A Primer on Detergents in Lubricating Oils

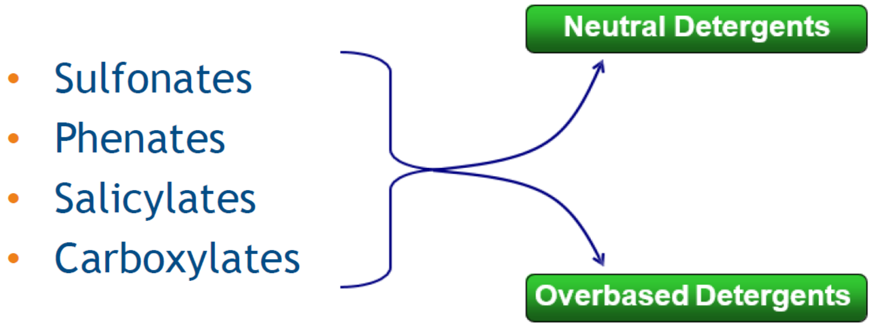
Introduction

Detergents provide a means for dissolving otherwise insoluble metallic salts, like calcium or magnesium carbonate, in lubricating oil. Therefore, they function like an alkaline source for the engine, neutralizing corrosive combustion acids that would dissolve key metal parts and eventually lead to engine failure.

Detergents also prevent the build-up of harmful deposits on the rings and in the grooves of the engine pistons. These deposits on the rings can cause them to stick, loss of compression (power) and increase blow-by, which in return reduces the piston cooling effect further carbonizing unburned fuel and lubes, increasing cylinder liner heat effected surfaces, which ultimately reduces the cylinder oil film thickness and starts the downward spiral of liner conditions and catastrophic wear, poor emissions quality, fuel economy, and eventual engine failure.

Types of Detergent

The detergent chemistry primarily involves sulfonates, phenates, salicylates and carboxylates. Depending on applications, they can further be classified as neutral or overbased detergents.



Neutral Detergents – Preparation

- Neutral detergents can be formed by chemical reaction between the organic acids and metal hydroxide.

$$\underset{\text{Metal Base}}{M^{n\oplus}(OH)_n^{\ominus}} + \underset{\text{Organic acid}}{ROH} \xrightarrow{\text{Heat}} \underset{\text{Oil soluble metal salt}}{(RO)_n^{\ominus}M^{n\oplus}} + \underset{\text{Water}}{H_2O}$$

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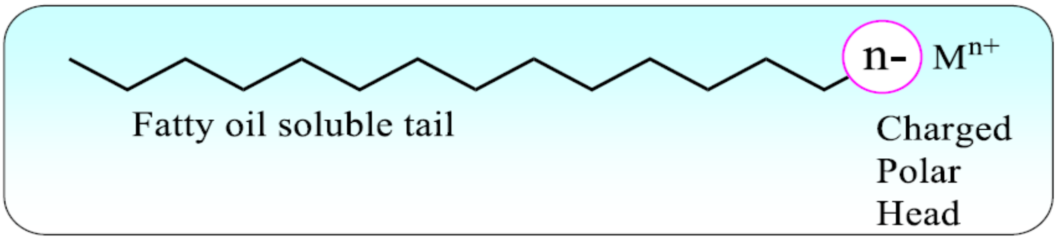
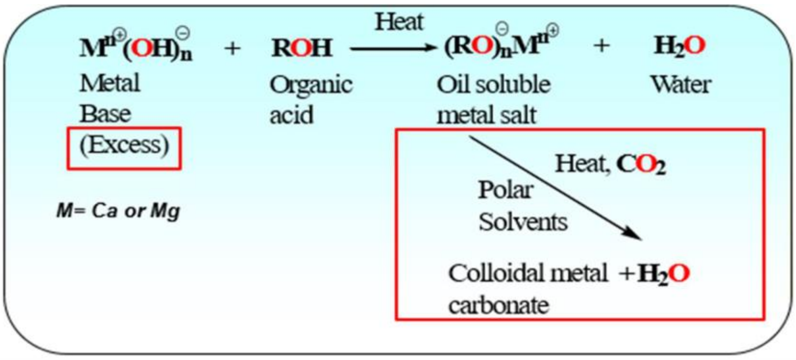
- **R** contains oil soluble carbon tail and polar head; it can be represented schematically as below.



- They are described as “neutral” because only enough base is used to neutralize the acid, no more.

Overbased Detergents – Preparation

- First stage is the same as the above (for neutral detergents).



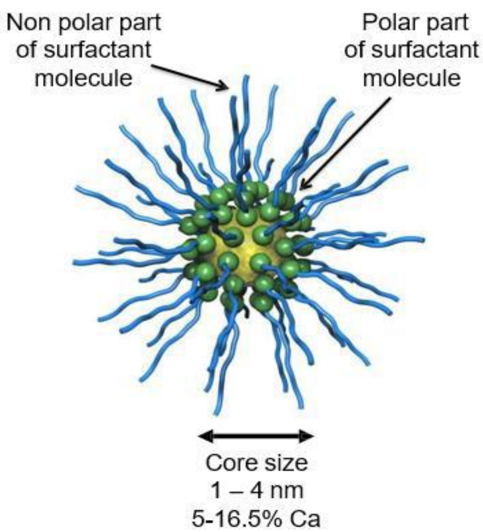
- Excess base is formed from further chemical reactions with carbon dioxide to form metal carbonates, in an oil soluble form.
- Termed overbased because far more base is used than that required to neutralize the acidic surfactants.

Detergent Structure

Chemically, detergent comprises three parts:

1) a long non-polar hydrocarbon tail which is responsible for their being soluble in lubricating oil;
2) a polar head, which serves as a linking group to the third part; and
3) the calcium carbonate base which is sequestered in the center of the molecule

The amount of carbonate base present in the molecule is tailored to the specific application for which the detergent is intended.



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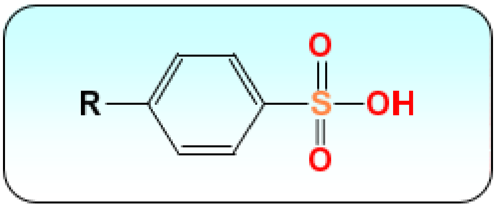
The colloidal base and surfactant (which is the soap molecule) work in synergy.

Advantages and disadvantages of main commercial types of detergents

Sulfonates

Advantages

- Excellent detergency
- Can be overbased to give very high base contents (e.g. up to 50% $CaCO_3$)
- Relatively cost effective



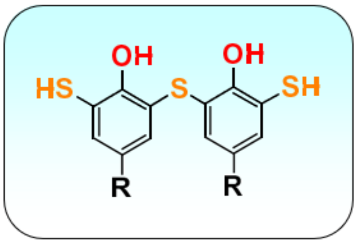
Disadvantages

- No antioxidancy

Phenates

Advantages

- Antioxidant performance
- Good detergency



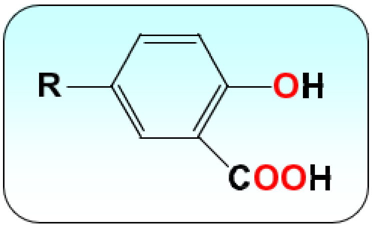
Disadvantages

- Cannot get such high base levels as sulfonates
- But can use a carboxylic acid co-surfactants
- Relatively expensive

Salicylates

Advantages

- Good antioxidant
- Good detergency
- Sulphur free



Disadvantages

- Cannot get such high base levels as sulfonates
- Less cost effective

For more details, please refer to the Typical Overbased Detergent Property Comparison **(Table 1)** and Range of typical detergent lubricant additives **(Table 2)**

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Functions of a Detergent

Detergents offer a number of performance attributes, including detergency, antioxidancy, TBN delivery and friction modification. Choices of detergent type and level are highly dependent on specific applications, and combinations are needed to optimize performance and cost.

For marine lubricants, overbased sulfonates and overbased phenates are frequently used together to utilize the high alkaline reserve and high-temperature detergency of sulfonates and the antioxidant property of phenates against adverse effects from the use of high sulfur and asphaltene-containing fuel (although with the IMO 2020, the use of the high-sulfur fuels may be reduced). However, overbased detergents' colloidally dispersed structure may be disrupted by interaction with certain polar species, such as water, additives, or other types of detergents, leading to gel formation and precipitation.

As marine lubricants are frequently exposed to seawater, the hydrolytical stability of the detergents and their compatibility are crucial. The hydrolytical stability of detergents is strongly influenced by the structure of the alkyl side chain of the soap molecules, such as branching. Longer side chains with certain degrees of branching can effectively increase the stability of its colloidally dispersed structure, thus improving the hydrolytical stability and detergency. Furthermore, metallurgy variances in engine designs, such as aluminium versus articulated steel diesel pistons, complicate proper detergent selection.

Piston and ring cleanliness are influenced by detergents. The photograph depicts a piston with excessive carbonaceous deposits which typically is caused by operations without an effective detergent. To prevent such deposit build up, lubricating oils are typically formulated with sulfonates that are high in soap content but relatively low in metallic base.

However, because there is still a need to neutralize harmful combustion acids, the solution is to use several different types of sulfonates: those that are rich in soap to protect against engine deposits, and those that are rich in metallic base to protect against corrosive wear from combustion acids.

Deposit Build-up Problems in the Industry

After vessels started to switch to low-sulphur fuels in order to comply with the IMO 2020 emissions regulations, there were some cases of excessive deposit build-up on the piston rings, leading in the more severe cases, even to ring breakage.

In many such cases, the initial investigations revealed that the reserve base were still normal / adequate in the used oil. While poor fuel quality could possibly one of the causes, many of these cases are still pending further investigations to understand the root cause or causes.

It is noted that even with superior detergency qualities, lubricants per se, cannot solve these if there are inherent problems pertaining to fuels quality/stability/compatibility. Yet, chemistry and technology-wise, effective selection of detergent components in lubricants (including ash-less detergents), can, at least, be expected to help minimise the severity of such problems.

Table 1. Typical Overbased Detergent Property Comparison

Properties	General Ranking
Polarity of soap molecule polar group	A > B > C
Detergency (high to low)	A > B > C
Dispersancy (high to low)	A > B > C
Antioxidation (good to poor)	C > B >A
Corrosion inhibition (good to poor)	A > B > C
Ease of overbasing (easy to difficult)	A > B > C
Acid neutralization rate (fast to low)	C > B >A
Hydrolytical stability (high to low)	A > B > C

Sulfonate: A, Salicylate: B, Phenate: C

Table 2. Range of typical detergent lubricant additives

Parameter	Range		
	Sulfonates	Phenates	Salicylates
TBN	0–500	50–400	50–400
Metal ratio	1–30	0.8–10	1–10
Soap content, %	10–45	30–50	10–45
Metal cation	Ca, Mg, Na, Ba	Ca, Ba, Mg	Ca, Mg
Molecular weight sulfonic acid	375–700	—	—
Alkylphenol	—	160–600	—
Carboxylic acid	—	—	250–1000
Sulfur, %	0.5–4.0	0–4	—

If you have any enquiries on technical issues, please consult our Product and Formulation Manager or our global technical team at technical.engineer@gulf-marine.com

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