

# SURFACTANTS FOR PARTICLE REMOVAL IN DRY-CLEANING WITH HIGH-PRESSURE CARBON DIOXIDE

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Amino acid based surfactants have been investigated for dry-cleaning with carbon dioxide. For the production of amino acid based surfactants, renewable, low-cost raw materials are used. Furthermore, these surfactants have a low toxicity, are biodegradable and not skin irritating. These characteristics make the amino acid based surfactants attractive for dry-cleaning with carbon dioxide.

The amino acid based surfactants give good results for dry-cleaning with liquid CO<sub>2</sub>. The surfactant Amihope LL (*N*-lauroyl-L-lysine) gives the best cleaning-results. Using this surfactant, an important process parameter is the addition of water. The addition of water is required for sufficient removal of non-particulate soils. It has, however, a negative influence on particulate soil removal. Therefore, a 2-bath process was proposed. The first bath has optimal conditions for particulate soil removal (no addition of water); the second bath has optimal conditions for non-particulate soil removal (water is added). The 2-bath process gives excellent results: the result for particulate soil removal is 84 % compared to the results for PER (perchloroethylene) in a commercial dry-cleaning apparatus, the result for non-particulate soil removal is 98 % compared to PER and the overall result is 92 % compared to PER.

## INTRODUCTION

The currently most used dry-cleaning solvent is perchloroethylene (PER), which is toxic, environmentally harmful and suspected to be carcinogenic. Carbon dioxide could be an ideal solvent to replace PER; carbon dioxide is non-toxic, non-flammable, ecologically sound, and available on a large scale. A disadvantage of CO<sub>2</sub> is its limited ability to dissolve polar molecules. The characteristics of CO<sub>2</sub> can be modified by the addition of a co-solvent. For dry-cleaning with CO<sub>2</sub>, various co-solvents have been investigated of which 2-propanol (IPA) was the most suitable [1]. For most non-particulate soils, the results using CO<sub>2</sub> and IPA were comparable to the results using PER. For particulate soils, however, the cleaning-results using CO<sub>2</sub> and IPA were worse than when PER was used.

Particulate soils can be removed from textile by mechanical action and/or surfactants. Relatively large particles (>20 µm) can be removed in CO<sub>2</sub> by increasing the mechanical action [2]. Increasing the mechanical action has, however, no positive influence on the removal of relatively small particles (< 20 µm) [2].

In order to remove small particles in CO<sub>2</sub>, surfactants have to be used. There is increasing interest in the use of amino acid based surfactants [3]. For the production of amino acid based surfactants, renewable, low-cost raw materials are used [4]. Furthermore, the surfactants have

a low toxicity, are biodegradable and not skin irritating. These characteristics make the amino acid based surfactants attractive for dry-cleaning with carbon dioxide. In this work, various amino acid based surfactants have been investigated. Furthermore, experiments analyzing the influence of the amount of water added to the system have been conducted.

## **EXPERIMENTAL**

### **Apparatus**

The experimental set-up is shown schematically in Figure 1. In a typical run, test fabrics attached to filling material are placed in the vessel. The cleaning vessel is closed and filled with a measured amount of CO<sub>2</sub>. After the circulation pump is turned on, the CO<sub>2</sub> flows from the vessel through the filter, the pump, and the heat exchanger back into the vessel. The apparatus is described in more detail in [1].

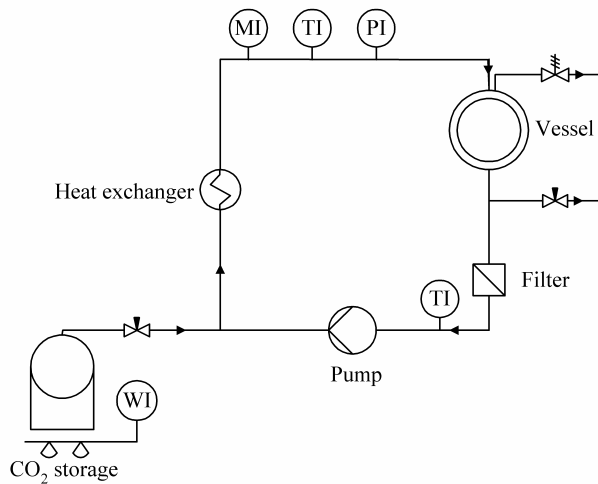
### **Materials**

To monitor the washing-results, soiled test fabrics have been used. The test fabrics have been purchased from the Center for Testmaterials B.V. (Vlaardingen, The Netherlands). Ten different kinds of test fabrics are used in the experiments described in this paper: sebum (skin fat) coloured with carbon black particles on wool (SW) and on polyester (SP); clay particles on wool (CW) and on polyester (CP); egg yolk on wool (EW) and on polyester (EP); butterfat with colorant on cotton (BC) and on polyester cotton (BPC); vegetable oil coloured with chlorophyll on cotton (OC) and on polyester cotton (OPC). The test clothes are divided into two different types: clothes soiled with non-particulate soil (EW, EP, BC, BPC, OC, OPC) and clothes soiled with particulate soil (SW, SP, CW, CP). SW and SP are soiled with both particulate (carbon black) and non-particulate soil (sebum). SW and SP are, however, considered as clothes with particulate soil, because studies on the removal of pure sebum and pure carbon black indicated that the removal of pure sebum does not pose a problem using liquid CO<sub>2</sub>, whereas pure carbon black does.

Carbon dioxide grade 3.7 is obtained from Hoek Loos B.V. (Schiedam, The Netherlands). 2-Propanol (IPA) from J.T. Baker (Deventer, The Netherlands) with a stated purity of 99%+ is used as co-solvent. The following surfactants from Ajinomoto Co., Inc. (Tokyo, Japan) were used: Amisoft LS-11 (*N*-(1-oxododecyl)-L-glutamic acid, monosodium salt), Amisoft HS-11 (*N*-(1-oxooctadecyl)-L-glutamic acid, monosodium salt), Amisoft LT-12 (*N*-(1-oxododecyl)-L-glutamic acid, comp. with 2,2',2''-nitrilotris[ethanol] (1:1)) and Amihope LL (*N*-lauroyl-L-lysine). Furthermore, tap water was used.

### **Measuring**

To determine the washing-result, the colour of the test fabrics was measured before and after washing. The way of measuring is described in more detail in [2].



**Figure 1: Experimental set-up**

The Cleaning Performance Index (CPI) is calculated to determine the washing-results. Here, the CPI is defined as:

$$CPI = \left[ 1 - \frac{\Delta E_{washed-unsoiled}}{\Delta E_{soiled-unsoiled}} \right] \times 100\% \quad (1)$$

where  $\Delta E$  is the measured colour difference in the  $L^*a^*b^*$  colour space [5].

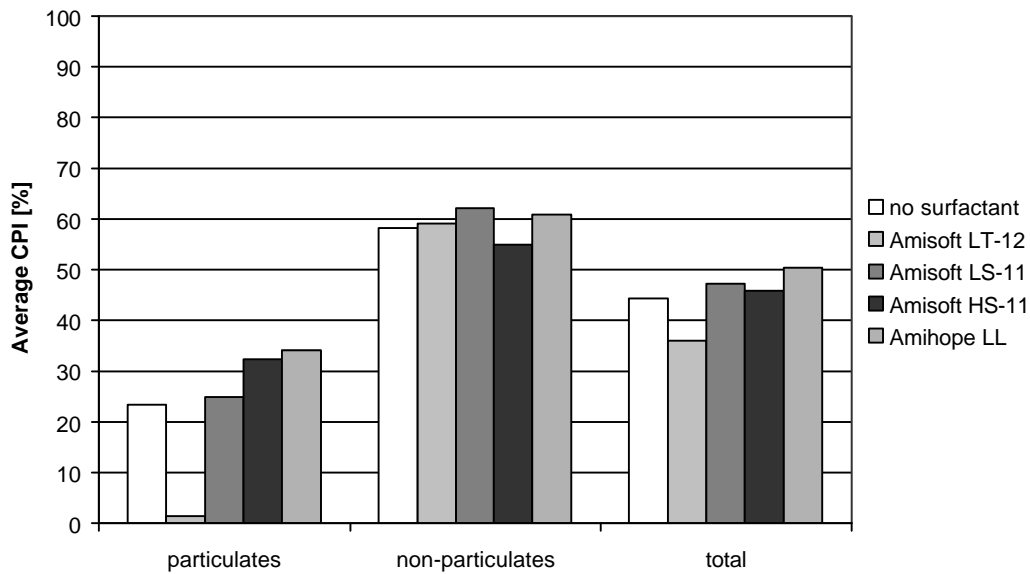
### Experiments with PER

In addition to the experiments using  $CO_2$ , the soiled fabrics have also been cleaned in PER with surfactants. This was done at a local dry cleaner's using a standard dry-cleaning procedure and apparatus, and no spotting. Spotting is a pre-treatment in which the pure detergent is physically brought into contact with the fabric.

### RESULTS AND DISCUSSION

For all experiments, the average CPI for relatively small particulate soils,  $CPI_{part}$  (the average CPI of the SW, SP, CW and CP test fabrics), the average CPI for the non-particulate soils,  $CPI_{n-p}$  (the average CPI of the EW, EP, BC, BPC, OC and OPC test fabrics), and the total average CPI,  $CPI_{total}$  (the average CPI of the ten used test fabrics), were calculated. In Figure 2, the cleaning-results are shown for the solid anionic surfactants Amisoft LS-11 and Amisoft HS-11, the liquid anionic surfactant LT-12 and the solid amphoteric surfactant Amihope LL. In the experiments, 6 kg  $CO_2$ , 25 g water, 250 g IPA and 10 g surfactant was used. Cleaning-tests with these surfactants were performed at 5.7 MPa and 293 K. The cleaning-time was 30 minutes.

During all experiments with solid surfactants, the surfactants were not completely solubilized in the liquid  $CO_2$ ; small surfactant particles were visible. The liquid surfactant Amisoft LT-12 was also not completely solubilized in the  $CO_2$ : after cleaning and rinsing fatty surfactant stains remain on the fabrics.



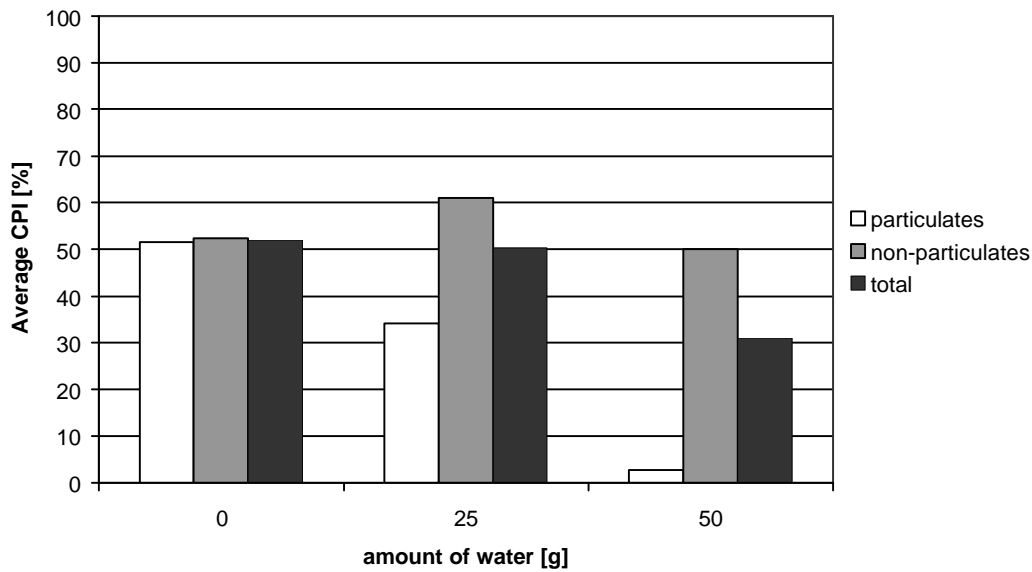
**Figure 2: Average CPI using the surfactants Amisoft LT-12, Amisoft LS-11, Amisoft HS-11 and Amihope LL**

Most surfactants have little influence on the removal of non-particulate soils. For the removal of particulate soil, Amisoft LT-12 has a clear negative influence, Amisoft LS-11 has a small positive influence, Amisoft HS-11 and Amihope LL have a large positive influence. Amihope LL gives the best overall result.

The charged surfactant molecules or particles may be responsible for the removal of the soil particles from the textile by adherence of the surfactant to the soil particles and/or fabric. If this leads to similar charging of the soil particles as well as the fabric, then this may establish an element of repulsion. This repulsion, together with mechanical action, may lead to the removal of small soil particles.

### Amount of water

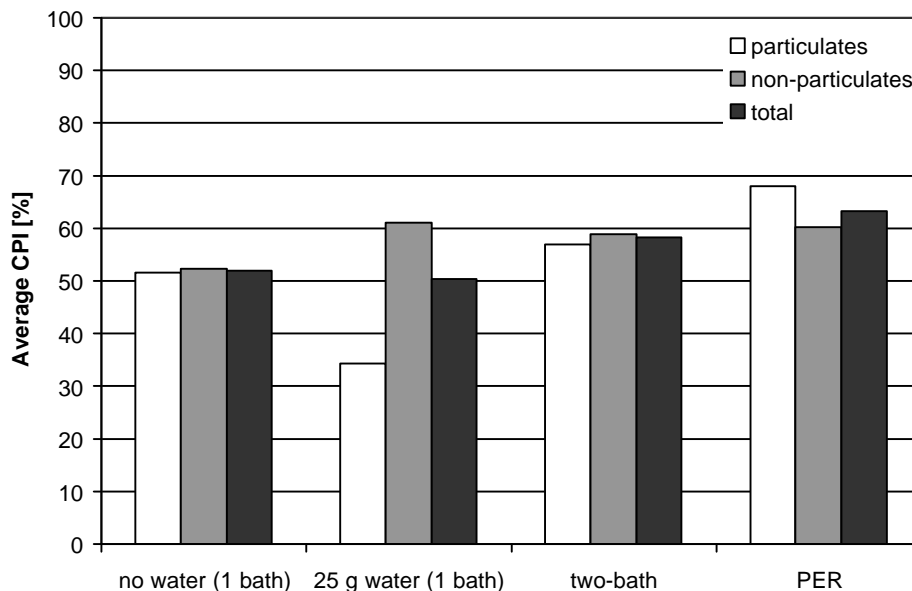
Experiments with varying process parameters show that most parameters have little or no influence on the cleaning-results for CO<sub>2</sub> using Amihope LL. These experiments showed, however, that the amount of water has a distinct influence on the cleaning-results. The amount of water added during the experiments was 0, 25 or 50 gram. 6 Kg CO<sub>2</sub>, 250 g IPA and 10 g Amihope LL was used. During the experiments, the temperature was 293 K and the pressure 5.7 MPa, the cleaning time was 30 minutes. As shown in Figure 3, the addition of water has a drastic influence on particulate soil removal; the CPI<sub>part</sub> decreases from 52 % when no water is added to 3 % when 50 g water is added. For non-particulate soil removal, however, the addition of some water is needed: the CPI<sub>n-p</sub> increases from 52 % when no water is added to 61 % when 25 g water is added. The addition of more water (50 g) has a negative result on non-particulate soil removal (the CPI<sub>n-p</sub> decreases from 61 % to 50 %).



**Figure 3: Average CPIs as function of the amount of water**

Since water has a negative influence on particulate soil removal, but a positive influence on non-particulate soil removal (up to a certain amount), a 2-bath process may be best for dry-cleaning with CO<sub>2</sub>. The first bath has optimal conditions for particulate soil removal; no addition of water. The second bath has optimal conditions for non-particulate soil removal: some water is added.

During the experiment using the two-bath process, the first bath had a temperature of 286 K and the pressure was 4.8 MPa; 6 kg CO<sub>2</sub>, 5 g Amihope LL and 250 g IPA was used; the cleaning-time was 30 minutes.



**Figure 4: Average CPIs for 1-bath CO<sub>2</sub> dry-cleaning (with/without water), 2-bath CO<sub>2</sub> dry-cleaning and dry-cleaning with PER**

In the second bath, the temperature was 298 K, the pressure 6.4 MPa; 6 kg CO<sub>2</sub>, 250 g IPA and 25 g water was used; the cleaning-time was 30 minutes. After each bath, the fabrics were rinsed with fresh carbon dioxide. The results of this experiment are given in Figure 4, which also shows the result for 1-bath dry-cleaning with and without water (already shown in Figure 3) and the results for dry-cleaning with PER in a commercial dry-cleaning apparatus.

Figure 4 shows that the results using the 2-bath process are good; particulate soil removal is even better than in the 1-bath process without water and is 84 % compared to PER, non-particulate soil removal is 98 % compared to PER. This results in an overall result which is 92 % compared to when using PER in a commercial dry-cleaning apparatus.

## CONCLUSIONS

Amino acid based surfactants can be used for dry-cleaning with liquid CO<sub>2</sub>. The surfactant Amihope LL (*N*-lauroyl-L-lysine) gives the best cleaning-results. Using this surfactant, an important process parameter is the addition of water. The addition of water is required for sufficient removal of non-particulate soils. It has, however, a negative influence on particulate soil removal. Therefore, a 2-bath process was proposed. In this process, the first bath has optimal conditions for particulate soil removal (no addition of water); the second bath has optimal conditions for non-particulate soil removal (addition of water). The 2-bath process gives excellent results: the result for particulate soil removal is 84 % compared to PER, the result for non-particulate soil removal is 98 % compared to PER and the overall result is 92 % compared to PER.

## ACKNOWLEDGEMENTS

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