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PAT (Process Analytical Technologies) for improving the process chemistry understanding of anti-wear and anti-oxidation additives

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1. Introduction

In this paper we will illustrate and discuss the results of an exploratory study focused on the acquisition of a better understanding of the process chemistry of "overbased detergents" (**OD**). These are anti-wear and anti-oxidation additives for motor lubricating oils. They are constituted of colloidal nanoparticles of amorphous calcium carbonate that are stabilized by surfactants based on alkyl salicylate calcium salts. The production of OD requires two major chemical steps: a) neutralization of alkyl salicylic acid (dope acid, **DA**) by calcium hydroxide (lime); b) transformation of lime in calcium carbonate (in the amorphous form) by reaction with carbon dioxide (carbonation phase).

The reaction pathway of the dope acid neutralization is illustrated in Fig. 1a.

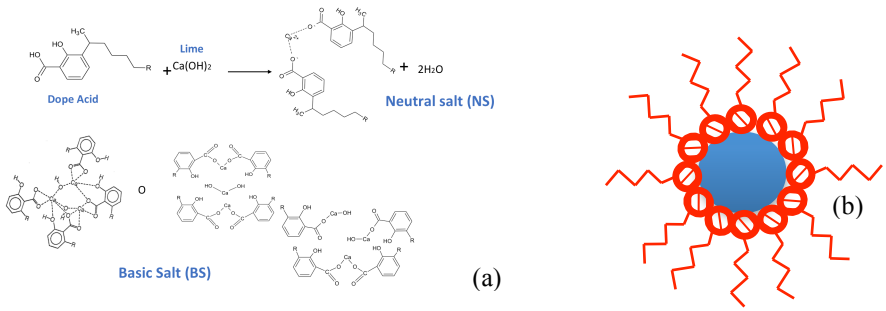

Figure 1. (a) Reaction pathway of the neutralization of DA; (b) micelle with the core of a water saturated solutions of $Ca(OH)_2$.

During the neutralization step, micelles, with a polar core of a water saturated solution of $Ca(OH)_2$, are formed; the micelles are stabilized by an external layer of basic and neutral salts as schematized in Fig. 1b. The calcium carbonate is formed during the carbonation step by feeding CO_2 and methanol, that acts as a promoter of the carbonation reaction, as discussed below. During the carbonation phase part of the BS is transformed into NS and calcium carbonate accordingly to Fig. 2.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad BS + CO_2 \rightarrow CaCO_3 + H_2O + NS$$

Figure 2. The main stoichiometric reactions leading to $CaCO_3$ formation.

An experimental campaign was carried out on a batch pilot plant monitored with PAT technologies based on MIR-FTIR and NIR spectroscopic characterizations. The spectra were analysed by using chemometric tools: Principal Components Analysis (PCA) and Multivariate Curve Resolution (MCR). In particular, the MCR

tool applied to the MIR-FTIR spectra proved to be very effective in order to acquire a better knowledge both on the chemical reaction mechanism and on the reaction kinetics.

2. Methods

The experimental campaign was carried by using a batch pilot plant in operation at the manufacturing plant laboratories Infineum Berre l'Etang (Infineum France SNC). The process variables investigated were: temperature, CO_2 flowrate, polarity of the liquid reaction environment (relative % of xylene ad methanol), and supply order of the reactants. A couple of experiments were also carried out in order to investigate the effect of operating in excess of CO_2 (overcarbonation). The pilot plant was equipped with MIR-FTIR and NIR probes that allowed to acquire in-line MIR and NIR spectra in real time. The quality attributes, like DLS, calcium%, basic index, viscosity and sediment % were measured off-line.

3. Results and discussion

In this short abstract, it is enough to mention an important result obtained through the MCR analysis of the MIR-FTIR spectra. We identified two intermediate species, bis-methyl calcium carbonate and calcium methoxide, that are consistent with the reaction pathway schematized in Fig. 3.

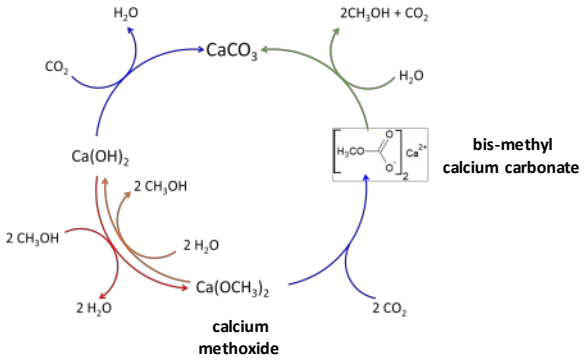

Figure 3. The proposed reaction mechanism for the formation of calcium carbonate.

Figure 3 shows that two possible paths can co-exist. The first one accounts for the direct carbonation of calcium dioxide, the second one foresees the formation of calcium methoxide that is transformed in bis-methyl calcium carbonate. This intermediate can react quickly with water leading to the formation of calcium carbonate, methanol and carbon dioxide. In the second path, the methanol plays the role of reaction promoter. The proposed reaction mechanism of Fig. 3 can also explain the observed time dependent changes in concentrations of methanol, calcium carbonate and water as it will be discussed in the oral presentation.

4. Conclusions

The integration of PAT and of chemometric tools have proved to be very useful and effective to acquire a better understanding of the process chemistry of overbased detergents. In particular, the role of methanol has been cleared out.

The results have also demonstrated the feasibility to develop intelligent process monitoring system to early identify potential condition for quality out-of-spec.