THE REMOVAL OF MINERAL OILS FROM THE SURFACE OF METALLIC CONTACTS OF Ag AND Cu BY SUPERCRITICAL CO_2

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ABSTRACT

In the process of making metal contacts for the electronics industry there is an operation in which they are stained with lubricating oil. Today, it is removed by organic solvents, but due to their negative environmental impact and high energy cost involved in their regeneration, this research studies their replacement by CO_2 under supercritical conditions. The contacts were impregnated with 3% of lubricating oil and were set forming a fixed bed in the extractor. Then, the effects of temperature, pressure, solvent flow rate, and the addition of cosolvents were investigated. The pressure was increased between 120 and 300 bar. Within this range, solubility and extraction yield increased as pressure did because of the direct raise on the CO_2 density. The raise in temperature (37-110ºC) and flow rate (1-5 $g\cdot min^{-1}$) caused an unexpected effect. In both cases, the oil removal yield increased. This was attributed to the formation of a chemisorbed oil layer on the metal surface whose desorption was favoured at high temperature and turbulence. Within the cited interval of explored variables, it was not possible to overcome 95% lubricant elimination. Therefore, it was explored the addition of a cosolvent. Pure ethanol between 2.5 and 10% was studied. The lower the temperature was, the larger amounts of ethanol were needed. Thus, the combination of a temperature of 110 ºC plus the addition of 5 % ethanol resulted in the total cleaning of both type of contacts. These results were confirmed by electronic microscopy images.

INTRODUCTION

Metal contacts are elements used in the electronics industry as raw material. They can be made of a single metal or alloys of several of them.

In the process of cold forming metal contacts, there is a stage in which they are impregnated with a lubricant oil. Afterwards,the contact surface, as precision parts, must be thoroughly cleaned so that the oils must be removed.

Currently, organic solvents are being used to remove the oil, but the process is expensive due to the high cost associated with solvent recovery, usually by distillation. In addition, this extraction method is starting to be abandoned due to the harmful effects solvents produce on the environment.

Therefore, the aim of this work was to replace the organic solvent by supercritical CO_2 which is non toxic, simply removable from the contacts and easily recoverable from the oil. The use of $SCCO_2$ as solvent in the electronic industry at industrial scale is very limited. There are only a few number of applications, almost all based on the removal of solid particles and fat attached to the surfaces of different particles, which is known as degreasing . In addition, almost all publications in this field are patents [1] [2].

MATERIALS AND METHODS

Pure Ag and Ag-Cu alloy contacts were given by Doduco (Spain). A picture is shown in Figure 1.

Figure 1. Metal contacts used in this work.

High purity CO_2 was supplied by Air Products, Spain. Pure ethanol (Merck, Spain) was used as modifier. SAE 30 given by Dudoco was the lubricating oil.

The assays were conducted in a high pressure apparatus with CO_2 continuous flow. 30 g of contacts soaked with 1 g of oil were arranged in a fixed bed within a vessel equipped with temperature control. The CO_2 previously pressurized and heated, entered from the bottom and passed over the bed under different operating conditions for distinct periods of time. The amount of extracted oil was weighted at constant periods of time. The CO_2 consumed was measured in a mass flow meter. When the end of the operating time was reached, the depressurization began. Then, the contacts were taken for subsequent electronic microscopy images to see any oil residues on the surface.

When ethanol was used as cosolvent, a parallel pumped introduced it at the corresponding weight percentage. Both the CO_2 and the ethanol mixed in a T union before entering the vessel.

RESULTS AND DISCUSSION

The lubricating oil solubility (which corresponds to the slope of the extraction curve in the initial moments of the process when CO_2 is saturated) augmented while increasing pressure as a result of the increased density of the supercritical fluid (see Figure 2).

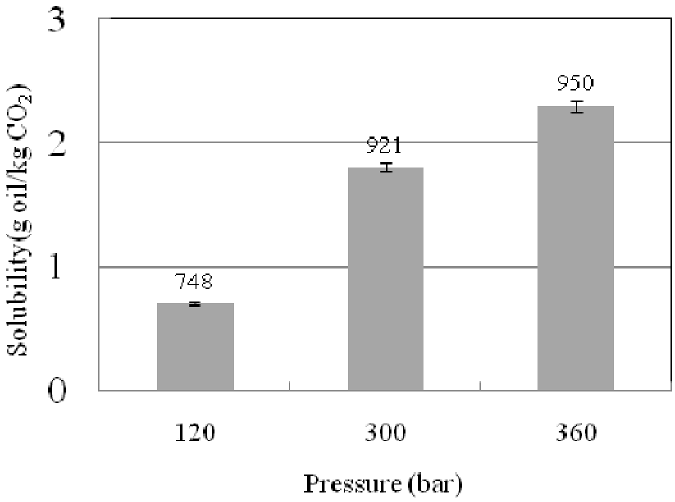

Figure 2. Pressure effect on oil solubility at 37 ºC and 2 g min^{-1}. Density values over the bars are expressed in kg m^{-3}.

Figure 3 shows that both the oil solubility and the extraction yield increased when temperature was raised. It is possible that crossover zone was exceeded so that the increased oil volatility predominated versus the reduced density. A second explanation is that the lubricating oil formed a strongly adsorbed monolayer on the metal surface whose desorption was favoured at high temperatures.

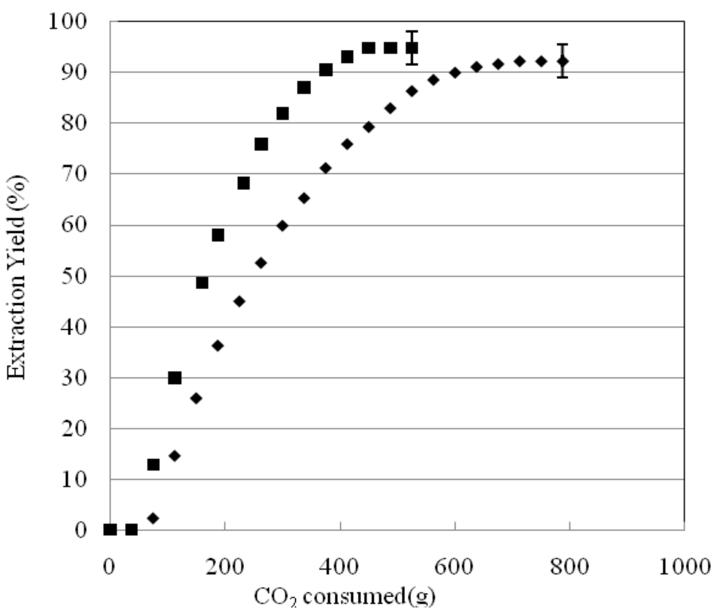

Figure 3. Temperature effect on oil extraction. ♦ 37 ºC, ■ 110 ºC at 300 bar and 2.5 g min^{-1}.

We also studied the effect of the CO_2 flow. Low flows were expected to achieve the saturation of the CO_2 so less amount of this gas was needed to achieve high yields. However Figure 4 shows the opposite. Increasing the flow, decreased the slope of the extraction curve because saturation was not reached, but provoked a strong turbulence that could have helped the desorption of the oil layer adhered to the metal surface, resulting in higher extraction yields.

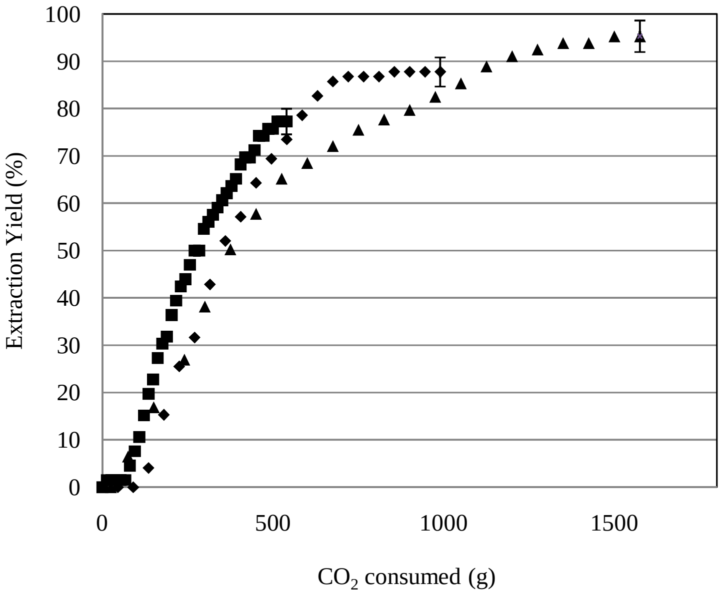

Figure 4. Effect of increasing CO_2 flow rate on oil extraction. ■ 1 g min^{-1}(8 h run), ♦ 3 g min^{-1} (5 h run), ▲ 5 g min^{-1} (5 h run).

Since even at the most extreme conditions explored in this work, it was not possible to totally remove the lubricant oil, a co-solvent was used. Thus, various percentages of ethanol were added to the CO_2. This alcohol is by far the most frequently used for the extraction oils and greases [3]. Besides, it is very volatile so easily removable from the metal on contact with air after the extraction. The investigations with this cosolvent were run at different temperatures at constant pressure (300 bar). The achieved extraction yields at a fixed operation duration are shown in Figure 5.

The presence of increased amounts of ethanol in the solvent mixture favoured the removal of the oil at both temperatures. However, if the proportion of ethanol was less than 10%, high temperatures (110ºC) were required to achieve the total removal of the lubricant oil. The electronic microscopy images of the surface of the contacts shown in Figure 6 corroborated this result. The contacts that were cleaned with pure CO_2 or at low temperatures, even with ethanol, showed oil residues. Only by the combination of high temperature and the use of ethanol, it was possible to remove all the lubricating oil.

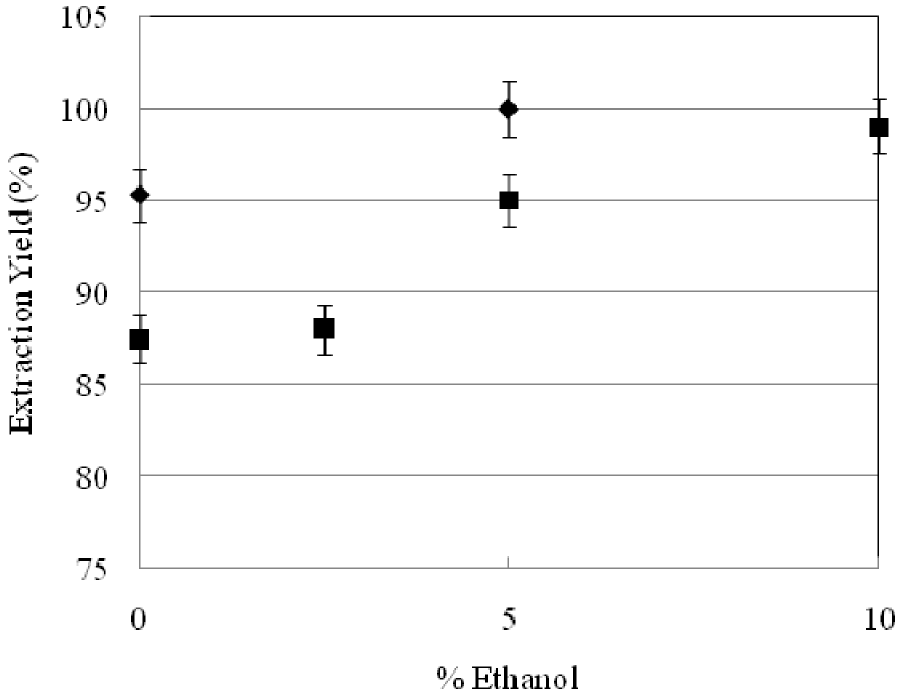

Figure 5. Ethanol effect in lubricating oil extraction yield. ■ 37 ºC, ♦ 110 ºC at 300 bar and 3 g min^{-1}, four hour runs.

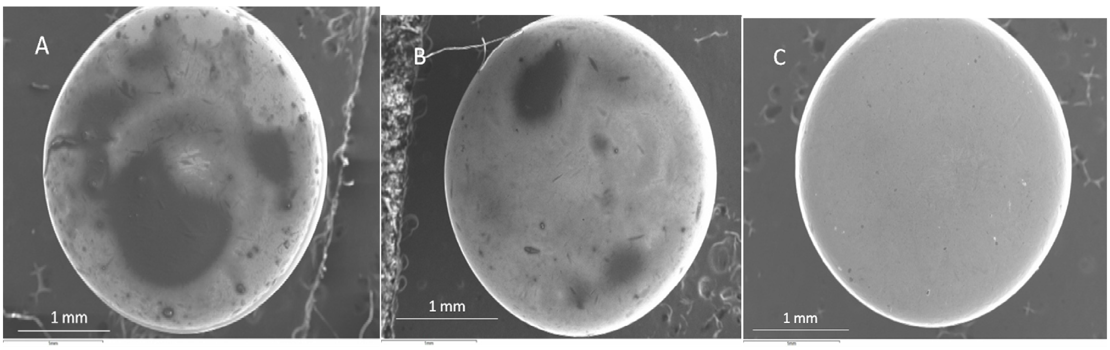

Figure 6. Electronic microscopy images of the top surface of the contacts. A) using 10% ethanol at 37 ºC; B) using pure CO_2 at 110 ºC; C) using 5% ethanol at 110ºC. Other conditions: 300 bar and 3 g min^{-1}.

CONCLUSIONS

This work shows that the CO_2 at supercritical conditions was able to solubilize the lubricating oil, although its removal was not complete under the conditions explored. Pressure improved the extraction due to density augmentation. Increased temperature and flow rate promoted the desorption of the strongly adsorbed oil layer on the metal surface. However, only with the addition of a polar cosolvent, such as ethanol, in combination with high temperature resulted in the total elimination of the oil.

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