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Journal:	*Tribology Transactions*
Manuscript ID:	UTRB-0866.R2
Manuscript Type:	Manuscript for Publication Only
Date Submitted by the Author:	11-May-2012
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Keywords:	Metalworking Fluids - see Metalworking, etc. < Lubricants, Oil Condition Monitoring < Maintenance, Water, Water-Based < Lubricants

Extending the Useful Life of Metalworking Fluids in a Copper Wire Drawing Industry by Monitoring their Functional Properties

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ABSTRACT

Three metalworking fluids (MWFs) from a copper wire drawing industry were monitored for a two-year period by studying changes in their functional properties: two semi-synthetic oil-in-water (O/W) emulsions used in smoothing and wire drawing processes and one synthetic fluid used in the casting process. The parameters measured were: zeta potential, droplet size distribution, surface tension, contact angle, foaming power and optical characterization of the creaming stability. Experimental results showed that zeta potential, droplet size distribution and creaming stability are the key parameters to monitor MWF life span and to extend its lifecycle. Surface tension, contact angle and foaming power showed large variation with time, and did not reflect adequately the change of functional properties of the MWFs. Furthermore, the influence of several parameters on MWF properties with the purpose of reducing the foaming power was studied. Commercial concentrates and several types of water (decalcified, tap and distilled) were utilized to formulate the fluids and their properties were compared to those of the plant MWFs.

KEY WORDS

Metalworking fluid; Oil-in-Water Emulsion; Copper Wire Drawing; Monitoring; Zeta Potential; Stability; Droplet Size Distribution; Foaming Power

INTRODUCTION

Oil-in-water (O/W) emulsions are used as metalworking fluids (MWFs) in industrial processes such as cutting, rolling, grinding or drawing, producing a substantial impact on tool life and workpiece quality (Brinksmeier, et al. *(1)*). These O/W emulsions consist of mixtures of oil, surfactants, additives and water and are used as lubricants and cooling agents at the machine-workpiece interface providing also chip removal, corrosion protection and microbial growth control. These fluids lose their functional properties with use from thermal and mechanical stress and are classified as hazardous substances that must be treated before being discharged (Cañizares, et al. *(2)*; John, et al. *(3)*). Moreover, spent MWFs cause high levels of pollution and rancid odors because of the presence of complex chemicals, biocides, etc., that require careful treatment and disposal (Cheng, et al. *(4)*).

The most common processes to treat waste O/W emulsions are membranes (Bailey *(5)*; Belkacem, et al. *(6)*; Benito, et al. *(7)*; Chakrabarty, et al. *(8)*; Hilal, et al. *(9)*; Lee, et al. *(10)*; Lipp, et al. *(11)*; Lobo, et al. *(12)*), chemical destabilization (conventional coagulation or electrocoagulation; Allende, et al. *(13)*; Cañizares, et al. *(2)*, *(14)*; Ríos, et al. *(15)*; Yang *(16)*), centrifugation (Allende, et al. *(13)*; Cambiella, et al. *(17)*) and vacuum evaporation (Gutiérrez, et al. *(18)*, *(19)*). Several hybrid processes, combining physical and chemical methods, may also be used and the effluent may be either recycled to the process or discharged, with environmental and economical benefits (Benito, et al. *(20)*, *(21)*; Fernández, et al. *(22)*; Gutiérrez, et al. *(23)*, *(24)*; Karakulski and Morawski *(25)*–*(27)*; Matos, et al. *(28)*).

In copper industries MWFs are used in drawing operations to control friction between the workpieces and the drawing die, to dissipate heat generated during drawing, and to improve the surface quality of the workpiece (Karakulski and Morawski *(25)*, *(27)*). These MWFs are used in processes of *rolling* (to transform the copper ingots into a continuous rod), *smoothing* (the rod is transformed in a copper wire) and *drawing* (to obtain copper wire with a smaller diameter) (Gutiérrez, et al. *(24)*). They become less effective with use, affecting the workpiece surface, and their loss of stability in the emulsion lifetime may be related to interfacial properties (Benito, et al. *(29)*; Brinksmeier, et al. *(1)*; Cambiella, et al. *(30)*; Canter, et al. *(31)*; Fernández, et al. *(22)*).

Oil droplets present in MWFs are normally negatively charged because of the use of anionic surfactants in their formulation (Benito, et al. *(29)*) and the adsorption of hydroxyl ions onto the droplet surface at working conditions (pH = 8.5–10). Thus, electrostatic repulsive forces between oil droplets lead to emulsion stability. However, stability depends on the cationic ions present, such as Cu^{2+}, including those causing water hardness (mainly Ca^{2+} and Mg^{2+}): when cationic concentration is high enough, the surface charge of the oil droplets is close to zero and the emulsion may be destabilized (Ríos, et al. *(15)*; Zhao, et al. *(32)*; Zimmermann, et al. *(33)*, *(34)*).

In this work, the evolution of two semi-synthetic O/W emulsions and a synthetic fluid used in a copper wire industrial plant was followed in a time span of two years by measuring six parameters: zeta potential, droplet size distribution, surface tension, contact angle, foaming power and creaming stability. The appropriate parameters were selected for MWF monitoring to implement corrective and preventive actions to extend fluid lifecycle, such as MWF upgrading with emulsifiers. The MWF must be replaced when its characteristics are not suitable for a given operation.

Simultaneously with life span analysis, new MWFs were formulated using commercial concentrates and different kinds of water, with several cationic ions present, and their properties were compared to those of the monitored plant MWFs. The aim of this second set of experiments was to formulate new metalworking fluids to replace those used in the industrial plant, with similar properties but with lower foaming power, which is undesirable due to problems in the production process.

MATERIALS AND METHODS

Metalworking Fluids Monitored

MWFs were provided by a local northern Spanish company from its continuous-casting copper plant. Copper cathodes are first melted in a shaft furnace (*smelting*). The liquid copper flows between a water-cooled hollow casting wheel and belt and is transformed into a continuous 80×60 mm rod (*casting*). This rod goes through a rolling mill which reduces its diameter to 8 mm (*rolling*), followed by a *pickling* treatment with isopropyl alcohol to prevent oxidation. The 8 mm wire rod undergoes a *smoothing* process to make a 2 mm wire, which is subsequently processed in a *wire drawing* machine to obtain copper wire of 0.25 mm diameter. The resulting wire is processed in an *annealing* furnace to improve product quality.

MWFs used in this study were collected from different parts of the process:

i. A synthetic fluid used in the casting process (casting fluid), made from a 1.5–3% v/v commercial concentrate Multiroll Cu (Zeller+Gmelin GmbH & Co. KG, Eislingen, Germany) in water. This fluid had a translucent color during its life time and no copper was present.

ii. A semi-synthetic O/W emulsion used for lubrication and cooling in the smoothing process (smoothing emulsion), with 12% v/v mineral oil Unopol G 560 (Carl Bechem GmbH, Hagen, Germany) in water. This emulsion had a green color and its copper concentration increased with use, up to 500–600 mg/L.

iii. A semi-synthetic O/W emulsion, used in the wire drawing process (wire drawing emulsion), made from a 8% v/v commercial concentrate Multidraw Cu MF (Zeller+Gmelin GmbH & Co. KG, Eislingen, Germany) in water. This concentrate is based in naphthenic hydrocarbons and contains both anionic and non-ionic surfactants. The initial white color of this emulsion turned into blue because of copper solubilization along its life span. Its copper concentration might reach 1,000 mg/L.

Commercial Metalworking Fluids Formulated at Laboratory Scale

Several commercial MWFs were characterized and results compared with the monitored ones. The purpose was to check whether the commercial MWFs showed lower foaming power, keeping constant other basic properties, so that they might be used to replace the MWFs of the industrial process, thus achieving source reduction. MWFs from the wire drawing and the casting processes were selected for this purpose.

A commercial concentrate Multidraw Cu MF-S was used to formulate the commercial emulsions and their properties were compared with those of the monitored wire drawing emulsion (Multidraw Cu MF). The effect of water quality used in the formulation and the presence of copper in the emulsion properties were also studied. Four kinds of emulsions were prepared with each one of the three concentrates. All of them consisted of an 8% v/v commercial concentrate in water. The first commercial emulsion was prepared using decalcified water in absence of copper. The second emulsion was similar but with addition of copper to a concentration of 100–500 mg/L. The third emulsion was formulated with 20% of local tap water and 80% of distilled water, in absence of copper. The fourth emulsion was made as the third one, but copper being present. After emulsions formulation all their properties were measured.

A Multiroll Cu LF-Special concentrate was used to formulate the commercial casting fluid. A second synthetic fluid was formulated with the commercial concentrate used in the process, Multiroll Cu. Both emulsions were made from a 1.5% v/v commercial concentrate in decalcified water. All their properties were also measured.

Measurement of Interfacial Properties of Metalworking Fluids

Optical characterization of O/W emulsion creaming stability was determined with a Turbiscan LAB Expert (Formulaction Co., L'Union, France) by static multiple light scattering (MLS). MLS consists of sending a light beam through a cylindrical glass cell containing the sample. The light source is an electro luminescent diode in the near infrared (NIR, $\lambda = 880$ nm). The semi-synthetic emulsion sample was placed without dilution in a cylindrical glass cell and two synchronous optical sensors received the light transmitted through the sample (180° from the incident light), and the light backscattered by the particles (or droplets) in the sample (45° from the incident light). The optical reading head scans the height of the sample in the cell (about 42 mm), acquiring transmission and backscattering data every 40 µm. These profiles build up a macroscopic fingerprint of the sample at a given time. Transmitted and backscattered light were monitored as a function of time and cell height for 3 days at 30–40 ºC (Allende, et al. *(13)*; Matos, et al. *(28)*).

A Zetasizer NanoZS (Malvern Instruments Ltd., UK) was utilized for the zeta potential (ζ) measurements of MWFs. Three replicate measurements were conducted for each sample at a constant temperature of 40 ºC.

Droplet size distributions (DSD) were determined for the two semi-synthetic emulsions following the laser light scattering technique and using a Mastersizer S long bench equipment (Malvern instruments Ltd., UK). DSD measurements were performed 10 min after the emulsion had been stirred with a Heidolph DIAX 900 homogenizer at 20,000 rpm. The emulsions were diluted with deionized water to prevent multiple scattering effects and then they were circulated through the measuring zone using a Hydro SM small volume sample dispersion unit. Several measurements were made for each emulsion at different dilutions and no significant changes in droplet size distributions were observed for dilute emulsions ranging from 1:10 to 1:100 dilution ratios. Droplet size results are reported as the volume-weighted mean diameter, $D_{[4,3]}$.

Surface tension was determined following the Du Noüy's platinum ring method at 40 ºC. Two instruments were used: a Krüss K-8 tensiometer during the first part of the monitoring (18 months), and a Sigma 700 tensiometer (KSV Instruments Ltd., Finland) during the last six months. Both instruments gave similar results.

Contact angles (θ) on copper surfaces were measured using a KSV CAM 200 Optical Contact Angle Meter (KSV Instruments Ltd., Finland). MWF droplets were placed on the copper plates by a syringe and allowed to spread freely on the surface. Spreading images were captured by a high resolution CCD camera at 10-s intervals for 180 s. Contact angles were determined using the KSV CAM 200 software. After use, the copper plate was rinsed with nitric acid, isopropanol and hexane, and then placed in an oven for ten minutes at 100 ºC.

The MWF foaming power was measured by placing 30 mL of fluid in a graduated cylinder and stirring it with a Heidolph DIAX 900 homogenizer at 20,000 rpm for 1 min. Foam volume was monitored as a function of time for 20 minutes. The foaming power was determined graphically, plotting the area of foam volume *vs.* time.

Conductivity and pH were simultaneously measured with a Crison MM40 multimeter.

RESULTS AND DISCUSSION

Monitoring

The wire drawing emulsion had been replaced a few days before the monitoring time started, while the smoothing emulsion had been replaced just at the start of the monitoring time. However, at the end of the monitoring time it was necessary to replace both semi-synthetic emulsions because of their loss of functional properties. The casting fluid (synthetic) was also replaced at the end of this study. Arrows in Figs. 1–6 indicate MWF replacement.

Zeta Potential (ζ)

The three MWFs followed the same trend, as shown in Fig. 1. The zeta potential increased with use, decreasing its absolute value, indicating MWF destabilization: smoothing and wire drawing emulsions reached even 0 mV or positive values as they aged. Once the emulsion was replaced, its absolute value increased again, around –50 mV. The two semi-synthetic emulsions showed a higher destabilization compared to the synthetic fluid. This might result from copper particles present in the wire drawing and smoothing emulsions that would affect the stability of the oil droplets.

Some authors have confirmed that zeta potential is the main indicator of emulsion stability, and in one study it was determined that when $\zeta > -10$ mV the emulsion is completely destabilized and is not suitable for the copper rolling process (Fernández, et al. *(22)*).

In the present work, the two semi-synthetic emulsions were used, even if ζ was close to 0 mV, but they had no optimum functional performance and their replacement is recommended if creaming stability measurements indicated emulsion destabilization.

Droplet Size Distribution (DSD)

DSD was determined only for semi-synthetic emulsions because the synthetic fluid had no oil in its original formulation. It provided important information on emulsion performance with time. A similar behavior was observed for both emulsions. Mean droplet size ($D_{[4,3]}$) increased with time reaching high values as the emulsion aged. A decrease in droplet size was observed when the emulsions were replaced (Fig. 2). The increase in the mean droplet size could result from the coalescence of oil droplets, which corresponds to the low zeta potentials observed. The two peaks observed at 3.5 and 20 months for the wire drawing emulsion are probably due to the fortuitous presence of a high number of copper particles: conductivity values for these two months reached even 8,000 or 9,000 mS/cm (see Fig. 5). Once emulsions were replaced, they became more stable showing a decrease in the mean droplet size and a maximum zeta potential absolute value.

Surface Tension

Surface tension measurements are shown in Fig. 3. Large variations with time were observed. For the casting fluid, surface tension increased slightly, as expected when the fluid is at the end of its life span. Furthermore, surface tension decreased with time for the two semi-synthetic emulsions, just before they were replaced. This behavior is likely due to the free oil film formed at the emulsion surface when the emulsion aged, decreasing the surface tension.

Contact Angle

Fig. 4 shows the contact angle as a function of time for the three monitored MWFs. A large variation was observed in all cases. It may be caused by changes in conductivity (Fig. 5), because of the steady increase of copper concentration with time. Low values of this parameter are required for a good process performance. A decrease in surfactants concentration because of the high temperatures reached in the rolling process causes the contact angle to increase and periodic additions of surfactants improved wettability (Fernández, et al. *(22)*). The addition of antifoam agents during monitoring time might also have an effect on this parameter. The contact angle fluctuated in a range of 50–60º for semi-synthetic emulsions. The casting fluid showed lower values, between 25–40º.

The variations of pH and conductivity with time are shown in Fig. 5. Conductivity increased with time for wire drawing and smoothing emulsions due to the increase in copper concentration. Copper concentration reached 1,000 mg/L in the wire drawing emulsion and 500–600 mg/L in the smoothing emulsion. A sharp decrease in conductivity was observed for the three MWFs when they were replaced. The pH’s remained in the range of 8.5–9.5 in all cases with no significant variation when the MWF was changed.

Foaming Power

Fig. 6 shows the foaming power for the three MWFs. A large variation was observed for the three cases due to the changes in conductivity and the addition of antifoam agents during the monitoring time. The presence of free oil when semi-synthetic emulsions were at the end of their life span seemed to reduce their foaming ability, which reached values close to zero.

Optical Characterization of Creaming Stability

The creaming stability of the semi-synthetic O/W emulsions was analyzed with the Turbiscan LAB Expert apparatus. Fig. 7 shows the creaming stability measurements just before and after replacement of the wire drawing emulsion. It can be observed that backscattering decreased as time increased for the bottom and middle layers, Fig. 7a, which indicates an increase in droplet size caused by coalescence of oil droplets. No clear trend was observed with respect to creaming. Furthermore, Fig. 7b shows that the emulsion was stable because there were no changes in droplet size or creaming.

Fig. 8 shows stability measurements of the smoothing emulsion. The stability measured three months after the emulsion was replaced is presented in Fig. 8a. A creaming zone was observed at the top of the measurement cell because of oil droplets density separation, forming a top oil layer. However, the emulsion was stable and no significant changes were observed in droplet size or backscattering profiles in the middle zone of the measurement cell, remaining at a constant value around 25%. Fig. 8b indicates also emulsion stability towards the middle of the monitoring time. There were no changes in droplet size or backscattering in the middle zone of the measurement cell, remaining its value around 38%, a sign of emulsion stability. However, a creaming zone was observed again at the top of the cell with the simultaneous appearance of a clarification front at the bottom, which indicates that oil droplets migrate to the top of the cell, although this emulsion maintains the initial conditions when it is continuously recirculated in the industrial process. Fig. 8c corresponds to the stability at the end of the monitoring time. Backscattering profiles in the middle zone of the measurement cell increased with time, which meant an increase in droplet size as a result of coalescence, with simultaneous appearance of a clarification front at the bottom of the cell. In this case, there is a creaming zone not only at the top of the cell: migration of oil droplets occurs for the whole cell height. It is important to notice that a backscattering value up to 47% implies the presence of free oil in the emulsion due to the phase separation produced after a total destabilization.

Kinetic profiles would help to understand these results. Fig. 9 shows backscattering variation with time at the middle layers of semi-synthetic emulsions shown in Figs. 7 and 8. There is no significant backscattering variation with time for emulsions shown in Figs. 7b, 8a and 8b, which is an indication that there are not changes in droplet size, remaining the emulsions stable. However, a change in backscattering was observed for the emulsions shown in Figs. 7a and 8c, which means that the mean droplet diameter increases with time because of oil droplet coalescence. Furthermore, a backscattering increase with time was observed for the emulsion shown in Fig. 8c, whereas it decreases in the case of emulsion shown in Fig. 7a. The different backscattering behavior was due to oil droplet size of the O/W emulsions: according to the physical model on which the Turbiscan apparatus is based, backscattering increases with the particle mean diameter for particles smaller than the incident wavelength ($\lambda = 0.88$ μm) and it decreases with the mean diameter for particles larger than the incident wavelength. The emulsion shown in Fig. 8c has a volume-weighted mean diameter ($D_{[4,3]}$) of 0.75 μm, being 6.1 μm for the emulsion shown in Fig. 7a.

Therefore, when an emulsion presents a zeta potential close to zero and a Turbiscan profile where the backscattering changes sharply with time, this emulsion should be replaced.

Characterization of Commercial Metalworking Fluids Formulated at Laboratory Scale

Commercial concentrates were used to formulate MWFs using decalcified, tap and distilled water and taking into account the addition of copper. Their properties were compared with those monitored in the copper plant to improve performance and eventually to replace them for new ones with lower foaming power without modifying other main properties.

Commercial Wire Drawing O/W Emulsions Formulated

Fig. 10 shows large differences in the foaming power of O/W emulsions formulated with several types of water. Foaming power increased when copper was added. The emulsions formulated using Multidraw Cu MF-S showed better results reaching the lowest one when 80% distilled water was used.

Both concentrates, Multidraw Cu MF and Multidraw Cu MF-S, were similar with respect to other parameters (Fig. 11). As the foaming power decreased, without changing the other properties, the latter concentrate was considered suitable to replace semi-synthetic emulsion in use after 22 months in operation.

It is important to notice that zeta potential is influenced by the ions present in solution. Zeta potential absolute values were similar (60–70 mV) for semi-synthetic O/W emulsions formulated with both concentrates, using decalcified and distilled water (Fig. 11). However, absolute values increased up to 80–90 mV when these emulsions were prepared in presence of copper using both types of water. Moreover, the type of water used and the presence of copper had slight or no effect on surface tension and contact angle, keeping their values constant despite the changes produced in the formulation.

Commercial Casting Fluid Formulated

Table 1 shows a summary of the properties studied. Foaming power was considerably reduced, while the contact angle and surface tension had similar values for both concentrates (Multiroll Cu and Multiroll Cu LF-Special). In addition to the foaming power, zeta potential was quite different but, being a synthetic fluid, this parameter was not directly related to stability as in other cases. To sum up, as the foaming power was greatly reduced and the other parameters were rather similar, the formulated fluid could be used to replace the synthetic fluid being used for 18 months.

CONCLUSIONS

- Zeta potential, droplet size distribution and optical characterization of the creaming stability are suitable parameters to monitor MWF lifecycle. Moreover, surface tension, contact angle and foaming power measurements showed large variations with time, and they are inappropriate parameters for MWF performance assessment.
- The three aforementioned parameters can be selected for monitoring metalworking fluids performance in a copper wire drawing industry, resulting in increased MWF lifetime through

appropriate changes (*i.e.* periodic addition of surfactants or emulsifiers), or even prediction of the optimum time for emulsion replacement.

- A proper metalworking fluid formulation may reduce its foaming power without changing the other functional properties, improving the process performance and reducing the periodic addition of antifoam agents.

ACKNOWLEDGEMENTS

Financial support by the Consejería de Educación y Ciencia del Principado de Asturias (Plan I+D+i 2001–2004, Ref.: COF04-50, and PCTI Asturias 2006–2009, Refs.: PC06-011 and EQP06-024) is gratefully acknowledged.

REFERENCES

(1) Brinksmeier, E., Garbrecht, M., Heinzel, C., Koch, Th., and Eckebrecht, J. (2009), “Current Approaches in Design and Supply of the Metalworking Fluids,” *Tribol. Trans.*, **52**, pp 591–601.

(2) Cañizares, P., Martínez, F., Jiménez, C., Sáez, C., and Rodrigo, M. A. (2008), “Coagulation and Electrocoagulation of Oil-in-Water Emulsions,” *J. Hazard. Mater.*, **151**, pp 44–51.

(3) John, J., Bhattacharya, M., and Raynor, P. C. (2004), “Emulsions Containing Vegetable Oils for Cutting Fluid Application,” *Colloid Surf. A-Physicochem. Eng. Asp.*, **237**, pp 141–150.

(4) Cheng, C., Phipps, D., and Alkhaddar, R. M. (2005), “Treatment of Spent Metalworking Fluids,” *Water Res.*, **39**, pp 4051–4063.

(5) Bailey, P. A. (1997), “Treatment of Waste Emulsified Oils by Ultrafiltration,” *Filtr. Sep.*, **14**, pp 53–55.

(6) Belkacem, M., Hadjiev, D., and Aurelle, Y. (1995), “A Model for Calculating the Steady State Flux of Organic Ultrafiltration Membranes for the Case of Cutting Oil Emulsions,” *Chem. Eng. J.*, **56**, pp 27–32.

(7) Benito, J. M., Ebel, S., Gutiérrez, B., Pazos, C., and Coca, J. (2001), “Ultrafiltration of a Waste Emulsified Cutting Oil Using Organic Membranes,” *Water Air Soil Pollut.*, **128**, pp 181–195.

(8) Chakrabarty, B., Ghoshal, A. K., and Purkait, M. K. (2010), “Cross-flow Ultrafiltration of Stable Oil-in-Water Emulsion Using Polysulfone Membranes,” *Chem. Eng. J.*, **165**, pp 447–456.

(9) Hilal, N., Busca, G., Hankins, N., and Mohammad, A. W. (2004), “The Use of Ultrafiltration and Nanofiltration Membranes in the Treatment of Metal-Working Fluids,” *Desalination*, **167**, pp 227–238.

(10) Lee, S., Aurelle, Y., and Roques, H. (1984), “Concentration Polarization, Membrane Fouling and Cleaning in Ultrafiltration of Soluble Oil,” *J. Membr. Sci.*, **19**, pp 23–38.

(11) Lipp, P., Lee, C. H., Fane, A. G., and Fell, C. J. D. (1988), “A Fundamental Study of the Ultrafiltration of Oil-Water Emulsions,” *J. Membr. Sci.*, **36**, pp 161–177.

(12) Lobo, A., Cambiella, A., Benito, J. M., Pazos, C., and Coca, J. (2008), “Ultrafiltration of Oil-in-Water Emulsions with Ceramic Membranes: Influence of pH and Crossflow Velocity,” *J. Membr. Sci.*, **278**, pp 328–334.

(13) Allende, D., Cambiella, A., Benito, J. M., Pazos, C., and Coca, J. (2008), “Destabilization-enhanced Centrifugation of Metalworking Oil-in-Water Emulsions: Effect of Demulsifying Agents,” *Chem. Eng. Technol.*, **31**, pp 1007–1014.

(14) Cañizares, P., Martínez, F., Lobato, J., and Rodrigo, M. A. (2007), “Break-up of Oil-in-Water Emulsions by Electrochemical Techniques,” *J. Hazard. Mater.*, **145**, pp 233–240.

(15) Ríos, G., Pazos, C., and Coca, J. (1998), “Destabilization of Cutting Oil Emulsions using Inorganic Salts as Coagulants,” *Colloid Surf. A-Physicochem. Eng. Asp.*, **138**, pp 383–389.

(16) Yang, C.-L. (2007), “Electrochemical Coagulation for Oily Water Demulsification,” *Sep. Purif. Technol.*, **54**, pp 388–395.

(17) Cambiella, A., Benito, J. M., Pazos, C., and Coca, J. (2006), “Centrifugal Separation Efficiency in the Treatment of Waste Emulsified Oils,” *Chem. Eng. Res. Des.*, **84**, pp 69–76.

(18) Gutiérrez, G., Cambiella, A., Benito, J. M., Pazos, C., and Coca, J. (2007), “The Effect of Additives on the Treatment of Oil-in-Water Emulsions by Vacuum Evaporation,” *J. Hazard. Mater.*, **144**, pp 649–654.

(19) Gutiérrez, G., Benito, J. M., Pazos, C., and Coca, J. (2010), “Vacuum Evaporation of Surfactant Solutions and Oil-in-Water Emulsions,” *Chem. Eng. J.*, **162**, pp 201–207

(20) Benito, J. M., Ríos, G., Gutiérrez, B., Pazos, C., and Coca, J. (1999), “Integrated Process for the Removal of Emulsified Oils from Effluents in the Steel Industry,” *Sep. Sci. Technol.*, **34**, pp 3031–3043.

(21) Benito, J. M., Ríos, G., Ortea, E., Fernández, E., Cambiella, A., Pazos, C., and Coca, J. (2002), “Design and Construction of a Modular Pilot Plant for the Treatment of Oil-containing Wastewaters,” *Desalination*, **147**, pp 5–10.

(22) Fernández, E., Benito, J. M., Pazos, C., Coca, J., Ruiz, I., and Ríos, G. (2005), “Regeneration of an Oil-in-Water Emulsion after Use in an Industrial Copper Rolling Process,” *Colloid Surf. A-Physicochem. Eng. Asp.*, **263**, pp 363–369.

(23) Gutiérrez, G., Lobo, A., Allende, D., Cambiella, A., Pazos, C., Coca, J., and Benito, J. M. (2008), “Influence of Coagulant Salt Addition on the Treatment of Oil-in-Water Emulsions by Centrifugation, Ultrafiltration and Vacuum Evaporation,” *Sep. Sci. Technol.*, **43**, pp 1884–1895.

(24) Gutiérrez, G., Lobo, A., Benito, J. M., Coca, J., and Pazos, C. (2011), “Treatment of a Waste Oil-in-Water Emulsion from a Copper-Rolling Process by Ultrafiltration and Vacuum Evaporation,” *J. Hazard. Mater.*, **185**, pp 1569–1574.

(25) Karakulski, K. and Morawski, A. W. (2000), “Purification of Copper Wire Drawing Emulsion by Application of UF and RO,” *Desalination*, **131**, pp 87–95.

(26) Karakulski, K. and Morawski, A. W. (2002), “Treatment of Spent Emulsion from a Cable Factory by an Integrated UF/NF Membrane System,” *Desalination*, **149**, pp 163–167.

(27) Karakulski, K. and Morawski, A. W. (2011), “Recovery of Process Water from Spent Emulsions Generated in Copper Cable Factory,” *J. Hazard. Mater.*, **186**, pp 1667–1671.

(28) Matos, M., Lobo, A., Fernández, E., Benito, J. M., Pazos, C., and Coca, J. (2008), “Recycling of Oily Ultrafiltration Permeates to Reformulate O/W Emulsions,” *Colloid Surf. A-Physicochem. Eng. Asp.*, **331**, pp 8–15.

(29) Benito, J. M., Cambiella, A., Lobo, A., Gutiérrez, G., Coca, J., and Pazos, C. (2010), “Formulation, Characterization and Treatment of Metalworking Oil-in-Water Emulsions,” *Clean Technol. Environ. Policy*, **12**, pp 31–41.

(30) Cambiella, A., Benito, J. M., Pazos, C., and Coca, J. (2007), “Interfacial Properties of Oil-in-Water Emulsions Designed to be Used as Metalworking Fluids,” *Colloid Surf. A-Physicochem. Eng. Asp.*, **305**, pp 112–119.

(31) Canter, N. (2011), “Cover story: Monitoring of Metalworking Fluids,” *Tribol. Lubr. Technol.*, **67**, 3, pp 42–51.

(32) Zhao, Y. P., Turay, R., and Hundley, L. (2006), “Monitoring and Predicting Emulsion Stability of Metalworking Fluids by Salt Titration and Laser Light Scattering Method,” *Tribol. Trans.*, **49**, pp 117–123.

(33) Zimmerman, J. B., Clarens, A. F., Hayes, K. F., and Skerlos, S. J. (2003), “Design of Hard Water Stable Emulsifier Systems for Petroleum- and Bio-Based Semi-Synthetic Metalworking Fluids,” *Environ. Sci. Technol.*, **37**, pp 5278–5288.

(34) Zimmerman, J. B., Hayes, K. F., and Skerlos, S. J. (2004), “Influence of Ion Accumulation on the Emulsion Stability and Performance of Semi-Synthetic Metalworking Fluids,” *Environ. Sci. Technol.*, **38**, pp 2482–2490.

TABLE CAPTIONS

Table 1. Comparison of parameters for synthetic fluids formulated with Multiroll Cu and Multiroll Cu LF-Special.

FIGURE CAPTIONS

Fig. 1. Zeta potential as a function of time for wire drawing, smoothing and casting metalworking fluids.

Fig. 2. Mean droplet size ($D_{[4,3]}$) as a function of time for wire drawing and smoothing emulsions.

Fig. 3. Surface tension as a function of time for wire drawing, smoothing and casting metalworking fluids.

Fig. 4. Contact angle values as a function of time for wire drawing, smoothing and casting metalworking fluids over a copper surface.

Fig. 5. Conductivity and pH as a function of time for wire drawing, smoothing and casting metalworking fluids.

Fig. 6. Foaming power as a function of time for wire drawing, smoothing and casting metalworking fluids.

Fig. 7. Creaming profiles of the wire drawing emulsion just before (a) and after (b) being replaced.

Fig. 8. Creaming profiles of the smoothing emulsion: (a) three months after replacement; (b) at the middle of the monitoring time; (c) at the end of the monitoring time.

Fig. 9. Kinetic profiles at the middle layers of wire drawing (a) and smoothing (b) emulsions samples from Turbiscan data shown in Figs. 7 and 8, respectively.

Fig. 10. Foaming power of O/W emulsions formulated with Multidraw Cu MF and Multidraw Cu MF-S concentrates using several types of water, in absence and in presence of copper.

Fig. 11. Contact angle, surface tension and zeta potential of O/W emulsions formulated with Multidraw Cu MF and Multidraw Cu MF-S concentrates using several types of water, in absence and in presence of copper.

Table 1

	Contact angle (º)	Zeta potential (mV)	Surface tension (mN/m)	Foaming power (mL × min)
Synthetic fluid with 1.5% of Multiroll Cu (decalcified water)	49.5	–42.8	28.8	362
Synthetic fluid with 1.5% of Multiroll Cu LF-Special (decalcified water)	52.1	–27.3	31.2	30

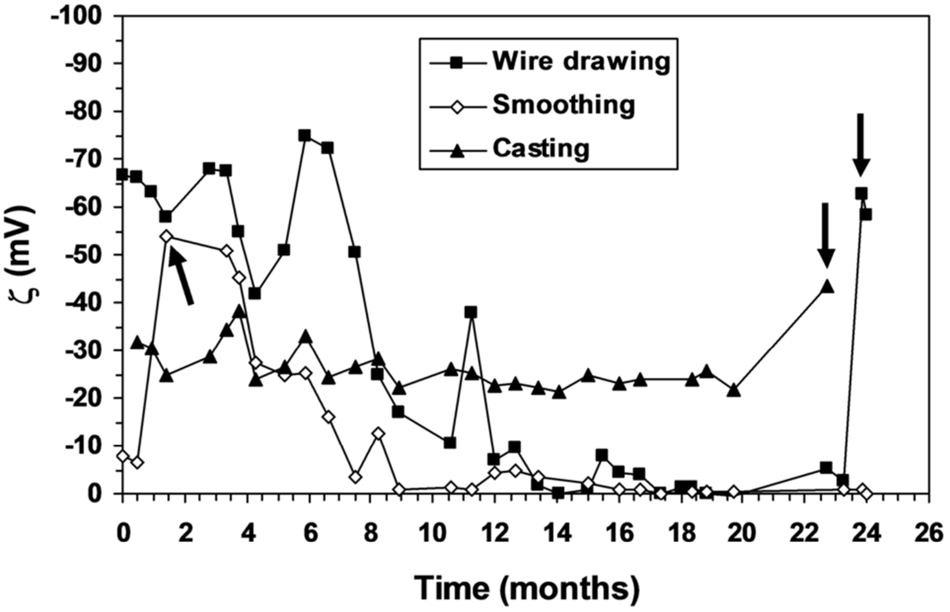

Fig. 1-Zeta potential as a function of time for wire drawing, smoothing and casting metalworking fluids
85x57mm (300 x 300 DPI)

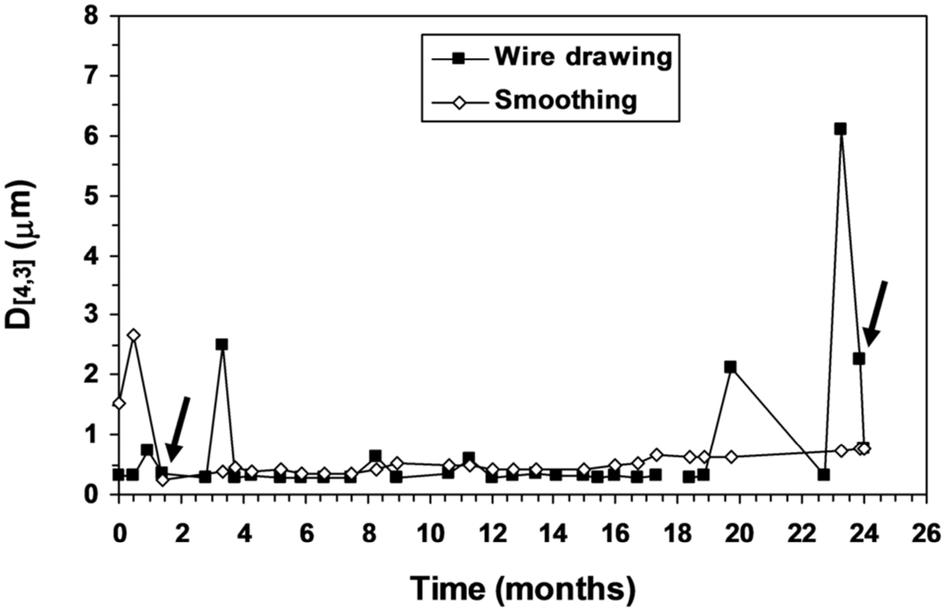

Fig. 2-Mean droplet size ($D_{[4,3]}$) as a function of time for wire drawing and smoothing emulsions
85x57mm (300 x 300 DPI)

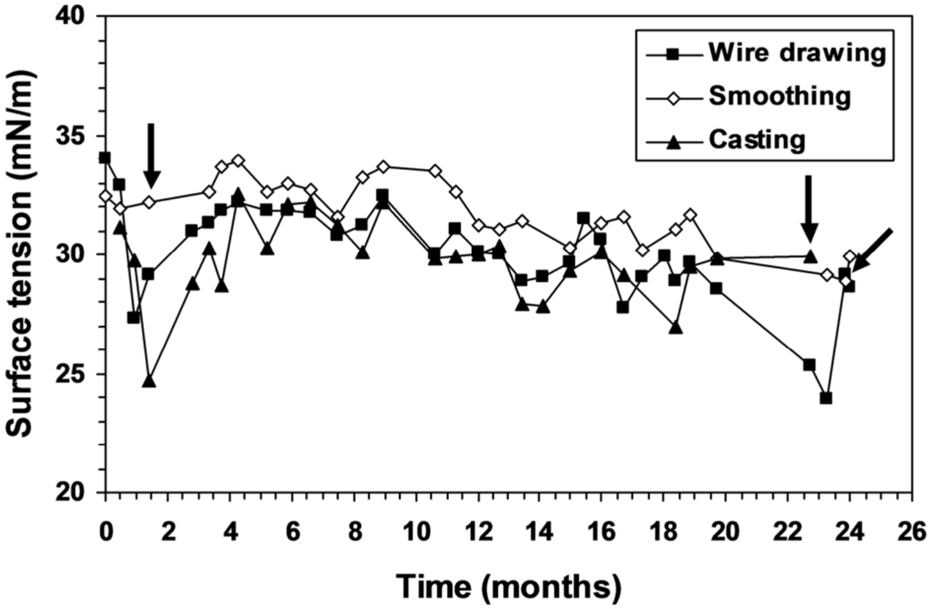

Fig. 3-Surface tension as a function of time for wire drawing, smoothing and casting metalworking fluids
85x57mm (300 x 300 DPI)

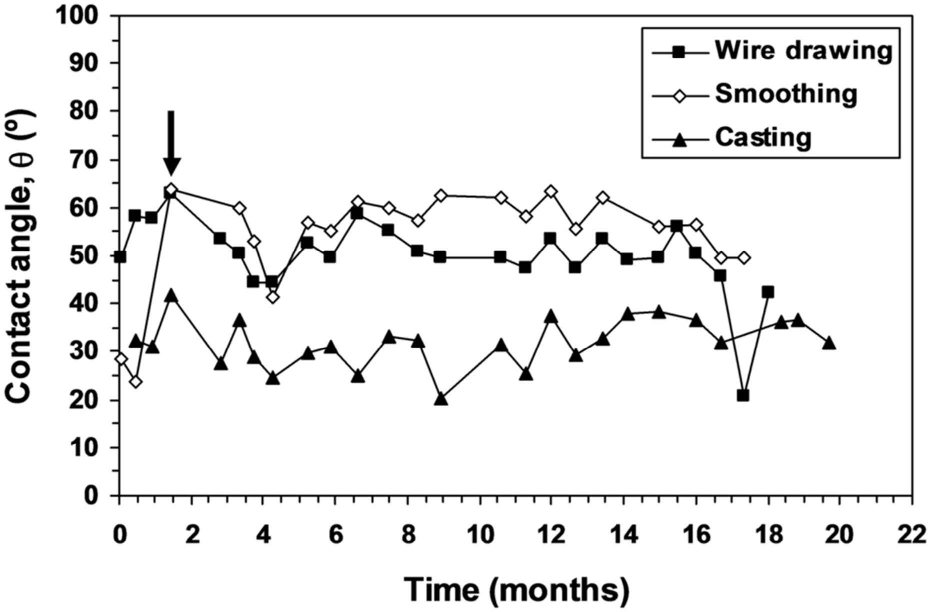

Fig. 4-Contact angle values as a function of time for wire drawing, smoothing and casting metalworking fluids over a copper surface
86x58mm (300 x 300 DPI)

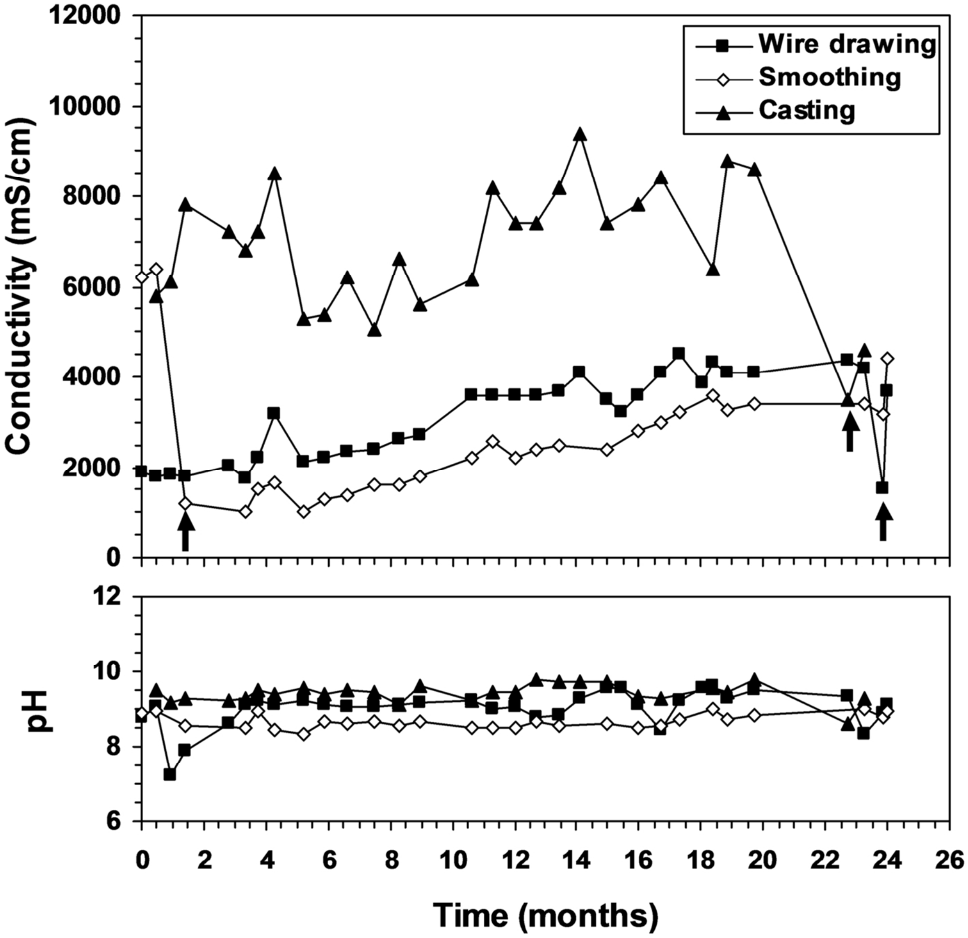

Fig. 5-Conductivity and pH as a function of time for wire drawing, smoothing and casting metalworking fluids
124x120mm (300 x 300 DPI)

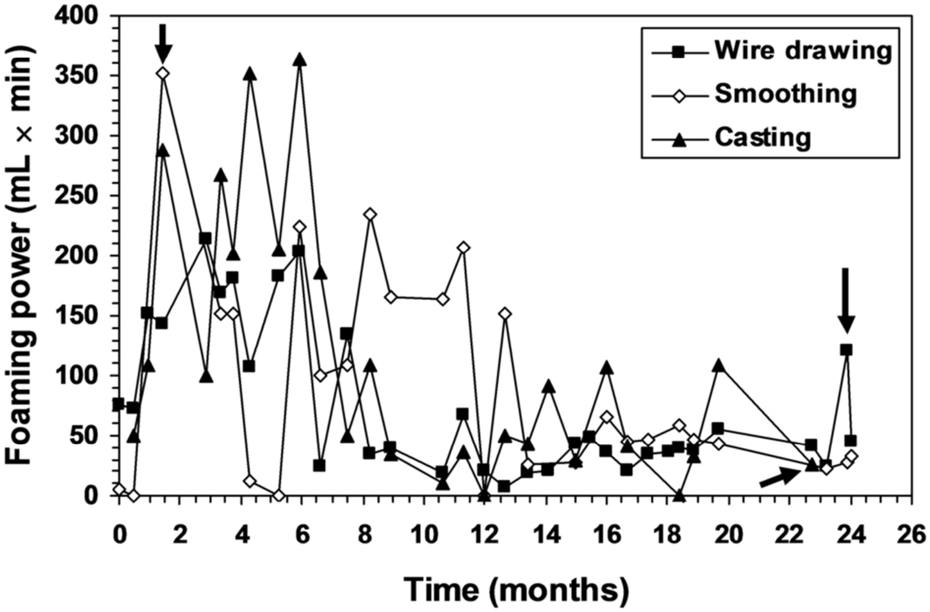

Fig. 6-Foaming power as a function of time for wire drawing, smoothing and casting metalworking fluids
86x58mm (300 x 300 DPI)

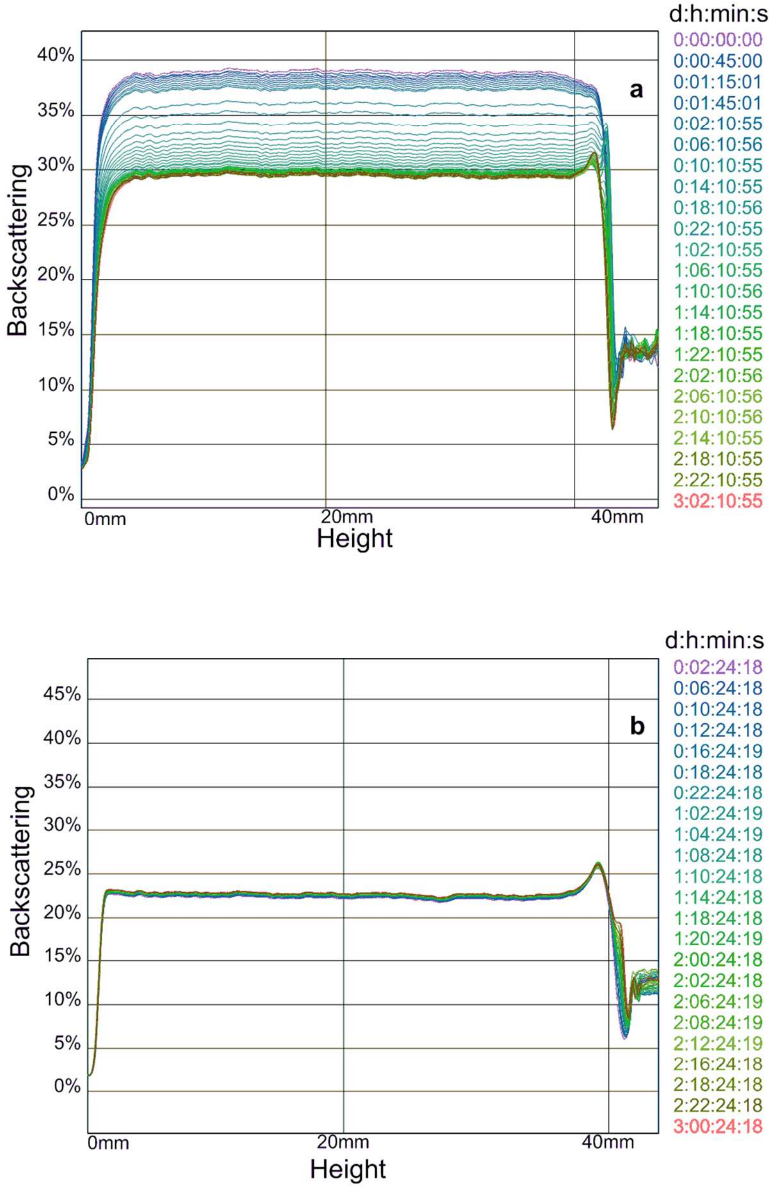

Fig. 7-Creaming profiles of the wire drawing emulsion just before (a) and after (b) being replaced
86x133mm (300 x 300 DPI)

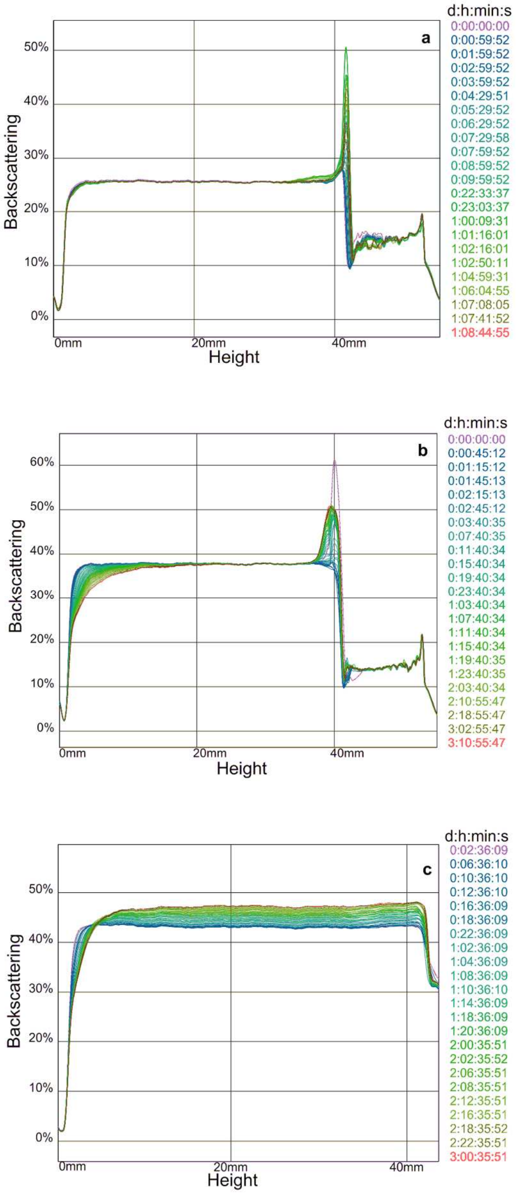

Fig. 8-Creaming profiles of the smoothing emulsion: (a) three months after replacement; (b) at the middle of the monitoring time; (c) at the end of the monitoring time
87x202mm (300 x 300 DPI)

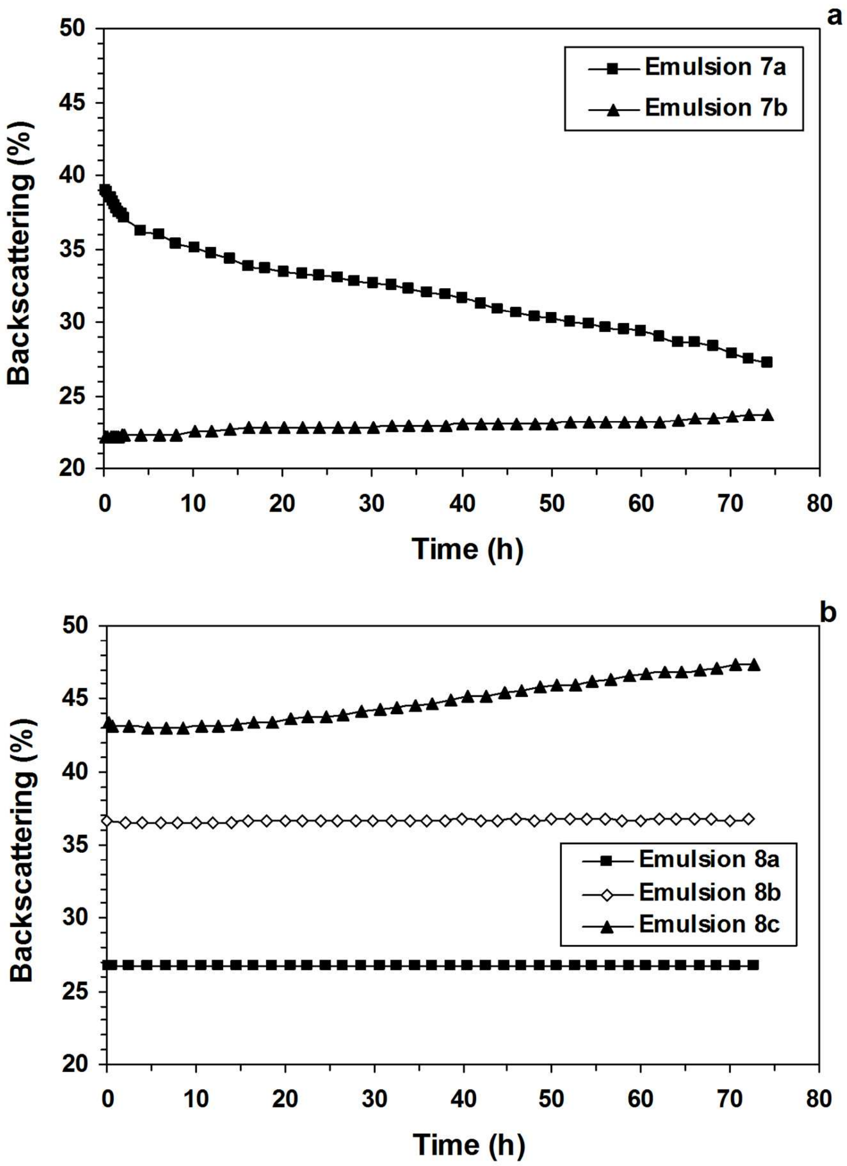

Fig. 9-Kinetic profiles at the middle layers of wire drawing (a) and smoothing (b) emulsions samples from Turbiscan data shown in Figs. 7 and 8, respectively
127x170mm (300 x 300 DPI)

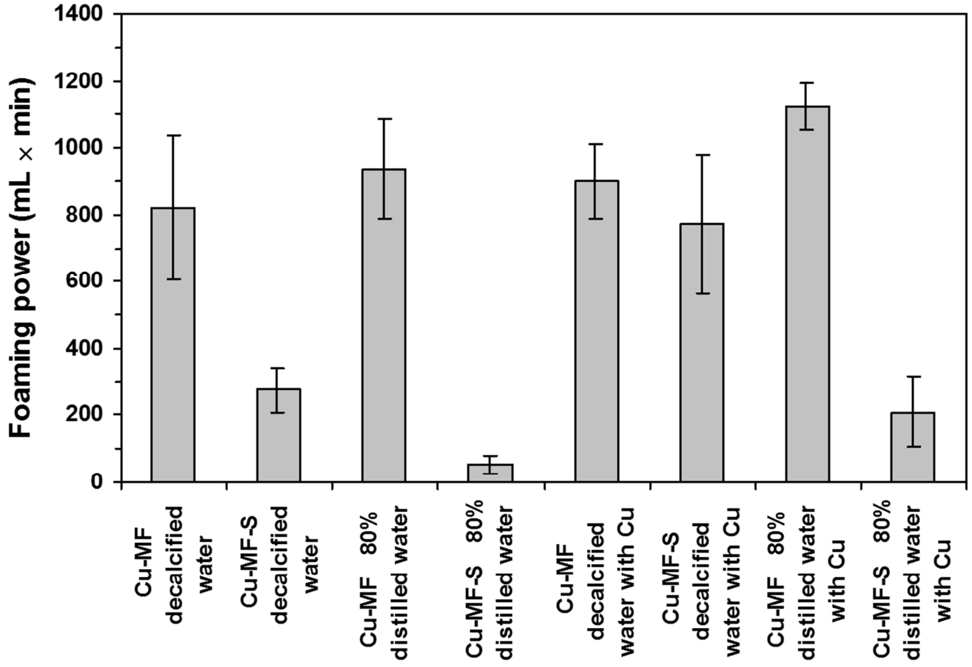

Fig. 10-Foaming power of O/W emulsions formulated with Multidraw Cu MF and Multidraw Cu MF-S concentrates using several types of water, in absence and in presence of copper
118x83mm (300 x 300 DPI)

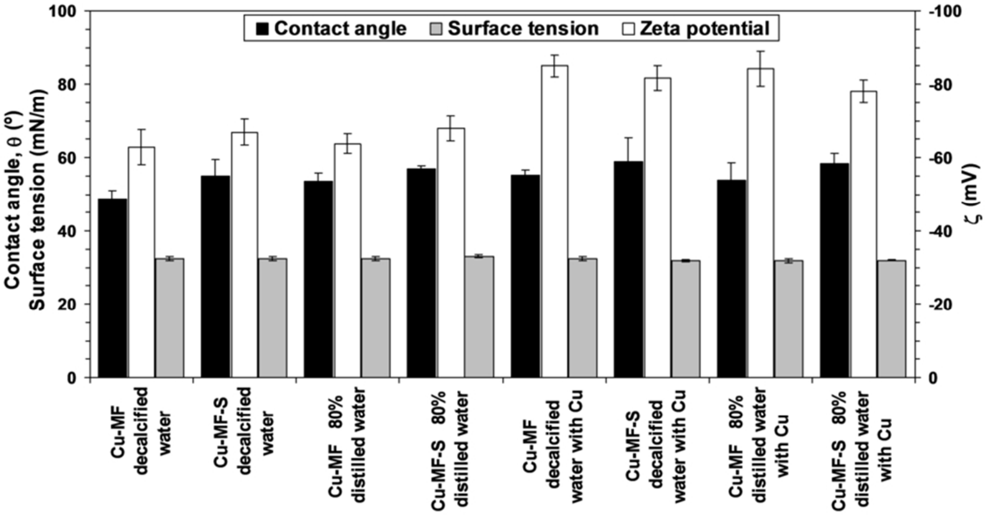

Fig. 11-Contact angle, surface tension and zeta potential of O/W emulsions formulated with Multidraw Cu MF and Multidraw Cu MF-S concentrates using several types of water, in absence and in presence of copper
81x43mm (300 x 300 DPI)