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Development of an alternative analytical methodology to monitor industrial degreasing baths by dynamic light scattering

Mathieu Menta [a, b, *], Jérôme Frayret [a], Bruno Grassl [a], Christine Gleyzes [b], Alain Castetbon [a], Martine Potin-Gautier [a]

[a] Université de Pau et des pays de l'Adour/CNRS, Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE), UMR 5254, IPREM, Hélioparc, 2 Avenue du Président Angot, 64053 Pau Cedex 9, France

[b] Ultra Traces Analyses Aquitaine (UT2A), 2 Avenue du Président Angot-Hélioparc, 64053 Pau Cedex 9, France

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ABSTRACT

In the metal finishing or aeronautical industries, efficient degreasing of metallic alloy surfaces is an essential step. This step was first performed with halogenated solvents. Legislation has involved since 1999 their replacement with green cleaners due to the hazardous effects of solvents on human health and on environment. Aqueous cleaners, commonly called detergents, are widely used as an alternative. The monitoring of such degreasing baths is usually realized by alkaline titration or conductimetry. However these techniques do not provide significant information on the state of degreasing baths. In this study a new method is proposed using dynamic light scattering (DLS). This technique can evaluate the size of the micelles formed in the degreasing bath. The free and "full of oil" micelles can be identified and quantified due to their different sizes. The contamination rate and the loss of detergent all along the use of the bath can be determined with these new indicators. After a validation step with prepared degreasing solutions, this method has allowed monitoring precisely industrial degreasing baths, reducing the frequency of the baths replacement, the volume of aqueous effluents and optimizing baths management.

1. Introduction

In the aeronautical industry, lubricants and greases are used during machining processes as cooling or corrosion protective agents (Cambiella et al., 2007; Trullols et al., 2006; Zhong et al., 2004). To make the surface treatments adhesive, these contaminants have to be eliminated from the surface of the piece by sequential and efficient cleaning processes. Petroleum and coal derivatives were the first employed for cleaning the surface (Wery, 1998). However, these solvents are flammable and manufacturers replaced them with organic chlorinated solvents, more precisely with trichloroethylene (Lavoué et al., 2003; Marshall, 2011; US Environmental Protection Agency, 1994). Many authors have evaluated the hazardous impacts of trichloroethylene (TCE) on human health and the environment (Carrieri et al., 2007; Fahrig et al., 1995; Kanako et al., 2000; Seo et al., 2008). Today, TCE is classified as carcinogenic and mutagenic (Verschoor and Reijnders, 2001). For these reasons, the European Community Directive no 1999/13/CE has mandated its replacement. The manufacturers associated with this study, Turbomeca and Messier-Dowty (SAFRAN Group, respectively from Bordes and Bidos, France), Lépine Industries (Orthez, France) and Aeroprotec (Pau, France) use aqueous cleaners (AC) environmentally more acceptable (Kikuchi et al., 2011) to replace TCE. An AC formulation is elaborated by taking into account several parameters such as the nature of the oil or the grease, the cleaning system, the composition of the metallic alloy and the subsequent process. A commercial AC formulation is usually constituted of surfactants and other minor compounds, such as alkaline compounds (to maintain the pH between 8 and 13 according to the treated alloy), corrosion inhibitors, water conditioners or chelators, charges, thickeners, salts and disinfectants (Bird, 1995; Mc Laughlin and Zisman, 2005). The degreasing efficiency mainly depends on the surfactant's properties. Surfactants are amphiphilic molecules characterized by a hydrophilic polar

* Corresponding author. Université de Pau et des pays de l'Adour/CNRS, Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE), UMR 5254, IPREM, Hélioparc, 2 Avenue du Président Angot, 64053 Pau Cedex 9, France. Tel.: +33 559 407 668; fax: +33 559 407 674.

E-mail address: jerome.frayret@univ-pau.fr (M. Menta).

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head group and a hydrophobic nonpolar tail. When the surfactant concentration is above the critical micelle concentration (CMC), surfactant molecules are rearranged in spherical aggregates called micelles (Lavoué et al., 2003; Wery, 1998). By this process, these components remove oil from the surface of an alloy and trap it in aggregates commonly named "full oil micelles". Surfactants reduce the surface tension of water, enhancing its penetration and stabilize the grease in the degreasing bath, creating an emulsion (Larpent, 1995; Lucena et al., 2005). Cationic surfactants are not employed in AC because the acidic pH of this kind of products can lead to the corrosion of metallic alloys. Anionic surfactants have good degreasing power and a good stability at high temperature and alkaline pH (Larpent, 1995). However, they present a high foaming power. To limit this effect, anionic surfactants are often associated with non-ionic ones (Lavoué et al., 2003; Wery, 1998).

The degreasing process for metallic surfaces can be applied either by immersion or sprinkling, according to the size and the geometry of pieces to treat. In these processes, the mechanical effect plays an important role in the detergent efficiency.

Monitoring the surfactant and oil contents in the degreasing bath is essential to optimize industrial processes. To perform this task several analytical approaches are usually employed. First, an Environmental Protection Agency (EPA) gravimetric method can be used. This approach is time consuming and negatively affects the productivity (Aguilera-Herrador et al., 2007). The second approach consists in the use of analytical tools recommended by AC providers: alkaline titration in aqueous media and conductivity measurements. However, Menta et al. have recently demonstrated the unsuitability of these techniques for a daily monitoring of the degreasing baths (Menta et al., 2012). Under industrial conditions, degreasing baths are complex solutions containing a mix of several oils and surfactants which are simultaneously measured by alkaline titration or conductivity measurement (Menta et al., 2012). These techniques give only the total concentration of both oils and surfactants but cannot distinguish the two species. The combination of alkaline titration and electrical conductivity measurements, using a six steps methodology, can nonetheless be used as a semi-quantitative method to estimate the oil and detergent contents (Menta et al., 2012). Other possibilities such as nuclear magnetic resonance (NMR) and hyphenation of chromatographic or related techniques (high-performance liquid chromatography, HPLC; capillary electrophoresis, CE) with mass spectrometry (MS) or UV detector have yet been used for surfactant monitoring (Aguilera-Herrador et al., 2007). However these techniques are expensive and time consuming (Garnier, 1995; Cutler and Kissa, 1987). For these reasons, these analytical approaches are not use in industry for routine analysis and check in real time the ageing of degreasing baths.

Due to recent legal restrictions about waste discharge, the reduction of aqueous effluents and volumes of waters and detergent used are economic and environmental objectives which industrial partners aim to respect. To reach these goals it is necessary for them to have tools and adapted methodologies. For these reasons, huge efforts are led on the implementation of cheap, fast and easy to use alternative analytical approaches.

As explained in previous paragraphs, the respective amounts of free and full oil micelles of surfactants are responsible for the efficiency of the degreasing step. However, no analytical tool was developed to analyze the evolution of their contents all along of the use of industrial baths. The characterization of such oil in water emulsions could be achieve using dynamic light scattering (DLS) detector which is a common tool to study the properties (size, size distribution, polydispersity) of this kind of sample. DLS manufacturers are currently realizing huge efforts to propose easy to use devices with decreasing prices to make this technique economically attractive for this kind of application. This work has been first focused on the evaluation of the suitability of DLS to estimate the bath ageing of degreasing baths. The validation of this methodology was realized with laboratory made solutions and then with industrial baths. The advantages of DLS for the monitoring of an industrial degreasing process and its optimization were then evaluated.

2. Material and methods

2.1. Apparatus

Surface tension was measured with a Tracker drop tensiometer from IT Concept (Longessaigne, France) using the rising drop method. The interfacial tension between the solution and air was determined by digital processing of the shape of a drop of the first fluid (air) formed within a quartz cell containing the second fluid (surfactant or detergent solution). The drop was illuminated with a CCD camera driven by a microcomputer using Windrop 1.1 software from IT Concept.

The size and the quantification of the free and full oil micelles were carried out by dynamic light scattering with a DLS Vasco-2 (Cordouan Technology, Pessac, France) equipped with the Rean® software using the Padé-Laplace inversion algorithm.

2.2. Reagents

Polystyrene standards (PS: 20, 50, 100 and 200 nm radius) from Duke Scientific Corporation (Fremont, USA) have been used to carry out hydrodynamic radius calibration and analytical procedure validation.

Two anionic and two non-ionic surfactants have been used to create well-contained degreasing baths. The surfactants, supplied by Sigma Aldrich, have been chosen because they possess various natural or chemical functions of the polar head groups and are constituent of common AC. The anionic surfactants are sodium dodecyl sulphate (SDS) and sodium dodecyl benzene sulphonate (SDBS), and non-ionic ones are Tween 80 and Tween 20. One water-soluble oil, Bacticool 2 (Bacticool, Condat) employed by industrials partners has been tested.

Mixtures of surfactant and oil were studied to evaluate the influence of surfactant and/or oil contents on the bath ageing and to validate the DLS methodology at the lab scale. Industrial samples from various processes were collected, filtered at 0.45 μm prior to the analysis to evaluate the suitability of the new methodology with real degreasing baths.

2.3. Procedures

Tensiometry was employed to determine the CMC of each surfactant. The surface tension of an air rising drop immerged in various surfactant solutions with increasing concentrations was determined at 25 °C. The CMC was estimated at the inflection point of the surface tension as a function of the surfactant concentration. Each solution was analysed three times to improve accuracy.

The method for ageing and contamination content determination consists in the analysis by DLS of less than 50 μl of sample. The measure is based on the analysis at 135° of scattered light fluctuations caused by the Brownian motion of particles in solution as a function of time.

The normalized intensity autocorrelation function, $g^{(2)}(\tau)$, derived from the scattered light intensity fluctuations is related to the electric field correlation function $g^{(1)}(\tau)$ by the Siegert relation (Chu, 1974)