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Biocides for Metal Working Fluids: India Outlook

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INTRODUCTION

Be it the automobile sector, the aerospace industry or any electrical equipment manufacturing site, the need and importance of metalworking fluids (MWF) are immense. They provide lubrication between the tool and the work piece, remove heat from surfaces, and flush away debris from the surface. But as important as they are, their formulation is also as critical and complex. MWF are generally divided into two categories, neat oils and water based MWFs. Water based MWFs are again divided into soluble oils, semi-synthetics and synthetics. The semi-synthetic fluids give much better efficacy and stability as compared to other fluids and so the demand and cost of these fluids is higher compared to other fluids.

The formulation of these fluids is very critical especially in Indian conditions because the MWFs are exposed to hostile working conditions yet they are expected to work effectively for long periods of time and give long sump lives and extended stability. Considering these aspects, formulating a robust MWF concentrate becomes a very important but highly challenging task in an Indian scenario. First of all, apart from making the emulsion of oil and water, many other additives are included in the formulation, e.g. amines, esters, biocides, corrosion inhibitors, emulsifiers, anti-foaming agents etc. Providing a stable and compatible formulation of these substances represents a challenge. The concentrate formulation makes just 3%-5% of the final diluted MWF emulsion that goes into actual use. This is because water based MWFs generally are diluted by up to 20-30 times before they are used in the machining area. The water quality, which is used for dilution, also plays an important role due to its variability. Also, MWFs are not disposed of just after one time use but are kept in sumps and are recycled multiple times until they start smelling or show major changes in their physical characteristics such as low pH, colour change, or slime formation. Also, MWFs are recycled for longer periods and come into repeated contact with workers, who generally display low hygiene awareness and therefore unknowingly contribute to fouling of the MWF.

For a metalworking fluid manufacturer, factors playing a role at customer's site are difficult to control. In order to make the fluid robust and qualitatively superior, a possible area of focus is to develop some tolerance in the concentrate formulation towards mishandling or the hygienically compromised working conditions prevalent in India.

The major hindrance for longer sump life generally comes from bacterial and fungal contamination of the fluid. In this scenario, the biocides as additives used in the formulation of MWFs play a very important role.

INDUSTRY SCENARIO OF INDIA FOR MWFs

Nearly all the MWF manufacturers use some form of biocides in their concentrates, but their performance varies. It would be wrong to deny the fact that most of them face microbial issues more often than expected. Earlier in India, mostly soluble oil based MWFs were used because they were cheaper, but they were expected to have lower sump lives. However, since the early 2000s, with the expansion of global MWF manufacturers in India, the use and demand for semi-synthetic MWFs have increased, and with that also the sump life expectation. Fig 1 shows a consumption based market segmentation of MWFs':

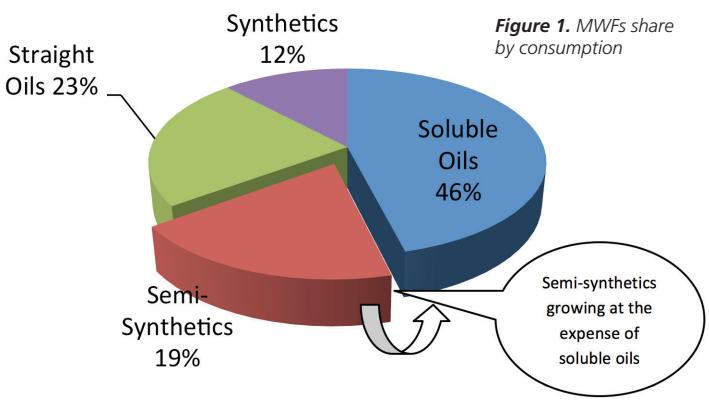

***Figure 1.** MWFs share by consumption*

This shift led to the increased importance for biocides resulting in willingness of manufactures to spend more on good quality biocides to increase their product performance. Biocides generally constitute 2-3% of the MWF concentrate formulation. Apart from this, some biocides like isothiozolinones are also added to the sumps directly. This dosing mechanism is called tankside additions. The tankside additions are generally performed when there is any untimely microbial issue (pH drop, foul smell, etc) in the running machine. The manufacturer generally provides these tankside biocides for free as part of their technical support to their customers. There are few limitations with tankside additions:

1. It constitutes additional cost.
2. It is not a permanent solution to the problem
3. Sometimes customers are reluctant to add biocides tankside because of safety concerns.

In these circumstances, there is a need for robust biocide in the concentrate MWFs formulation itself to drastically reduce the use of tankside biocides and save money for manufacturers.

Microbial issues in the coolant sump are universal and not only the small and local manufacturers are facing this problem, but even multinational companies are struggling to provide prolonged life to their semi-synthetic MWFs. A big limitation with multinational companies is that their formulations are decided globally but microbial problems are very much locally dependent (geography, climate, culture, plant design, plan operation etc.). In such a scenario, even though their product faces local microbial challenges, it becomes difficult for them to modify their formulation independently. On the contrary, local and small MWF manufacturers are independent and take decisions that satisfy their customer's need within their cost limits to stay and maintain their brand name in the market.

Based on complexities of chemistries, physics, formulation and microbiology disciplines involved in MWF design, focused microbiological knowledge is rather scarce. Despite the use of biocides (and unfortunately due to inappropriate biocide application), problems are faced very frequently. Although, these problems are considered seriously, unfortunately often temporary solutions are devised to these problems, which later sometimes lead to catastrophic results.

The above mentioned limitations in knowledge and focus results in the continuing use of traditional biocides which are cheap, well established but provide very limited protection against specific bacterial problems. This results in a strong focus on cost comparison with limited emphasis on thorough understanding, quality and innovation.

Based on above described scenario, it is obvious that the microbial control challenges in the use of MWFs is immense and needs to be addressed. The elaboration on biofilm, illustration of biocidal actives and their features, and examples provided in case studies shall contribute to advancing understanding of microbial control in MWF applications.

MICROBIAL CONTROL CHALLENGES:

Biofilms: A new concept in sump management

In metalworking fluids, one of the main issues is biofilm development'. The issue is hardly heard of, and remains largely unaddressed. Biofilms are cluster of different bacterial species which stick to each other on a surface under a complex matrix of extracellular polymeric substances (EPS). The EPS matrix consists of polysaccharides, proteins, DNA and RNA secreted by the microbial cells itself. In MWF operations, the typical surface on which biofilms form are usually the sump walls, the pipe interiors and machine surfaces (Fig 2). The biofilms generally can go undetected when located in places where the human reach is difficult and so are difficult to remove. The biofilm EPS matrix can protect microbes and make it more difficult for tankside biocide treatments to be effective. EPS matrix of a biofilm will limit the penetration of oxygen into them. In low oxygen environments, sulphate reducing bacteria (SRB) and iron-reducing bacteria (IRB) can proliferate. SRBs produce H_2S (hydrogen sulphide) gas which smells similar to rotten eggs and will reacts with and corrode metal surfaces of the machine. The SRBs and IRBs present inside the biofilms results in the formation of iron sulphide (FeS) which is black in colour and is a by-product of microbial corrosion. This causes discolouration in the emulsion (Fig 3). The H_2S gas produced in the sump can deactivate isothiazolinones which are commonly used as tankside biocide additions resulting in the need for higher and more frequent dosing.

Efficacy and limitation of commonly used biocides in India:

Triazine (1,3,5-tris(2-hydroxyethyl)-s-triazine): Some of the best selling products in the Indian MWF market today is the class of triazine based biocides either as stand-alone or in combination with a fungicide. Triazine can be considered as one of the commonly used biocides for MWF concentrate applications because it has high pH stability, a lower cost option, and it is well known and widely available. However, there are few limitations with triazine chemistry. First, triazine based biocides display an efficacy gap against sulphate reducing bacteria (SRB) and so, the fear of bio-film formation and fouling of fluids is always there. It is true that triazine acts well against many other bacterial species and provides decent protection. However, in order to make the fluid full-proof against microbial contamination, especially Indian conditions where the fluid management practices are below standards, triazine chemistries have not yielded adequate results. Triazine also display an efficacy gap against Mycobacterium species. These bacterial species are slow growing and are difficult to quantify thus are often not appropriately identified. However, they have been implicated in causing an occupational illness called hypersensitivity pneumonitis.

Another crucial problem associated with triazine is that its mechanism of action is by immediate excess release of formaldehyde. Although it results in faster killing of bacteria, formaldehyde, being very volatile, evaporates rapidly, which

strongly reduces the duration of the preservation period of the fluids.

BIT (1,2-benzisothiazolin-2-one): BIT based biocides are also used in many MWFs. They are considered because of better stability at high pH and temperature and ease of formulation. They constitutes a sustainable formaldehyde-free option. There are some challenges with BIT chemistry too. They are less effective against Pseudomonas species which are common in the Indian environment. Also, BIT are reported to display an efficacy gap against Mycobacterium species. BIT gets rapidly deactivated if the contaminated sump has SRB actively growing in it.

Oxazolidine and OIT
The combination of oxazolidines (4,4 dimethyl oxazolidine, Ethyldihydro-1H,3H,5H-oxazolo[3,4-c]oxazole) along with OIT (2-n-octyl-4-isothiazolin-2-one) has been found to be performing well in India and is increasing in popularity. Oxazolidines are highly active against bacteria. it is effective against SRBs and Pseudomonas species and having some efficacy against Mycobacterium species as well. Oxazolidines also have pH buffering capacity and are high pH and temperature stable. Oxazolidines also remain unaffected in the presence of low levels of sulphides. OIT is a very effective antifungal molecule. It is stable in alkaline MWF systems. When used in combination, OIT and oxazolidine, it provides a strongly extended sump life in typical Indian conditions.

Morpholines:
Morpholines (4-(2-nitrobutyl)morpholine, 4,4′-(2-ethyl-2-nitrotrimethylene)dimorpholine) are commonly used in MWF concentrates because they are very stable in MWF formulations. Morpholine constitutes a formaldehyde free option for the protection against wide range of bacteria, fungi and against Mycobacterium species under typical MWF use conditions. There are few problems associated with morpholine based biocides which includes odour, lachrymation, and possible skin sensitization. It may also react with nitrites of secondary amines to form nitrosamines which are known carcinogens.

Problems With Tankside Addition:
In India, one of the common practices that have developed over the years is the tankside addition of biocides for resolving untimely microbial spoilage issues. Although this practice provides immediate help, it has its own side effects. The biocides used in tankside such as isothiazolinones quickly inhibit the growth of microbes and then kill. During its action it also gets consumed. These biocides solve the problem for a short period of time, but as time passes, the dead bacteria become a nutrient source for other bacteria and fungi. Also, dead bacteria can contribute to increased biofilms mass. As non-oxidizing biocides don't help reduce biofilms EPS, biofilms can become even stronger. So, controlling the bacteria in the early stage of sump management is more important than a brute force method. It is very critical to do tankside addition as a supplement to concentrate-based microbial control on need basis.

CASE STUDIES:
A very famous multinational MWF manufacturer operating in India was facing the problem of a foul smell, microbial corrosion and instability in their semi-synthetic MWF fluids despite using Triazine based biocides at 3-4% concentration in the MWF concentrate. A recent microbial audit in one of their customer's plants showed the presence of biofilms and SRBs in their fluids (Fig 4 and 5). The samples also contained fungi and majority of microbes found in different samples were Gram negative bacteria capable of producing slime as well as some Gram positive bacteria.

Figure 2. *General biofilm in pipeline*

Figure 3. *SRB growth, blackening of SRB media due to H_2S formation*

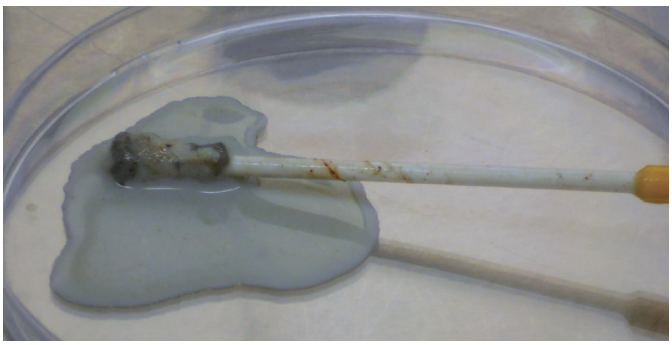

Figure 4. *Swab showing rusting and presence of biofilm in the MWF emulsion*

Figure 5. *Swab showing rusting and presence of biofilm in the sump surface*

A similar case was seen in an audit of another mid scale Indian MWF manufacturer where the issues of foul smell and fungal growth were faced in their semi-synthetic MWF at some of the machines running at their customers end in North India. They tried to rectify it using a high dosage of bis-morpholine, triazine and IPBC (3-iodopropynylbutylcarbamate) combinations doses. Although this provided temporary relief, after 5-6 months, they faced the same issue again. They asked for microbiological audit of the site. The fluid samples were taken and analysed. It was observed that the majority of the microbes found in different samples were Gram negative bacteria related to the Enterobacteriaceae family and few Gram positive bacteria. Most of the samples had 2-3 different morphotypes. Hard water as well as RO water had a contamination level of $>10^5$ CFU/ml per ml of sample. Also, after incubation, colonies of SRBs were observed.

They used tankside addition of DBNPA (2,2-dibromo-3-nitrilopropionamide) and got relief from foul smell almost immediately. In aqueous alkaline environments, DBNPA decomposes quickly and is deactivated by sulphide, so it will degrade rapidly in environments containing SRB. Ultimately, only carbon dioxide, ammonia, and bromide ion remain as end products. Similarly, they were using IPBC chemistry as fungicide in their concentrate formulation but when it was tested for the presence of IPBC using High Performance Liquid Chromatography (HPLC), it was observed that the IPBC concentration was lower than expected. The OIT chemistry was found to be quite stable in their MWF formulation compared to the IPBC.

CONCLUSION:

There are a lot of factors responsible for microbial contamination of a MWF emulsion in the sump. Microbes demand a more innovative and constantly evolving approach to prevent them from spoiling the MWF industry. Also, different geographies need different strategies to mitigate microbial problems since different geographies have different types of microbial flora. After analysing the market, problems, comparing and testing different biocide chemistries, it was observed is that there is a strong need and demand for a biocide that when added in concentrates will be robust enough to suppress the need for frequent tankside addition and which can withstand mishandling in the MWF system. Also, there is a need for a good quality fungicide that will be stable for a long time in the concentrate and can act in combination with bactericide.

Based on this knowledge, trials and testing were done to see which biocidal chemistry can fulfil these requirements. Working with available chemistries, it was found that in Indian conditions, to achieve microbial contamination and long term stability, a combination biocide should be used. Oxazolidines in combination with OIT perform better in the Indian scenario. This combination when used in new sumps or properly cleaned sumps works with maximum effectiveness and minimises biofilms formation. Biofilms can be removed from sumps during cleaning by adding suitable biofilm removal products in their washing water.

The proper cleaning of sumps is crucial because as these combinations controls the bacterial growth and not just kill it with brute force, any prior presence of bacterial contamination in the sumps reduces its effectiveness.

Finally, as wise men say "Prevention is better than cure", no matter how robust the metalworking fluid is, it is always better to maintain good plant hygiene and be aware of basic microbial knowledge. After all, a little knowledge is not always dangerous!

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