



Insight into the role of amines in Metal Working Fluids



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ABSTRACT

The influence of primary/tertiary amines in Oil-in-Water emulsions (as Metal Working Fluids (MWFs) towards brass) is evaluated in both pure water and 5% O/W emulsion. Physical properties, wetting, lubricating and corrosion behaviors are finely investigated. Experimental results show that the number of carbon atoms in amines plays a pivotal role in reducing the brass corrosion. Among the adopted amines, the cyclohexyldiethanolamine (CHDEA) seems to be the optimal one in both media: (i) it adsorbs easily onto the brass limiting corrosion and stain; (ii) it leads to stable emulsions; (iii) it does not affect the emulsion lubricant and wetting performances.

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1. Introduction

Oil-in-Water (O/W) emulsions are widely exploited in several fields such as cosmetic [1], pharma [2] and machinery industry [3–7]. In particular, when they are used as cutting or Metal Working Fluids (MWFs), the annual global consumption by the year 2007 was 640 million gallons and the estimated utilization in the US was about 100 million gallons [8]. However, the correct estimates for the utilization and hence the costs of cutting fluids cannot be presented on account of the diversity and pervasive nature of field processes. In this field, MWFs are used as lubricants, coolants, chip evacuators and corrosion inhibitors in metal cutting and forming operations, such as rolling, drilling, cutting or grinding [3,6,7,9]. In such operations a combination of lubricating properties, provided by the oil, and cooling properties, provided by the aqueous phase, are required. MWFs cost up to 15% of the entire machining process [3], so many attempts have been made to reduce their use limiting both the costs and the environmental concerns [6]. However, most of the machining operations still require the use of these fluids

where they improve the productivity, the quality of manufacturing, reduce cutting forces and vibrations and improve the tool life [3,6]. Thus, recently, lots of efforts have been made to formulate new eco-friendly products from renewable sources too [5,7].

MWFs should have the following characteristics to perform properly: good lubricating, anti-adhesion and wetting properties, good cooling action, high stability, low viscosity, good wetting properties, corrosion inhibition, non-toxic and non-flammable, economical in use and disposal [3]. Many additives are added to the final formulation to ensure these properties and so commercial products have usually a very complex composition with many components: biocides, defoamers, corrosion inhibitors, preservatives, emulsifiers and so on [4]. As well known from the literature [2,4,5,10], emulsifiers play a key role in the stabilization of the emulsion, preventing or retarding droplets coalescence. Thicker films and so higher stabilities have been achieved by using mixtures of anionic and non-ionic surfactants where both steric and electrostatic repulsion are exploited to avoid coalescence phenomena. Cationic tensides are not used in MWFs as they could be adsorbed onto negatively charged metal surfaces at the operational pH of these fluids, around 8.5/9 [7].

Moreover, the pH of MWFs is an important parameter for several reasons: particularly, the emulsion stability, the corrosion behavior and the bacterial growth are the most relevant. Anionic tensides are in the dissociated form only at pH values above their pK_a . Hence, high pH values provide negatives charges at the oil/water interface [4] and so increase the emulsion stability due to electrical repulsion

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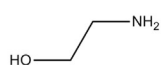
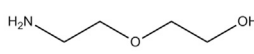
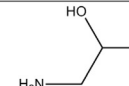
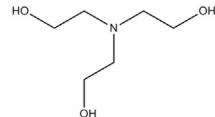
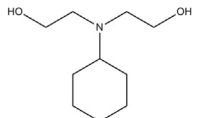
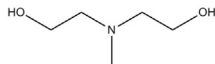
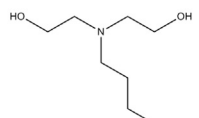
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Table 1
Brass composition.

	Weight percentage, %wt									
	Cu	Zn	As	Al	Fe	Mn	Ni	Pb	Sn	Others
Brass Alloy CW511L	62.5	36.5	0.1	0.1	0.1	–	0.3	0.2	0.1	0.2

Table 2
Chemical structure and pK_a values of the primary and tertiary amines tested in this work.

Sample		Chemical structure	pK_a
Primary amines	Monoethanolamine (MEA)		9.4
	Diglycolamine (DGA)		9.5
	1-amino-2-propanol (MIPA)		9.6
Tertiary amines	Triethanolamine (TEA)		7.7
	Cyclohexyl diethanolamine (CHDEA)		8.3
	Methyl diethanolamine (MDEA)		8.5
	Butyl diethanolamine (BDEA)		8.9

between oil droplets. Secondly, the variation of pH can strongly affect the corrosion of metals as widely evidenced in the Pourbaix diagrams [11]. For instance, in the case of iron in soft water, the metal is more corroded at pH values under 4, whereas the corrosion current drops for values higher than 10. For values between 4 and 10 the corrosion current is nearly constant [11]. Finally, bacterial and fungal growth rates are inhibited at high or low pH values [12]. Both NaOH [4] and aliphatic amines (such as triethanolamine (TEA)), can be adopted to adjust the pH value of a cutting fluid [7,13]. Generally, amines are preferred because the addition of ions to the emulsion increases the ionic strength of the aqueous phase leading to a higher coalescence tendency [2]. Furthermore, amines can also act as corrosion inhibitors in many environments, reducing the metals dissolution rate. Commonly, most of the effective and performing inhibitors are organic compounds having π bonds and heteroatoms like nitrogen, sulphur and oxygen in their structures [14]. The inhibition efficiency lies on their ability to get adsorbed on the metal surface [14–19]. Whereas lots of papers are focused on aliphatic amines as corrosion inhibitors of steel [14–16,20,21] and zinc [17], the situation is different for copper [22] and copper alloys, where heterocyclic compounds, such as di- [23], tri- [24–26] and tetrazole [27,28] derivatives, thiocarbamides [29] and benzylidene derivatives [30] are widely investigated.

The aim of the present work is to study the corrosiveness of both primary and tertiary aliphatic amines commonly used in MWFs

towards brass substrates. Firstly, the adopted amines were tested in water evaluating their role in limiting corrosion phenomena. Then, O/W cutting emulsions containing selected amines were prepared; emulsion stability and characterizations, lubricating performance and inhibition/corrosion properties were finely studied. To the authors' best knowledge no scientific results aimed at evaluating the corrosion features of different organic amines both in water and in the final emulsion on brass specimens are present in the recent literature.

2. Material and methods

2.1. Brass substrate

Brass samples (CW511L alloy) were supplied by BrawoBrass Working S.p.A. and their composition is reported in Table 1. Before being used, brass specimens were mechanically grinded with different grades of silicon carbide papers (800, 1200, 2400, 4000), rinsed with ethanol and thoroughly washed with double distilled water.

The sample morphology and elemental composition of brass specimens were determined by a Scanning Electron Microscopy (SEM) Zeiss LEO 1430 working at 30 keV, equipped with an Energy Dispersive X-ray (EDX) analysis system. Experiments were performed before and after a potentiodynamic polarization in 1% wt.

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