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Performances in Tank Cleaning

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ABSTRACT: There are several operations which must do to maximize the performance of tank cleaning. The new advanced technologies in tank cleaning have raised the standards in marine areas. There are many ways to realise optimal cleaning efficiency for different tanks. The evaluation of tank cleaning options means to start with audit of operations: how many tanks require cleaning, are there obstructions in tanks (e.g. agitators, mixers), what residue needs to be removed, are cleaning agents required or is water sufficient, what methods can used for tank cleaning. After these steps, must be verify the results and ensure that the best cleaning values can be achieved in terms of accuracy and reliability. Technology advancements have made it easier to remove stubborn residues, shorten cleaning cycle times and achieve higher levels of automation. In this paper are presented the performances in tank cleaning in accordance with legislation in force. If tank cleaning technologies are effective, then operating costs are minimal.

1 INTRODUCTION

1.1 *Chemicals characteristics*

The ability of a vessel to execute a successful tank cleaning operation is what makes that vessel better than its competitor. If the tank cleaning is successful, there is no waste. If the tank cleaning is not successful, everyoane feels the impact: time, manpower, cleaning chemicals, bunkers, equipment, off specification cargo and loss of earings. The basics of any tank cleaning procedure are tipically the same. There are technical publically tank cleaning guidelines, like: MIRACLE (Supplied and produced by Chemtec in Hamburg); Dr. Verway (CHEMTEC, Hamburg); MILBROS (Q88 Stamford, USA)(Sørensen O. et al.1959). All of these published guidelines basically provide the same informations in order to avoid the appearance of technological risks (Jensen B.B. et al. 2011-2012; Panaitescu F.V. et al. 2014).

One of the most important aspects of choosing the correct tank cleaning procedure is to recognise and understand the chemical properties of the previous cargo: volatility, solubility in water, viscosity, colour, drying cargo, polimerisable cargo, strong absorber. The most important aspects of understanding the chemical properties of the cargoes that are being cleaned from: volatile cargoes will tend to evaporate, but may be retained in organic coatings; non-volatile cargoes tend to be persistent, but are not retained in organic coatings; water soluble cargoes do not need cleaning chemicals to remove them, because they are completely removed just using water; viscous cargoes will usually need warmer washing water to make them easier to remove; coloured cargoes/residues will probably need a colour remover-bleach; drying oils and polymerisable cargoes will always need ambient temperature water washing; strong absorbers are a challenge. Some additional factors strongly influence the successful outcome of any tank cleaning operation: a) outside climate conditions; b) the monitoring cleaning process; c) the pre-loading inspection specifications for the next cargo. There are three levels of pre-loading inspection: load on top (LOT); visually clean/water white standard; chemically clean/wall wash standard.

1.2 *Tank cleaning operations*

There are various parameter that contribute to effective tank cleaning (Sørensen O. et al. 1959; Sinner, H. 1959). The content of tank cleaning plan is based on the cleaning processes model: MARPOL wash (Annex I, Annex II high viscosity) or solvent; cold/hot wash to continue; wash with chemicals; rinse (when chemical are used); repeat chemical wash/manual cleaning; steaming/fresh water; manual cleaning (CSM-L&I-IMEC.2016).

Tank cleaning operations are optimised when all cleaning steps are monitoring. After these steps, must be verify the results and ensure that the best cleaning values can be achieved in terms of accuracy and reliability.

2 OPTIMIZING TANK CLEANING OPERATIONS

2.1 *The steps of cleaning operations*

Tank cleaning operations are manually and mechanically. If the operation is made manually, changing to an automated method will yield many benefits: more consistent, improved worker safety by removing contact with hazardous chemicals, faster cleaning, reduced use of water, chemicals and lower wastewater disposal costs (http://www.tankjet.com, 2016). If the cleaning is made with machines, may be able to improve cleaning efficiency by making some simple changes or using different equipment. Technology advancements have made it easier to remove stubborn residues, shorten cleaning cycle times and achieve higher levels of automation (http://www.tankjet.com, 2016).

The new advanced technologies in tank cleaning have raised the standards in marine areas.There are many ways to realise optimal cleaning efficiency for different tanks. The evaluation of tank cleaning options means to start with audit of operations: how many tanks require cleaning, are there obstructions in tanks (e.g.agitators, mixers), what residue needs to be removed, are cleaning agents required or is water sufficient, what methods can used for tank cleaning. After these steps, must be verify the results and ensure that the best cleaning values can be achieved in terms of accuracy and reliability.

Inspection of the cargo tanks is very important because it is the best indicator about whether the load port inspection will be successful or not (CSM-L&I-IMEC, 2016). If the cargo tanks and the deck look and smell clean and are well organised, the load port inspector will have a better feeling about vessel and the final results will be favorable.

Inspection of the cargo tanks includes: a) tank hatch (hatch gaskets, odour when the hatch is first opened, overall appearance of the hatch, the conditions of coating, signs of corrosion); b) deck head (sign of condensation, cargo residues, visible salt crystals, coating breakdown); c) access ladder or platforms; d) bulkheads (check for evidence of previous cargo, discoloured patches, corrosion, coating breackdown/condition of the steel, other surface debrs, tank cleaning machine "shadow" areas); e) cargo lines (first foot samples are critical, because they are the first measure of how clean the cargo lines are; always clean them in the same way that the cargo tanks are cleaned cold water/hot water/cleaning chemicals, steaming lines cleaning free from inorganic chlorides; this step includes also flexi cargo hoses which are used during cargo operations; after cleaning and prior to loading must verified that all drain valves are kept open; at the end of cleaning, the lines must be blown back to the tanks).

2.2 *The selection of equipments*

It is important to optimise the tank cleaning process to ensure repeatable tank cleaning performance in the shortest possible amount of time (Jensen, B.B.B. et al. 2011-2012).

For this, tank cleaning process must be automated. Process control depends upon reliable real-time in-line measurements using electronic sensors to monitor and verify the performance of tank cleaning systems. It is important to choosing the right system to monitor and control tank cleaning automated system and to define the objectives for monitoring and control. These help to understand the available options and advantages (cleaning consistency, reduced labour costs and increased production time, less downtime, higher energy savings and reduced water and cleaning fluid consumption).

There are many possibilities to choose tank cleaning products and the maximum tank diameter each unit can clean (http://www.tankjet.com, 2016).

Final decision will be determined by tank size and level of cleaning required. For the selection process there are the folowing things which must comply (http://www.tankjet.com, 2016):

- *High impact cleaning* is required to remove stubborn residues such as layers of a dried substance (tank cleaners in this category generally use high pressure and/or high flow);
- *Medium impact cleaning* is required when good impingement is needed to remove residues (tank cleaners that provide medium impact generally use solid stream nozzles at medium flows and pressures);
- *Low impact cleaning* is used for light cleaning when some impact is required (low flow/medium pressure and high flow/low pressure nozzles are used to achieve low impact cleaning);
- *Rinsing* is used when distributing cleaning solution throughout the tank without impact provides sufficient cleaning.

2.3 *Methods of research*

There are three clasical methods of applying cleaning chemicals to the cargo tanks and a new vision for monitoring and test analysis of samples-VISIBLE and

ULTRA-VIOLET spectroscopy (UV-VIS) (table 1). The clasical cleaning methods are: re-circulation (figure 1), injection (figure2), direct spraying (CSM-L&I-IMEC, 2016). The important objectives for cleaning by recirculation are: the process can't stopped (once the cleaning has started, it is very straightforward to handle); work easy facilities (easy calculation for cleaning chemicals depending on work solution); easy to maintain heat during recirculation (unless the vessel is equipped with heating coils or aqn extremely efficient heater system). The important objectives for cleaning by injection are: provides a constant supply of "fresh" cleaning solution; utilises maximum washing water temperatures; depending on the efficiency of injection pump; the concentration of the cleaning chemical mixture is not really confirmed (the clening chemical concentrate is pumped into a water moving volume); can use much higher volumes of cleaning chemicals concentrate; the contact time between cleasning chemical solution and cargo tank surface is much lower (30 ... 60 minutes). Direct spraying is primarily used for spot cleaning of areas that are in the shadow of the tank cleaning machines, unless the tank cleaning machines are damaged or broken.

For monitoring and test analysis of samples in the VSIBLE region of the light spectrum, regular glass sample cells should be used. They are marked with "G'letter. The apparatus is spectrometer. For monitoring and test analysis of samples in the ULTRA-VIOLET region of the light spectrum, only sample cells made from quartz glass can be used. They are marked with "Q"letter. It is important to use the correct sample cell, otherwise the data generated might not be valid.

Tank cleaning result tests are: Permanganate Time Test-PTT (is based on the ability of potassium permanganate, $KMnO_4$, to oxidise hydrocarbon impurities that could be present in the wall wash liquid; if PTT is a reaction in a neutral solution, the value of $KMnO_4$ is small and changes its colour from pink-orange to yellow-orange)(MARPOL); Hydrocarbons Test (water miscibility)(is the qualitative detection of non-water-soluble contaminants; Chloride Test (is used the judge the presence of chlorides on bulkheads; Chloride levels vary from 0.1 ppm to 5 ppm); Colour Test (APHA); UV-Test (is used to identify hydrocarbons and chemicals); The Acid Wash Test (is used to determine the presence of Benzene, Toluene, Xylenes, refined solvent Naphthas, similar industrial aromatic hydrocarbons, impurities in methanol); NVM (Non Volatile Matters) Test (is used to determine if there are non-volatile impurities on the tank surface by weights).

Table 1. VISIBLE and ULTRA-VIOLET spectroscopy.

Tank cleaning Test	VIS	UV
Absorbance	Units	wavelenght (nm), Absorbance (A)
1. Inorganic chlorides	ppm***	Cargo quality for potable ethanol methanol
2. PTT*	%	SHELL CHEMICAL Analyse (alcohols, ketone)
3. APHA colour	APHA	routine wall wash inspection prior to loading potable ethanol and HMD*****
4. Hydrocarbons	FTU***	water insoluble hydrocarbons

* PTT = permanganate time test
** APHA = colour test
*** ppm = parts per miliion inorganic chlorides
*** FTU = formazine turbidity unit
*****HMD = Hexamethylene diamine

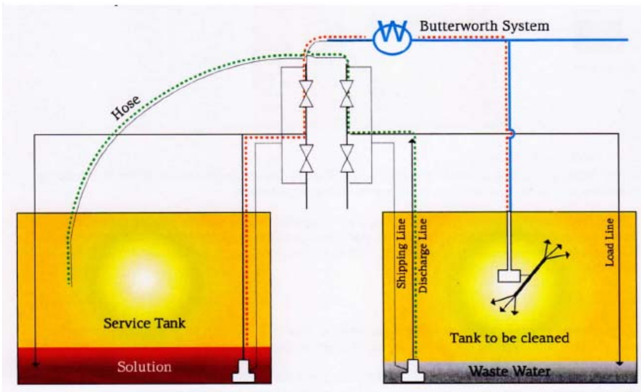

Figure 1. The principle of Re-circulation .

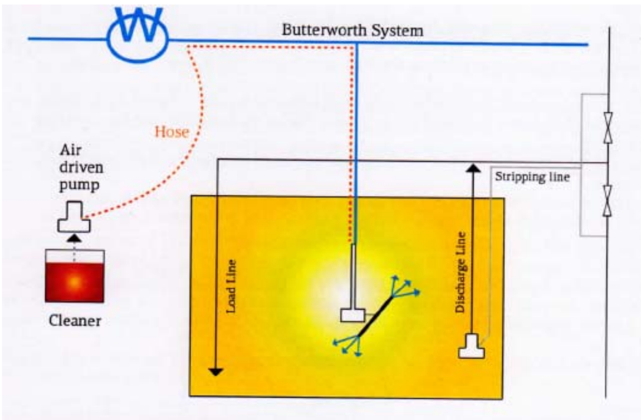

Figure 2. The principle of injection.

The test procedure for analysis may vary slightly from place to place, but the principle is always the same. In this case study are used for each test different samples where are mixed with different solution for relevant presence of residues (on chlorides, silver nitrate solution, on PTT, potassium permanganate solution, the hydrocarbons test contains traces of hydrocarbon based cargoes that are soluble in the methanol or acetone).

In the chemical tanker area, UV spectroscopy is a more widely accepted technique for analysing the quality of loaded cargo. When a UV light source is passed through a test sample, the different chemical groups that make up the sample, absorb different amounts of the UV light (absorbance) (CSM-L&I-IMEC, 2016). Each chemical substance has its own unique UV fingerprint and this permit to identify the presence of these chemical substances in the test samples.

The most commonly chemicals are: methanol, benzene, styrene monomer, phenol, fatty acid methyl ester-fame, pyrolysis gasoline, acetone, multiple hydrocarbons, unknows.

3 EXPERIMENTAL DATA AND RESULTS

3.1 *Visible spectroscopy tests*

Visible spectroscopy tests are: inorganic chlorides, PPT, APHA colour, hydrocarbons. In this paper, for each test are used different quantities of test sample, put into separate, clean measuring cylinders and add different solutions to identified chemical products. The effects and results are analysed with spectrometer, at different reaction times (minutes) (Table 2).

Table 2. Visible spectroscopy tests

Test	Add solution	Time	Results
	ml/%/g	minutes	nm, A, ppm, %, FTU
1. Inorganic chlorides	25 (5 drops silver nitrate (2%/5%)+ 5 drops 20% nitric acid)	15	420 nm 0.099 A* 1.0 ppm
2. PPT	500 (0.02% $KMnO_4$+ 0.1g solid KMnO4)	< 20 > 50	< 32% > 32% 530 nm
3. APHA colour	methanol/acetone		5...15 APHA (low levels)
4.Hydrocarbons	100 (solvent+water)	15... 20	400 nm 0.025 A 1...2 FTU (slight hydr.) 3...600 FTU (increasing hydr.)

* Absorbance

3.2 *UV spectroscopy tests*

The typical "aromatic"activity was tested for chemicals: methanol, benzene, styrene, phenol, more UV traces of chemical cargoes (figure 3, figure 4, figure 5, figure 6, figure 7) with spectometer. One important aspect of UV spectroscopy is the concentration of the identified groups (i.e. to be able to quantify how much benzene is present in the sample). For this, was analysed how 10 ppm of benzene, styrene and phenol in methanol not only give different shaped peaks, but also different sized peaks as well (figure 8).

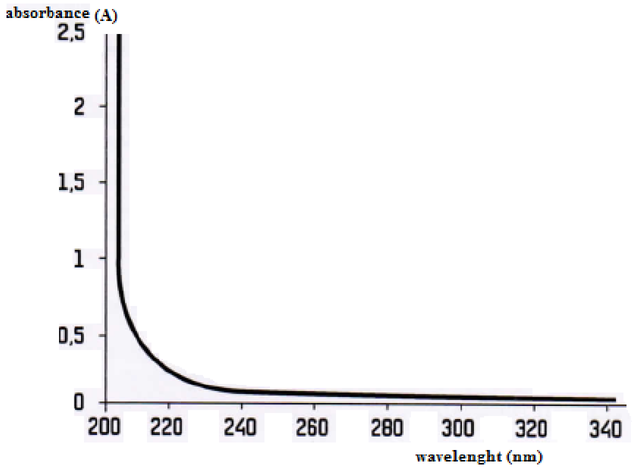

Figure 3. Pure methanol.

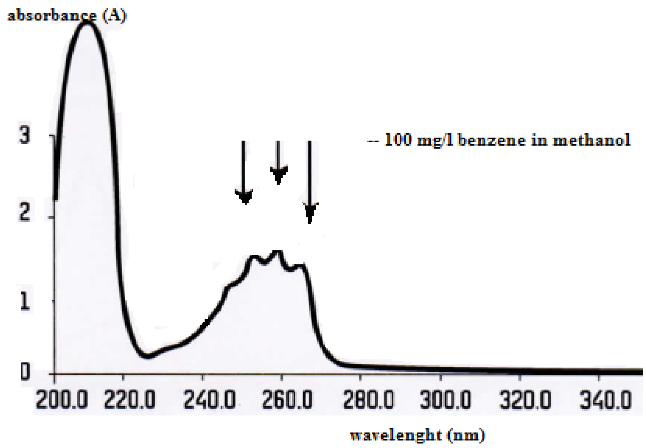

Figure 4. Benzene in methanol.

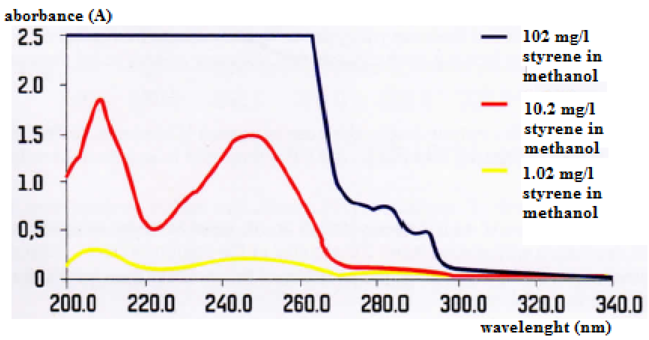

Figure 5. Styrene in methanol.

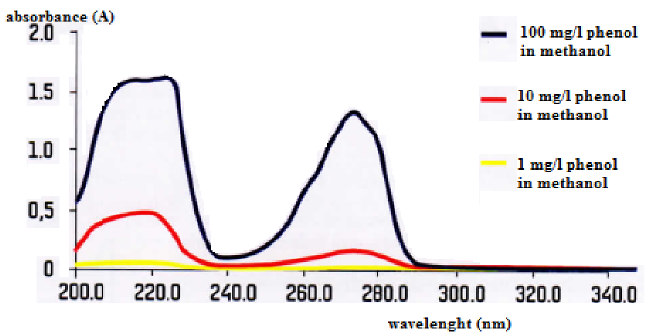

Figure 6. Phenol in methanol.

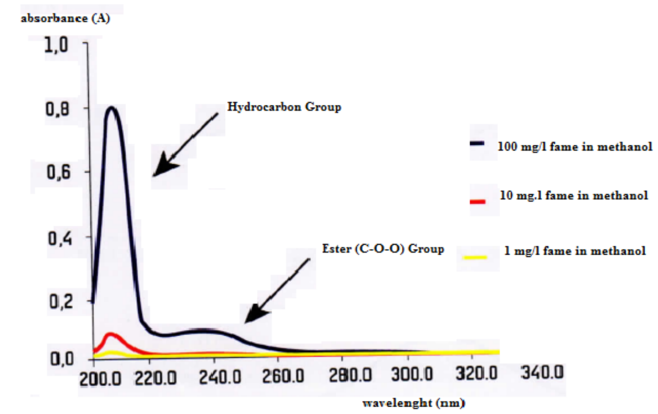

Figure 7. Fame in methanol.

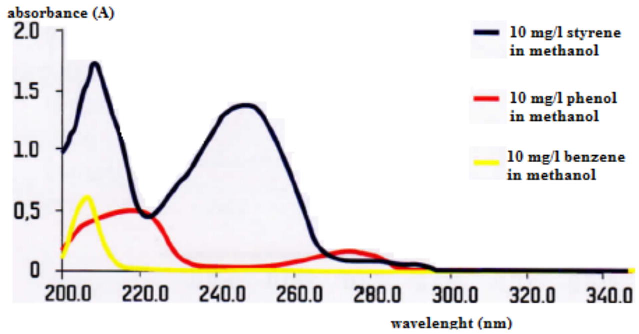

Figure 8. The concentration of the identified groups.

The grafic interpretations have shown that UV spectroscopy is very important to identify chemical groups and to determine concentartions of these groups (CSM-L&I-IMEC, 2016).

4 CONCLUSIONS

In general, the tank cleaning monitoring procedures depend on the cargoes properties to be cleaned, on the surrounding conditions, on the available equipment and last but not least the requirements of the products to be loaded. A variety of chemical cleaning agents is available for most application problems. Cleaning agents must be IMO approved. After analise of experimental data, can observe:

1 For visible spectroscopy

– at inorganic chlorides test- after 15 minutes out of direct sunlight, any presence of a white colour indicates the presence of inorganic chlorides in the test samples and using spectrometer, can be quantified these;
– at PPT , after 10 minutes visually check the appearance of each sample (typically is 50 ... 60 minutes); after 50 minutes, if was found > 32%, the result should be repored as PTT is greater than 50 minutes; if the test sample was analysed after 20 minutes and the was found < 32%, the result should be repored as PTT is less than 20 minutes. In case study, the spectrometer reading to how the colour of a methanol wall wash fades, regarding at 32% - still contains a trace of pink and regarding at 21 % - is closest to the recommended colour. Without the spectrometer, the method of determining of PTT is to prepare the colour standard described by requirements.
– at colour test, the result is in accordance with requirements in units APHA;
– at hydrocarbons test results (Table 2), can directly reading on spectrometer, in units of turbidity FTU, if it is a slight presence of hydrocarbons, or it indicates an increasing presence of hydrocarbons; in this case study, be accepted as “pass”.

2 For UV spectroscopy

– for benzene in methanol there are two areas with strong activity between 200...220 nm (benzene is a pure hydrocarbon) and 240 ...260 nm (three small peaks with pure benzene and the indicative of all Aromatics);
– for styrene in methanol there is strong UV activityin two specific regions at 210 nm (hydrocarbon, ethylene group) and between 240...260 nm (Aromatics);
– for phenol in methanol there is Aromatic activity around 240...260 nm, but in this case study, it has been shifted to higher wavelenght areas, 260 .. 280 nm (because the OH group from formula of phenol is directly attached to the benzene ring (Sørensen et al. 2016).

There are more UV traces of chemical cargoes (fatty acid methyl ester-fame, pyrolysys gasoline-pygas, acetone, multiple hydrocarbons, unknows).

In literature are published more informations about additional poits for UV tests (NVM-Non-volatile- matter, AWC-acid wash colour test) and washing water analysis (http://www. alfalaval. com. 2016).

REFERENCES

CSM-L&I-IMEC, 2016. Chemical tanker training. In *Student guide-tank cleaning*, Constanta:pp. 30-58.

http://www. alfalaval. com. 2016. Tank cleaning -planning. In *Th.Ah. Tank cleaning-guide*: pp. 2-7.

Jensen, B.B. et al. 2011-2012. Tank Cleaning Technology: Innovative application to improve clean-in-place (CIP). In *EHEDG* 2012: pp. 26-30.

Panaitescu, F.V., Panaitescu, M., Voicu, I.&Panaitescu, I.I. 2014. Training for environmental risks in the Black Sea Basin. In *the International Journal on Marine Navigation and Safety of Sea Transportation TransNav*, vol.8, no.2 2014.

Sinner, H. 1959. The Sinner Circle “TACT”. In *Sinner's Cleaning Philosophy*, Henkel.

Sørensen, O. & Andersen, J. Acc. 2016. Controlling hygienic tank cleaning using hygienic sensors to monitor tank cleaning. In *Alfa Laval Magazine-Thinking Ahead* :pp. 5-7.

http://www.tankjet.com..2016. Optimizing tank cleaning operations. In *Optimizing tank cleaning catalog no15, Introduction*:pp.1-8