again, they are depending on solvent being volatile and forming a condensed area on interior surfaces. The inherent problem with his is the delivery of a wetting or emulsifying agent to the surface when the solvent has already evaporated, overall using a higher boiling solvent will result in better removal of hydrocarbons.

The biggest problem with this and the microemulsion systems is there is no actual control over pyrophoric materials or H_2S.

Measuring Results

Paratene® D740 and D742 have radically different chemistry and different objectives. Paratene® D740 is intended to remove light hydrocarbons and react with hydrogen sulphide and pyrophoric substances. Paratene® D742 is intended to remove heavy hydrocarbons and disperse solids.

H_2S measurements can be carried out using standard measuring techniques. No interferences from the D740 have been seen in normal application. When the H_2S levels in the escaping vapour have been reduced to zero it is probable that most if not all of the H_2S has been removed from the system.

LEL is a misused term for hydrocarbon vapour. The presence of light hydrocarbons in the vapour will be reduced to zero when the lighter materials have been washed out by the Paratene® D740. As the system heats up additional hydrocarbon vapour may be released by the vaporization of heavier and heavier substances. A lack of measurable "LEL" when the system is hot is a strong indication that all of the available hydrocarbons have been removed.

Paratene® D740 is a wetting agent and detergent - it is not a solvent degreaser. Thus where hydrocarbon and heavy deposits are present it cannot remove the hydrocarbon and H_2S trapped in heavy layers of deposits nor can it neutralize pyrophoric material trapped in the same sort of deposits.

Paratene® D742 is a degreaser and controls Benzene and other hydrocarbons. The progress of D742"s degreasing action can be monitored by the change in oil content of the solution. Measuring benzene content and total oil content is difficult. The formation of a micro emulsion is spontaneous and locks in some of the hydrocarbons. Mixing a small amount of the condensate returns with an insoluble solvent such as chloroform will extract much of the organic material. The water and solvent can then be separated by centrifugation.

The amount of water recovered can be subtracted from the original and the amount of organic material calculated. The degree of solids being carried can also be determined.

Benzene measurements are more difficult. First, if the system is above 80°C all of the benzene in the system is a vapour. At temperatures between 20 and 40°C Paratene D742 will encapsulate a portion of the available benzene. In some cases, particularly mists, the aromatic glycol ether in Paratene D742 will give false positive readings for benzene in instruments using a photo ionization detector[10]. The photo ionization detector will saturate with the glycol ether and give increasingly large false positive values. When the detectors were compared with gas chromatographic measurements the detectors were giving false positives for benzene when the aromatic glycol ether was present.

The best measurement for benzene has remained a portable gas chromatograph.

Cleaning system recommendation

Based on the experience gathered in field operations, the best way to apply Paratene D740 and Paratene D742 is in a series application. Paratene D742 should be applied first and the returns monitored for hydrocarbon content either by centrifuge or by transmittance. When the returns become clear, the system should then be switched to D740 until the measured amine levels reach 300ppm at all sample points. Contact times depend on the size of the system, number of injection points, available steam composition and pressure.

Additional Cleaning Applications for Paratene® D740 and Paratene® D742

Paratene® D740 and Paratene® D742 are water based degreasing additives that were designed for steam application but can be used in a multitude of other cleaning applications.

Paratene® D740

D740 is a blend of surfactants designed to improve the wetting of solids and surfaces. It is mildly oxidizing and can react with hydrogen sulphide and pyrophoric materials.

Paratene® D740 is soluble in water, acids and caustic solutions. It will improve the wetting of all these solutions and aid in the removal of hydrocarbons as well as improving the reaction rates of acids on many difficult to wet scales. For this application D740 should be added at between 0.2 and 0.5%.

D740 can aid in removal of residual hydrocarbon vapours from vessels and systems. It can be applied in water or in alkaline solutions as a wash or rinse. For this application the D740 should be applied at 2 – 5%.

Paratene® D742

Paratene® D742 is a powerful concentrated water based degreaser. It can be used diluted at a rate of 5 – 50% dilution in water to remove hydrocarbons and heavy oil deposits from piping, towers, exchangers, tanks and vessels.

When applied at concentrations of 20% or higher Paratene® D742 will suppress hydrocarbon emissions particularly BTEX's. This makes D742 and excellent choice for degreasing the interior of tanks. (10 litres of BTEX will be controlled per 100 litres of applied D742.) Paratene® D742 contains no inorganic phosphates and is completely biodegradable. This makes it an excellent choice as a degreasing solution in external and environmentally sensitive applications.

[1] Loucks, Charles M., Brown, William B. 1963 "Chemical cleaning of metal surfaces employing steam" United States DOW CHEMICAL CO 3084076 http://www.freepatentsonline.com/3084076.html

[2] Mestetsky, Pat A. (St. Charles, IL) 1997 "Method of cleaning contaminated industrial equipment" United States United Laboratories International, LLC (St. Charles, IL) 5686297 http://www.freepatentsonline.com/5686297.html

[3] Hart, Paul R. (The Woodlands, TX) 1997 "Refinery vessel cleaning treatment" United States Betz Dearborn Inc. (Trevose, PA) 5611869 http://www.freepatentsonline.com/5611869.html

[4] Mehta, Nishaneth K. (Houston, TX), Krajicek, Richard W. (Houston, TX) 1994 "Process for vessel decontamination" United States SERV-Tech, Inc. (Houston, TX), 5356482 http://www.freepatentsonline.com/5356482.html

[5] Sears, Sean E. (Wichita, KS, US), Roberts, Kevin L. (The Woodlands, TX, US) 2005 "Method of cleaning vessels in a refinery" United States, Refined Technologies, Inc. (Wichita, KS, US), 6893509 http://www.freepatentsonline.com/6893509.html

[6] Shulman G.P., Link W.E. "Thermal Decomposition of Dimethyllauryl amine oxide" Journal of American oil Chemists, Vol 4, no.4 April 1964. Pg 329-331

[7] Singh S.K., Bajpai M., Tyagi V.K. "Amine Oxides: A review" Journal of Oleo Science Vol. 55, No. 3, 99-119 (2006)

[8] Walker R.,Steel A.D., Morgan T.B. "Deactivation of Pyrophoric Iron Sulfides" Ind. Eng. Chem. Res. 36, 3662 – 3667 (1997)

[9] Rickard D.,Luther G.W. "Chemistry of Iron Sulfides" Chem. Rev. 107, 514-562 (2007)

[10] Private correspondence with Robert Craig Dragger Safety Inc.