Objective of tank cleaning is the next cargo

The relationship between cargo tank coatings and tank cleaning is inextricably entwined. Failure to understand the impact of either, can lead to prolonged and inefficient tank cleaning or in the worst case, cargo contamination claims*.

What should also be considered is that the primary role of the coating is to prevent corrosion of the steel structure of the vessels. The paint manufacturers strive to produce coatings with the best all-round corrosion protection and chemical resistance that are effective for the trading patterns in which the vessels are trading in.

When the vessels move out of these trading patterns, for whatever reason; operational or commercial, the largest impacts are felt. This is the time when the greatest understanding of the relationship between cargo tank coating and tank cleaning is required.

It should be noted at this time that this discussion does not look at stainless steel, Teflon, or rubber coatings.

Cargo tank coatings

It is fair to say that all cargo tank coatings are to some extent, a compromise; the 'perfect' coating does not really exist.

Increasing the pigment volume concentration (PVC) in organic coatings can improve the apparent chemical resistance, but not for every cargo. Increasing PVC will also generally increase the permeability of the coating, which allows for a freer movement of cargoes 'in and out' of the coating. This reduction in residency time tends to reduce the contamination potential for volatile cargoes. However, the increase in permeability may also make the coating more sensitive to water, which could be quite disastrous.

One should also consider cross link density, which has a significant impact on both the chemical resistance and the flexibility of organic coatings. In general, the higher the cross link density, the better the chemical resistance, but the lower the flexibility.

There appears to be a trend emerging linking chemical resistance and flexibility and perhaps one characteristic will suffer - or be compromised - at the expense of the other?

When one considers that the chemical resistance may have to be compromised in order to produce a durable coating that does not crack as soon as the vessel starts to operate, the specific resistance of chemical and oil products to the coating becomes extremely important.

This is also the most logical reason why many coating manufacturers supply a range of different coatings that can be almost tailored to meet the exacting requirements of any specific trade pattern.

Organic coatings

There are two types of organic coating in common use today, phenolic epoxy and straight (amine cured) epoxy, which are primarily different in their chemical resistance; with phenolic epoxies providing a much higher level of chemical resistance compared to straight epoxies.

Phenolic epoxies are more expensive than straight epoxies because chemical resistance comes at a premium. As such, phenolic epoxies tend to be utilised far more widely in the chemical trade as opposed to straight epoxies which tend to be utilised in the vegetable oil, easy chemicals and CPP (Annex I) trades.

MarineLine is something of an enigma because while it is considered as an organic coating, this is not strictly correct, because of its make-up; however, for the sake of this discussion, it will be considered as an organic at this time.

MarineLine is neither a phenolic nor a straight epoxy and its chemical resistance is said to be derived from a very high cross link density, balanced with unique characteristics, which allow flexing of the product after it has been applied and post cured.

Inorganic coatings

In two words - zinc silicate. This coating type is quite different from organic coatings because the chemical resistance comes from the fact that the fully cured coating is inorganic and the vast majority of liquid cargoes shipped are organic. In other words, the coating and the cargo being carried are chemically opposite and this fact is extremely important.

Again one should also consider the permeability of the coating, because this property does change during the life of zinc silicate coatings. New zinc silicate is extremely porous, and there are some who say it would be a better coating if it stayed like this, based on the free movement of cargoes in and out of the coating and little or no retention of those cargo residues.

However this is not the case. Zinc silicate is quite reactive, which also restricts the type of products that can be carried and upon exposure to water, cargoes and the atmosphere, there is a steady build up of zinc salts, which reduces the permeability of the coating, at the same time increasing the resistance to organic cargoes.

Zinc salts can cause other problems and there is tendency to try and remove them by scrubbing or using cleaning materials that actually dissolve the salts, but as long as there is sufficient 'free' zinc available in the coating, the salts will return and it is perhaps better to deal with the coating including the salts than to try and change the characteristics of the coating.

Looking briefly at MarineLine again, it should be noted that this coating is actually based on silicon chemistry, which arguably puts MarineLine into the inorganic coatings category. Bearing this in mind, it should be considered that the high level of chemical resistance that the manufacturers claim for their coating is based not only on the high level of cross linking, but also on the fact that the coating and the cargoes being carried, as noted for zinc silicate, are chemically opposite.

MarineLine is treated as an organic coating.

Coatings and cargoes

The nature and chemical resistance of the different coating types determines which cargoes can or cannot be carried in those coatings.

As discussed the vast majority of bulk liquid cargoes are organic in composition and as such it is fair to assume that there is a natural affinity between these cargoes and the organic coatings. If one then looks at the permeability of organic coatings it can be quickly understood that aggressive and penetrating organic solvents are not ideally suited to organic coatings.

Many phenolic epoxies can actually be used to carry such cargoes, but there are restrictions, particularly after the cargoes are discharged and it is actually noted that some coating manufacturers are now prohibiting the carriage of such organic solvents even in the phenolic epoxies.

Straight epoxies can be almost immediately destroyed in such solvents and are thus considered unsuitable.

But apart from the carriage of aggressive organic solvents, most epoxy coatings are quite versatile and suitable for the carriage of a wide range of cargoes; non aggressive organic solvents and derivatives, clean and dirty petroleum products, acidic and alkaline based products, vegetable oils, waxes.

In terms of tank cleaning, most epoxy coatings are very smooth, which generally restricts the amount of clingage of previous cargoes and as such surface tank cleaning materials tend to very effective at removing previous cargo residues. It is also found that epoxy coatings are quite resistant to extremes of pH, so there are less risks using alkaline or acid based tank cleaning materials certainly compared with zinc silicate, which is also important to consider.

The absorption of certain previous cargo residues into organic coatings is of most concern when formulating tank cleaning plans, because removing these residues is not easy. Unsaturated and aromatic based cargoes are particularly challenging because once they have been absorbed into the coating, these residues can stay there for a long time, if the coating is not exposed to conditions that actively desorb these residues.

It is a popular misconception that if an organic coated vessel is loaded with intermediate or buffer cargoes after the carriage of an absorbing cargo, the residues of the absorbing cargo will be removed and will no longer pose a threat to a cargo that is particularly sensitive to these residues. This is not strictly correct, as it depends completely upon the chemical nature of the intermediate cargo and has resulted in cargo claims in the past.

There are really only two ways of removing residues absorbed into an organic coating.

The first is to raise the temperature of the steel inside the cargo tank to a level where the residues are evaporated from the coating. This is feasible for low boiling residues, but not practical for residues with a boiling point in excess of around +75 deg C.

The second is to load the cargo tank with a cargo, usually solvent based, that will extract the residues without itself becoming contaminated with the residues.

The tendency is to over-clean organic coatings because of their noted resistance to most cleaning materials and this is another area where problems can occur, particularly if the vessel is cleaning to a wall wash standard. As the washing temperature increases, the coatings will start to open and absorbed residues will be liberated, however it has to be considered that the residues may have been accumulating for many voyages and while the most volatile residues will be liberated first, the heavier residues, azeotropes and/or reaction products of the previous cargoes, may stay behind in the coating, even after prolonged hot washing.

Solvents may also be used to clean the coating, because they can actively penetrate inside the coating and remove the most stubborn residues that remain after cleaning with water/detergents. It should always be considered that not all of the residues will be removed in one go and wall wash samples may fail, even after cleaning with a solvent.

What should also be noted after cleaning organic coatings at high temperature or with a solvent is that the coating will be softened for a period of time after the cleaning has been completed. During this time the coating will cool down and harden and it is very common to see wall wash results improve over a period of time, without any additional cleaning.

The most important consideration when cleaning an organic coating is the quality of the next nominated cargo and the understanding of the nature of the residues that may be absorbed in the coating from previous voyages. If the next nominated cargo is particularly sensitive to aromatic residues and the previous cargo was a medium boiling point aromatic solvent, it is unlikely that any amount of tank cleaning will remove sufficient of the previous cargo to prevent contamination of the next cargo.

This challenge has been made more difficult by the ever increasing demands on the quality specification of shipped cargoes - not just chemical but also fuel based - and also the analytical capabilities of the laboratories who analyse and certify the quality of these cargoes. In the past, parts per million levels of contamination were considered to be quite strict, but now many contaminants are measured in parts per billion levels and as such, it is now far more common for cargoes to be rejected, even though vessels are cleaning longer and harder than they ever did in the past.

In order to put this into perspective;

- One part per million is equal to one second in 11½ days.
- One part per billion is equal to one second in 31½ years.

This is not strictly a reflection on the quality of the crews on board the vessels, it is purely the fact that the receivers are able to analyse the cargoes to far more stringent levels and in fact, one of the most successful tank cleaning operations today prior to the carriage of the most sensitive cargoes, does not involve any tank cleaning at all, it is more preventative management and involves loading intermediate lower grade cargoes that remove residues known to be a threat to the higher grade cargoes.

In complete contrast, zinc silicate is totally different.

First, the number of cargoes that are acceptable for loading in zinc silicate is considerably smaller, primarily because of the nature of the zinc, which reacts with products that have anything but an almost neutral pH.

A pH range of 5 - 9 is normal for most zinc silicates so this immediately rules out all alkaline and acid based products and also vegetable oils that have a significant fatty acid content.

It is found that most fuels are neutral pH, so clean and dirty petroleum products do not pose any problems, but where zinc silicate really comes into its own is in the carriage of aggressive organic solvents, because the zinc silicate is chemically opposite and thus completely unreactive to any neutral organic product, solvent or otherwise.

Tank cleaning zinc silicate is also completely different to cleaning organic coatings because while zinc silicate absorbs organic solvents, it does not retain them. Perhaps more significantly though, unlike the surface of organic coatings the surface of zinc silicate is far from smooth; in fact in many cases it is extremely rough to the touch.

The latter point creates very challenging tank cleaning issues because it is found that non volatile cargo residues are readily adsorbed on to the surface of the coating and also absorbed into the matrix of the coating.

So when cleaning from oils it is extremely is potentially very difficult to clean. This problem is made more challenging for two reasons:

1) Surface active cleaning materials (detergents) are exactly that; surface cleaners; and it is known that previous cargo residues are trapped within the coating matrix.
2) The most effective solutions for cleaning oil based residues usually employ ingredients containing caustic or meta-silicate, which have a pH in the region of 12 or 13 and are thus prohibited for use on zinc silicate.

> “It is fair to say that all cargo tank coatings are to some extent, a compromise; the ‘perfect’ coating does not really exist.”

One other point to note at this time is the effect of fuel generated inert gas in zinc silicate coated cargo tanks, prior to loading and during the discharge of flammable clean petroleum products. In short, inert gas is acidic and with prolonged contact to the coating it is quite common to observe yellow/brown dust on the surface of the cargo tanks, which is most likely a reaction product of the zinc silicate and the acidic inert gas.

This powder massively increases the surface area of the coating and significantly increases the potential of previous cargoes becoming adsorbed to the surface and trapped just underneath the surface layer. The only way to remove this problem is manual scrubbing, which is time consuming and limited in its effectiveness.

The last coating type is MarineLine

Theoretically, this coating utilises the benefits of organic coatings and zinc silicate coatings in one system.

In the first case, the coating is very smooth and as a consequence the majority of cargoes will run off the surface without causing a retention problem. High melting or particularly viscous products will of course cling to the surface, but temperature alone is generally sufficient to tackle this issue.

The next consideration is the chemical composition of MarineLine. It is accepted that the product is treated as an organic coating, because during application, the product is mixed with various organic solvents in order to expedite application. However, as noted, once these solvents are removed during drying and post curing, the backbone of the MarineLine coating is silicon; not carbon.

If MarineLine is then considered to be an inorganic coating, it would be expected to be particularly resistant to organic solvents; and indeed this is found.

Without the pH limitations of zinc silicate, it would also be expected that the number of products suitable for carriage in MarineLine is much higher compared to zinc silicate and again this is true. The manufacturers state that the product is actually suitable for acid carriage, which is a bold statement, when one considers that acid transportation has been the almost exclusive domain of stainless steel for many years.

The potential of a smooth surfaced coating with good resistance to penetrating organic solvents and not restricted by pH is immediately obvious in several trade patterns and the author is currently investigating this potential further.

In summary

Understanding how cargoes behave and/or react with the various coating types - always bearing in mind that any cargo absorbed into or adsorbed onto the surface of that coating will behave differently when it reacts with a different cargo - is essential if an efficient and economical tank cleaning procedure is to be carried out.

How the previous cargo residues are expected to be presented - absorbed, adsorbed, retained in a surface profile - is critical to the correct choice of tank cleaning chemical and the duration of each cleaning cycle. And of course the resistance of the cargo tank coating to the cleaning chemical is also extremely important, not only to effectively remove the previous cargo residues, but also to prevent short and long term damage to the coated surface.

Finally the quality of the next loaded cargo should never be overlooked, particularly if it is known that a coated surface is contaminated with a previous cargo residue. The objective of any tank cleaning procedure is to clean to a condition where the next cargo can be loaded without risk of contamination. By careful understanding and appropriate monitoring of each tank cleaning step, this objective is readily attainable. TO

This article is the second in a series written by Guy Johnson, BSc (Hons) MRSC CChem CSci, director L&I Maritime (UK).

Videotel adds Tank Cleaning to its titles

With the introduction of the second version of TMSA earlier this year, Videotel, has added to its range of training titles with 'Tank Cleaning Practice'.

The programme describes different types of tank cleaning, from a quick wash between compatible products, to the complex washing procedures required between incompatible products. It also looks at how decisions are made about which type of cleaning process to use.

Captain Milind Karkhanis, vice president, Videotel Training Services, said: "Tank cleaning is one of the most important aspects of cargo transportation. Our programme outlines the key processes and procedures that are prerequisites for safe and effective tank cleaning, emphasising the importance of crew familiarisation and training."

In making these programmes, Videotel has been working with INTERTANKO and other leading training establishments and operators to guarantee that these products support the INTERTANKO TOTS (Tanker Officer Training Standards) scheme. TOTS provides the tanker industry with a standard that ensures tanker officer competence through training, both on board and onshore.

Videotel's tanker training programmes are available on video and DVD and are suitable for use in training sessions on board ship and are accompanied by detailed support booklets. Computer-based training (CBT) interactive versions are also produced for independent study, wherever the trainee may be.

NAVADAN appoints sales manager

Effective 1st December Capt Thomas Marvig Rasmussen has been appointed as sales manager for NAVADAN APS.

With his background as master and operations manager in companies such as Norient Product Pool and Weco-Shipping/Dannebrog Rederi in Denmark, he has gained substantial knowhow of the markets' requirements for chemicals and the chemical tank cleaning solutions that are offered on a worldwide basis by the company.

NAVADAN's head Frank R. Tschicaja