Dry-cleaning with high-pressure carbon dioxide

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Proefschrift

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Summary

Dry-cleaning with high-pressure carbon dioxide

Dry-cleaning is a process for removing soils and stains from fabrics and garments which uses a non-aqueous solvent with detergent added. 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, cheap, non-corrosive, available on a large scale, and can therefore serve as a permanent sustainable alternative for the currently used solvents.

In this work, a dry-cleaning process using high-pressure carbon dioxide has been investigated and optimized.

A disadvantage of CO_2 is its limited ability to dissolve polar molecules. However, the characteristics of CO_2 can be modified by the addition of a co-solvent. Various co-solvents have been investigated of which 2-propanol (IPA) was the most suitable. For most non-particulate soils, the results using CO_2, water and IPA were comparable to the results using PER. For particulate soils, however, the cleaning-results using CO_2, water and IPA were worse than with PER.

Particulate soils can be removed from textile by mechanical action and/or surfactants. Only relatively large particles (>20 μm) could be removed in CO_2 by increasing the mechanical action. A model for quantifying the amount of mechanical action has been developed. This model was used to predict the optimal process conditions for the removal of relatively large particles, which is at maximal mechanical action. It was concluded from the model and experiments that the level of highest mechanical action in CO_2 was obtained in a two-phase environment at low pressure and temperature and that 75 RPM was the optimal number of revolutions in our system (inner-drum diameter 21 cm).

Unfortunately, increasing the mechanical action had no positive influence on the removal of small particles (< 20 μm).

In order to remove small particles in CO_2, surfactants have to be used. The addition of anionic surfactants had a distinct positive influence on the removal of particulate soil. For most anionic surfactants, however, the use of a co-solvent (which is required to remove non-particulate soils sufficiently) had a pronounced negative influence on the cleaning-results for particulate soil.

Amine surfactants also had a positive influence on the removal of particulate soils. For most amines, the use of co-solvent IPA hardly influenced the removal of particulate soil. The best overall result using CO_2 and an amine surfactant in the experimental set-up was 87 % compared to the PER bench mark.

Unfortunately, amines are skin irritants which makes them less suitable for dry-cleaning. It is for this reason that we searched for alternatives. Amino acid based surfactants have been studied. 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 are not irritating to the skin. These characteristics make the amino acid based surfactants attractive for dry-cleaning with carbon dioxide.

The amino acid based surfactants gave good results for dry-cleaning with liquid CO_2. The surfactant Amihope LL (*N*-lauroyl-L-lysine) gave the best cleaning-results. An important process parameter using this surfactant was the addition of water. The addition of water is required for sufficient removal of non-particulate soils. However, when no water was added to the system, there was a large increase in particle removal. Therefore, a 2-bath process was proposed. The first bath is for particulate soil removal and has optimal conditions for particulate soil removal; the second bath has optimal conditions for non-particulate soil removal. The 2-bath process using Amihope LL gave good results: the result for particulate soil removal was 84 % compared to the results for PER, the result for non-particulate soil removal was 98 % compared to PER and the overall result was 92 % compared to PER.

All surfactants that gave good results for particulate soil removal (anionic, amine and amino acid based surfactants) were, surprisingly, hardly soluble in CO_2 and were (largely) present as solid particles.

The mechanisms that may play a role in particulate soil removal using the surfactant Amihope LL were investigated. The cleaning action of the surfactant is probably a combination of adsorption and mechanical action. Adsorption of surfactant may cause a wedge between the fibre and the particles. Furthermore, adsorption of surfactants may reduce the Van der Waals attraction between the fibre and the soil. Surfactant particles were present in all experiments that gave good results for particle removal. The presence of surfactant particles may create more mechanical action and may cause an abrasive effect by the surfactant particles on the soil particles.

An economic evaluation shows that the costs for dry-cleaning using the optimized CO_2-process are equal to the costs of the PER-process. Recycling of the surfactant and the co-solvent can lower the costs of the CO_2-process further.

Maaike van Roosmalen

Samenvatting

Chemisch reinigen met hogedruk koolzuur

Chemisch reinigen is het proces waarbij vuil en vlekken van kleding en andere weefsels verwijderd worden en waarbij gebruik wordt gemaakt van een oplosmiddel dat niet op water is gebaseerd met daaraan toegevoegd een detergent. Het op dit moment meest gebruikte oplosmiddel voor chemisch reinigen is perchloorethyleen (PER). PER is giftig, schadelijk voor het milieu en verdacht carcinogeen. Koolzuur zou een ideale vervanger kunnen zijn voor PER; koolzuur is niet giftig, niet vlambaar, milieuvriendelijk, niet corrosief en beschikbaar op grote schaal, en kan daarom dienen als permanent duurzaam alternatief voor de op dit moment gebruikte oplosmiddelen.

Het doel van dit proefschrift is om chemisch reinigen met CO_2 vanuit een nieuw chemisch en technologisch standpunt te bekijken.

Een nadeel van het gebruik van CO_2 is de beperkte oplosbaarheid van polaire verbindingen in CO_2. De eigenschappen van CO_2 kunnen worden veranderd door het toevoegen van een co-solvent. Diverse co-solvents zijn onderzocht, waarvan 2-propanol (IPA) het meest geschikt bleek te zijn. Voor de meeste vlekken waren de reinigingsresultaten met CO_2, water en IPA vergelijkbaar met de resultaten voor PER. Voor vlekken veroorzaakt door vaste vuildeeltjes waren de resultaten met CO_2, water en IPA echter slechter dan met PER. Vuildeeltjes kunnen van textiel verwijderd worden door mechanische actie en/of een oppervlakte-actieve stof (ook wel wasactieve stof genoemd). Relatief grote vuildeeltjes (>20 µm) konden in CO_2 verwijderd worden door het vergroten van de mechanische actie. Een model is ontwikkeld voor het kwantificeren van de hoeveelheid mechanische actie. Dit model werd gebruikt om de optimale procescondities voor verwijdering van grote vuildeeltjes te voorspellen (dit is bij maximale mechanische actie). Vanuit het model en experimenten kon worden geconcludeerd dat het hoogste niveau van mechanische actie werd bereikt in een 2-fase systeem bij lage temperatuur en druk, en dat 75 toeren per minuut het optimale toerental in ons systeem was (diameter binnentrommel 21 cm).

Het vergroten van de mechanische actie had geen positieve invloed op de verwijdering van relatief kleine vuildeeltjes (<20 μm).

Om kleine vuildeeltjes te verwijderen in CO_2 moet gebruik worden gemaakt van wasactieve stoffen. Het toevoegen van anionogene oppervlakte-actieve stoffen had een duidelijk positieve invloed op het verwijderen van kleine vuildeeltjes. Helaas had bij deze oppervlakte-actieve stoffen het gebruik van een co-solvent (dat nodig is om de vlekken die niet veroorzaakt worden door vuildeeltjes te verwijderen) een uitgesproken negatieve invloed op de resultaten voor deeltjesverwijdering.

Oppervlakte-actieve stoffen met een aminogroep hadden ook een positieve invloed op de verwijdering van vuildeeltjes. Voor de meeste amines had het gebruik van de co-solvent IPA nauwelijks invloed op de deeltjesverwijdering. Het beste totaalresultaat met CO_2 en een amine in de experimentele opstelling was 87 % vergeleken met de reinigingsresultaten in een commerciële PER-machine.

Amines zijn helaas irriterend voor de huid wat ze minder geschikt maakt voor chemisch reinigen. Oppervlakte-actieve stoffen gebaseerd op aminozuren zouden een goed alternatief kunnen zijn; deze oppervlakte-actieve stoffen hebben een lage toxiciteit, zijn biologisch afbreekbaar en niet irriterend voor de huid. Verder worden voor de productie van deze stoffen duurzame en goedkope grondstoffen gebruikt. Deze eigenschappen maken de op aminozuren gebaseerde oppervlakte-actieve stoffen aantrekkelijk voor chemisch reinigen met koolzuur.

De op aminozuren gebaseerde oppervlakte-actieve stoffen gaven goede resultaten voor chemisch reinigen met vloeibaar CO_2. Amihope LL (N-lauroyl-L-lysine) gaf de beste reinigingsresultaten. Een belangrijke procesparameter bij het gebruik van deze wasactieve stof was het toevoegen van water. Het toevoegen van water is nodig voor de verwijdering van vlekken die niet veroorzaakt worden door vuildeeltjes. Het niet toevoegen van water had echter een grote positieve invloed op de verwijdering van vuildeeltjes. Een 2-badsproces zou hier uitkomst kunnen bieden: het eerste bad is voor de verwijdering van vuildeeltjes en heeft de optimale procescondities voor het verwijderen hiervan (o.a. geen water toevoegen), het tweede bad heeft optimale condities voor de verwijdering van vlekken die niet veroorzaakt worden door vuildeeltjes (o.a. wel water toevoegen). Het 2-badsproces met Amihope LL gaf goede reinigingsresultaten; het resultaat voor verwijdering van vuildeeltjes was 84 % in vergelijk met PER, het resultaat voor de verwijdering van vlekken die niet veroorzaakt worden door vuildeeltjes was 98 % in vergelijk met PER en het totaalresultaat was 92 % in vergelijk met PER.

Alle oppervlakte-actieve stoffen die goede resultaten gaven voor de verwijdering van vuildeeltjes (anionogene oppervlakte-actieve stoffen, amines en de op aminozuren gebaseerde oppervlakte-actieve stoffen) waren, tot onze verbazing, nauwelijks oplosbaar in CO_2 en waren (grotendeels) aanwezig als vaste deeltjes.

Het mechanisme dat een rol zou kunnen spelen in de verwijdering van vuildeeltjes met behulp van Amihope LL is nader onderzocht. De werking van deze oppervlakte-actieve stof is waarschijnlijk gebaseerd op een combinatie van adsorptie en mechanische actie. Adsorptie van de oppervlakte-actieve stof kan leiden tot een wig tussen de vezel en het vuildeeltje. Verder zou de adsorptie van oppervlakte-actieve stof de Van der Waals attractie tussen het vuildeeltje en de vezel kunnen reduceren. De aanwezigheid van de oppervlakte-actieve stof in de vorm van deeltjes zou meer mechanische actie kunnen creëren en tevens zouden deze deeltjes een schurende werking kunnen hebben.

Een economische evaluatie toont aan dat de kosten van chemisch reinigen met het geoptimaliseerde CO_2-proces gelijk zijn aan de kosten van het PER-proces. Het recycleren van de oppervlakte-actieve stof en co-solvent kan de kosten van het CO_2-proces verder verlagen.

Maaike van Roosmalen

Contents

Chapter 1

Introduction

1.1 Introduction

Dry-cleaning is a process for removing soils and stains from fabrics and garments which uses a non-aqueous solvent with detergent added [1].

The use of water as cleaning solvent for textiles causes dimensional changes (wrinkle, shrink, loose of shape) in yarns, fabrics and garments, because water tends to swell hydrophilic textile fibres. Non-aqueous solvents like hydrocarbons and halocarbons do not swell the fibres and have therefore no effect on the physical structure of the fabric.

1.2 History of dry-cleaning solvents [2,3]

The process of cleaning fabrics with non-aqueous liquids is believed to have begun in France in 1825. A worker in a dye and cleaning factory spilled lamp oil on a soiled tablecloth. When the tablecloth dried, the spots were gone. Turpentine and kerosene were used initially as dry-cleaning solvents, in the late 1800s, benzene, naphtha, and gasoline began to be used. In the 1920s, Stoddard (petroleum-based) solvent was introduced in the United States in order to minimize the fire hazards associated with use of the more volatile hydrocarbon-based solvents. Stoddard solvent, having a flashpoint of approximately 49°C, reduced the risk of fire and explosion, but did not eliminate it. Carbon tetrachloride, the first chlorinated solvent used for dry-cleaning, was introduced because of the high costs of hydrocarbon solvents and was widely used until the 1950s. Its use was discontinued because of its toxicity and its aggressiveness to metals, textiles, and dyes. Trichloroethylene was introduced in the 1930s. The use of perchloroethylene (PER) began to increase in the 1940s, and by the late 1950s it had virtually replaced carbon tetrachloride and trichloroethylene in commercial dry-cleaning.

Chlorofluorocarbon solvents (especially CFC-113) were introduced in the 1970s; however, because of environmental concerns (ozone depletion), their use is declining rapidly.

PER is currently the solvent of choice in most parts of the world, except in regions such as Japan, where petroleum-based solvents are used to clean approximate two third of the garments [4].

1.3 Dry-cleaning using perchloroethylene (PER) as solvent

1.3.1 Drawbacks of the use of PER [3]

PER has an extraordinary chemical stability and solvent power, and is non-flammable. However, significant adverse health and environmental effects have been discovered. PER can enter the body through both respiratory and dermal exposure. Symptoms associated with respiratory exposure to PER are: depression of the central nervous system, damage to kidneys and liver, confusion, dizziness, impaired memory, and headache. It can also cause eye, nose and throat irritation. Repeated dermal exposure may result in dry, scale, and fissured dermatitis. If PER is heated sufficiently, thermal decomposition will result in the formation of hydrogen chloride and phosgene gases. Moreover, PER is classified as probably carcinogenic to humans. PER is also an air pollutant and a groundwater contaminant. Many countries have imposed stringent regulations for the control of PER exposures and emissions; these regulations cause a growing technical expense.

1.3.2 Dry-cleaning process with PER [3]

First, garments are inspected and sorted according to weight, color, fabric, and finish. Garments with visible stains are then treated at the spotting station. Spotting involves the selective application of a wide variety of chemicals and steam to remove specific stains from the garments. Some of the more common chemicals and chemical families for spotting are chlorinated solvents, acetic acid, dilute hydrofluoric acid, hydrogen peroxide, and aqueous ammonia. Subsequently, clothes are manually loaded into the machine, followed by the solvent, to which detergent is added. The contents of the machine are then agitated for a period of time. Next, the clothes are spun at a high speed to remove the solvent.

The drying process of the clothes may occur in the same machine (dry-to-dry machines) or a different one (transfer machines). In the drying process, recirculated warm air vaporizes the residual solvent. Unheated air is subsequently passed through the system during the cool-down cycle. This step reduces wrinkles. In vented machines, this step is followed by passing fresh air through the system to freshen and deodorize the clothing; this is called the aeration step. Garments are then removed from the machine. Next, the garments are pressed.

Dry cleaner's use filtration and/or distillation to recover and purify the solvent. Filtration removes insoluble soils, nonvolatile residues, and loose dyes from the solvent and, in some cases, soluble soils. Distillation removes soluble oils, fatty acids, and greases not removed by filtration. Both filtration and distillation produce solid wastes containing PER. The equipment used for distillation and/or filtration is part of the PER-machine.

1.3.3 PER dry-cleaning machines [3]

Two basic types of machines are generally used in dry-cleaning: transfer and dry-to-dry. A picture of a PER-machine is shown in Figure 1. Transfer machines require manual transfer of solvent-containing clothing between the washer and the dryer. Transfer machines were used exclusively until the late 1960s. Dry-to-dry machines eliminate clothing transfer; clothes enter and exit the machine dry. Dry-to-dry machines can be vented or nonvented. Vented dry-to-dry machines exhaust residual solvent vapors directly into the atmosphere or through a vapor recovery system. Nonvented dry-to-dry machines are essentially closed systems, which are only open to the atmosphere when the machine door is open. These machines recirculate the heated drying air through a vapor recovery system and back to the drying drum, eliminating the aeration step. The two primary vapor recovery technologies used to recover PER vapor from dry-cleaning machines are the carbon adsorber and the refrigerated condenser. Carbon adsorbers remove PER molecules from the air by passing the PER containing air over activated carbon with a high adsorption capacity. Refrigerated condensers use a refrigerant to cool the PER containing air below the dew point of the vapor.

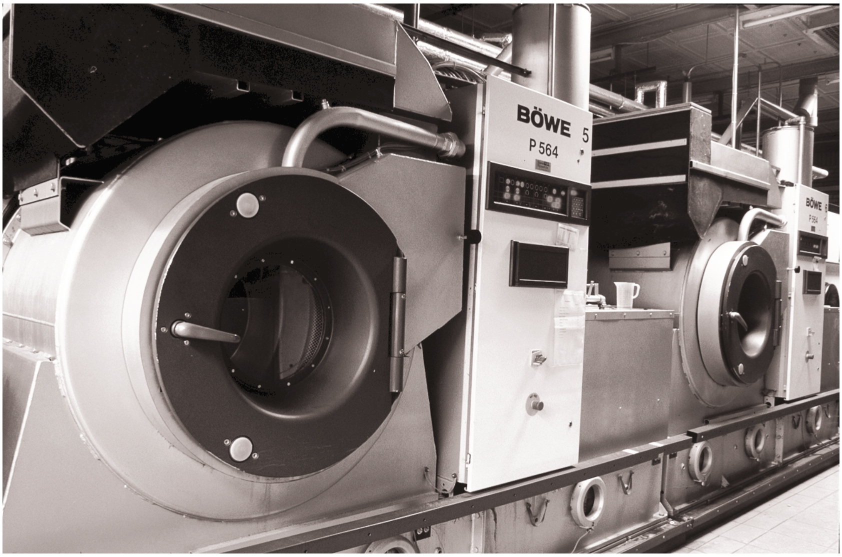

Photo: Piet Musters/ Delft Integraal

Figure 1: PER-machine

1.4 Alternatives to PER

Alternatives to PER are:

- Hydrocarbon solvents. In recent years, a new generation hydrocarbon solvents has been developed. These are paraffins having a carbon chain of eight to twelve carbon atoms e.g. n-undecane. These newer formulations are not as susceptible to explosions (having higher flashpoints), have lower volatilities and therefore lower emissions. Since they have lower volalities, the drying process takes longer than for PER. The hydrocarbon solvents are halogen- and aromatic-free. New equipment for hydrocarbon solvents has been developed to lower the danger of explosions. The hydrocarbon solvents are, however, flammable; PER is not. These solvents are less effective at removing oil and grease stains than PER [5]. While the new formulations of hydrocarbon solvents appear to be less toxic than their predecessors, further research should be done to answer remaining questions concerning the toxicity of the solvents. Furthermore, the use of these solvents can give the cleaned goods a smell [6].

- Water. Several studies report that 30 % to 70 % of the garments dry-cleaned using PER can be wet-cleaned satisfactorily while controlling fabric deterioration and shrinkage [5]. The problems using wet-cleaning are already mentioned before (shrinkage, loss of shape etc.).

  Furthermore, wet-cleaning is labor intensive (more finishing work). Water is also less effective at removing oil and grease stains than PER [5].
- New solvents like GreenEarth. GreenEarth is a silicone-based solvent. This solvent may, however, have possible health risks. Repeated inhalation or oral exposure of mice and rats to GreenEarth produced an increase in liver size. Furthermore, a statistically increase in the trend for uterine endometrial tumors was observed in female rats exposed for 24 months at 160 ppm.
- Carbon dioxide.

1.4.1 Carbon dioxide

In this work, carbon dioxide has been investigated as a dry-cleaning solvent. Carbon dioxide (CO_2) is a viable alternative for the currently used solvents. Carbon dioxide is non-toxic, non-flammable, ecologically sound, cheap, non-corrosive, and available on a large scale, and can therefore serve as a permanent sustainable alternative. Furthermore, it combines a low viscosity with a high diffusion coefficient which may enhance the cleaning efficiency (easier and faster penetration). An additional advantage of using CO_2 is that the fabrics will be dry after washing, because the carbon dioxide evaporates from the fabrics during depressurization of the cleaning-vessel. Therefore, no additional drying step is needed, which will save energy and time.

An important difference between dry-cleaning with PER or other currently used solvents, and dry-cleaning with CO_2 is that carbon dioxide dry-cleaning needs a substantially higher pressure than atmospheric pressure. Therefore, a new process for dry-cleaning had to be developed. An advantage of working with CO_2 under pressure is that it is quite easy to separate the CO_2 from the detergent formulation and the soil. If the pressure is lowered and the CO_2 becomes gaseous, few components will stay solubilized in the gaseous CO_2 phase. This will result in clean CO_2 and a compact, solvent free residue.

Commercial machines for dry-cleaning with high-pressure CO_2 are in principle available (Electrolux, Chart, Sailstar, Alliance, Comeco2). However, the availability of these machines does not imply yet that they are used on a large scale by dry cleaner's. There are two parameters that may accelerate the implementation of CO_2 dry-cleaning: low costs for CO_2 dry-cleaning, preferably cheaper than for PER, and the excellent cleaning-results, which should be comparable to the results in PER. The possibility of profits and good cleaning-results combined with a sustainable process and advanced technology may also attract newcomers to the business of dry-cleaning.

Stricter regulations on the use of PER will also accelerate the introduction of CO_2. These regulations would make dry-cleaning with PER more complicated and more expensive (because of investment costs for changing the existing machines). The EU directive to limit industrial emissions of volatile organic compounds includes that all dry-cleaning installations will have to meet fugitive losses of no more than 20 g/kg of textiles cleaned by end 2007. A complete ban on the use of PER would further accelerate the use of CO_2. In California, PER will be banned from 2020. Furthermore, from 2003 every new dry-cleaning machine installed in the district Riverside and San Bernardino (main parts of Los Angeles) has to operate PER free. Every PER dry cleaner in this area from November

2007 also has to limit the cancer risk to 25 within 1 million population [7]. Such laws do not exist in Europe or in The Netherlands yet. However, when the performance of CO_2 becomes comparable to that of PER, introduction of stricter laws may be expected. Environmentalism of existing dry-cleaners and new entrepreneurs, and of their customers may also play a role in the implementation of dry-cleaning with CO_2.

Cleaning-performance depends on four factors, also known as Sinner's factors. These are mechanical action, washing chemistry (the addition of compounds like surfactants, water and co-solvent), time and temperature. In this work, these parameters have been investigated and a new process based on the findings of these investigations has been designed. Aspects that can be designed on a routine like basis (like regeneration of the CO_2) have not been investigated. Furthermore, behaviour of the garments (wrinkling, shrinking etc.) was not a part of this investigation.
For cost estimation, an economic evaluation has been made.

The aim of this thesis is:
To approach the CO_2 dry-cleaning process from a new chemical and technological viewpoint.

1.5 Contents of this thesis

In Chapter 2, the experimental set-up used for the dry-cleaning experiments has been discussed. Chapter 3 describes the influence of mechanical action on the cleaning-results. With the aid of a model, the mechanical action on a piece of textile in a rotating drum has been described. Using the experimental set-up, the influence of various process parameters on the amount mechanical action has been studied.
CO_2 has a limited ability to dissolve polar soil molecules, therefore, polar compounds called co-solvents are added to the CO_2. In Chapter 4, the use of various short alcohols as

co-solvents has been investigated. Furthermore, the influence of process conditions (time and temperature) on cleaning-results has been considered.

In Chapter 5, various anionic and amine based surfactants have been investigated as surfactants for dry-cleaning with CO_2.

Chapter 6 describes the use of amino acid based surfactants in dry-cleaning with CO_2. Furthermore, it contains a process analysis for the cleaning process with amino acid based surfactants.

In Chapter 7, the possible cleaning-mechanisms using the solid amino acid based surfactants are discussed.

Chapter 8 compares the costs for the process using carbon dioxide with the costs for the conventional dry-cleaning process using PER.

References

[1] D.C. Tirsell, Dry cleaning, in: Ullmann’s Encyclopedia of Industrial Chemistry, Sixth Edition, 2000 Electronic release, Wiley-VCH Verlag GmbH, Weinheim 2000.

[2] IARC monographs on the evaluation of carcinogenic risk to humans: dry cleaning, some chlorinated solvents and other chemicals, Vol. 63, World Health Organization, International Agency for Research on Cancer, Lyon 1995.

[3] G.S. Earnest, A. Beasley Spencer, S.S, Smith, W.H. Heitbrink, R.L. Mickelsen, J.D. McGothlin, L.M. Ewers, Control of health and safety hazard in commercial drycleaners; Chemical exposures, fire hazards, and ergonomic risk factors, DHHS (NIOSH) Publication No. 97-150, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, 1997.

[4] J. Kurz, Global perspectives on our changing industry, presented on the U.S. Environmental Protection Agency Design for the Environment Conference, Washington DC, 1998.

[5] G.S. Earnest, R.T. Hagedorn, J.P. Flesch, Control of exposure to perchloroethylene in commercial drycleaning (substitution), DHHS (NIOSH) Publication No. 97-155, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, 1997.

[6] K.D. Hasenclever, Textilecleaning with solvents – is there a future?, in: Proceedings of the 41st wfk International Detergency Conference, Düsseldorf, Germany, 2003, p. 236.

[7] M. Seiter, Textile cleaning in liquid carbondioxide, in: Proceedings of the 41st wfk International Detergency Conference, Düsseldorf, Germany, 2003, p. 253.

Chapter 2

Experimental set-up

2.1 Apparatus

A simplified flowsheet of the experimental set-up is shown in Figure 1. The experimental set-up is also shown in Figure 2. The experimental set-up was designed and constructed at the Laboratory for Process Equipment, Delft University of Technology (Delft, The Netherlands). The cleaning-vessel was constructed at Van Steen Apparatenbouw B.V. (Pijnacker, The Netherlands). The vessel is shown in Figures 3 and 4. It has an inside diameter of 0.25 m, a length of 0.55 m and volume of 25 l. The wall thickness of the vessel is 15 mm. A rotating inner-drum is mounted inside the cleaning-vessel to provide the necessary mechanical action. This inner-drum, with a diameter of 0.21 m, a length of 0.295 m and a volume of 10 l, is perforated. The holes have a diameter of 4 mm with a distance of 7 mm from center to center. The inner drum has 3 baffles with a height of 25 mm. The inner drum is closed at the cloth input side with a lid. On the other side, the inner drum is connected to a rotating shaft. This shaft passes through the wall of the high-pressure vessel to the motor (SEW R32DT71D4, Vector Aandrijftechniek B.V., Rotterdam, The Netherlands) via a seal (Saint-Gobain Performance Plastics, Kontich, Belgium) made of Rulon “K” and bearings. The motor is PLC controlled (Getronics, Amsterdam, The Netherlands) and the machine can run complete washing programs. The vessel and the rotating drum are made from Stainless Steel 304. The vessel has a quick-closure (T.D. Williamson LTD., Swindon, United Kingdom), which allows easy and fast opening and closure of the vessel. This closure is also constructed from Stainless Steel 304.

Before the fluid from the vessel enters the pump, it passes through a filter in order to remove particles, threads etc.

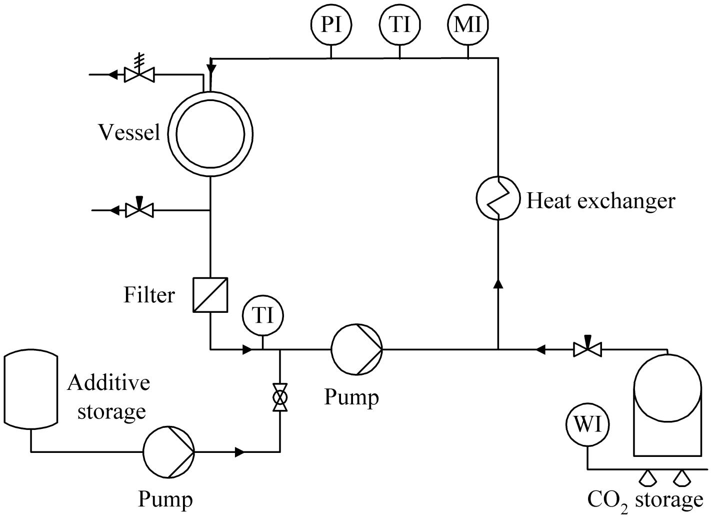

Figure 1: Flowsheet of experimental set-up

The filter house has a height of 130 mm and an outside diameter of 125 mm and is made of Stainless Steel 304. The filter plate has a diameter of 74 mm. The minimal pore size of the filter is 11 µm. The filter material (Krebsöge Filters GmbH, Radevormwald, Germany) consists of Stainless Steel. The filter house was designed and constructed at the Laboratory for Process Equipment, Delft University of Technology (Delft, The Netherlands).

The pump is a 1.5 HP MagnePump (Autoclave Engineers, Pennsylvania, USA).

During each cycle of circulation, the CO_2 passes through a heat exchanger contained in a cylinder with service fluid (water). The heat exchanger was designed to cool and heat CO_2. When the system is closed, the system pressure increases during heating of the CO_2 and decreases when the CO_2 is cooled down. The heat exchanger consists of a 4 m long spiral tube with an inner diameter of 11 mm (height 500 mm, diameter 80 mm), through which the CO_2 flows. Water flows through a PVC pipe (height 500 mm, diameter 120 mm) around the spiral. From this pipe, the water flows through a circulation heater/cooler (UC-022-1-H, Peter Huber Kältemaschinenbau GmbH, Offenburg, Germany) and back. The temperature of the water can be regulated between 263 K and 333 K.

The temperature, pressure, density, and mass flow are monitored. The mass flow is monitored by a MASSFLO® mass flow meter (N.V. Danfoss S.A., Brussels, Belgium), which also measures volume flow, density, temperature and has a totalizer. The mass flow meter consists of a MASS 2100, DI 15 sensor and a MASS 3000 signal converter. The pressure is measured using a Cerabar T pressure indicator (Endress+Hauser B.V., Naarden, The Netherlands). During the first two years of experiments, the temperature of the CO_2 was measured after the pump using an HMP-234-A humidity sensor (Vaisala, Helsinki, Finland). This sensor has been replaced by a PT 100 (CasCade Automation Systems B.V., Ridderkerk, The Netherlands) before the pump.

Additives can be gradually added to the circulation stream by means of a pump (LEWA EK-1, LEWA, Leonberg, Germany).

The external supply of CO_2 is a heated 2780 liter vessel containing CO_2 grade 3.7 supplied by Hoek Loos B.V. (Schiedam, The Netherlands).

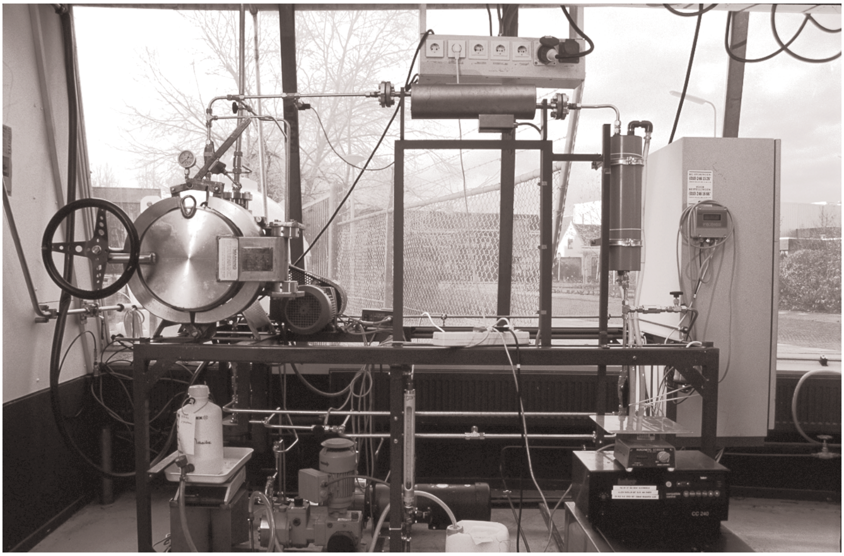

Photo: Piet Musters/ Delft Integraal

Figure 2: Experimental set-up

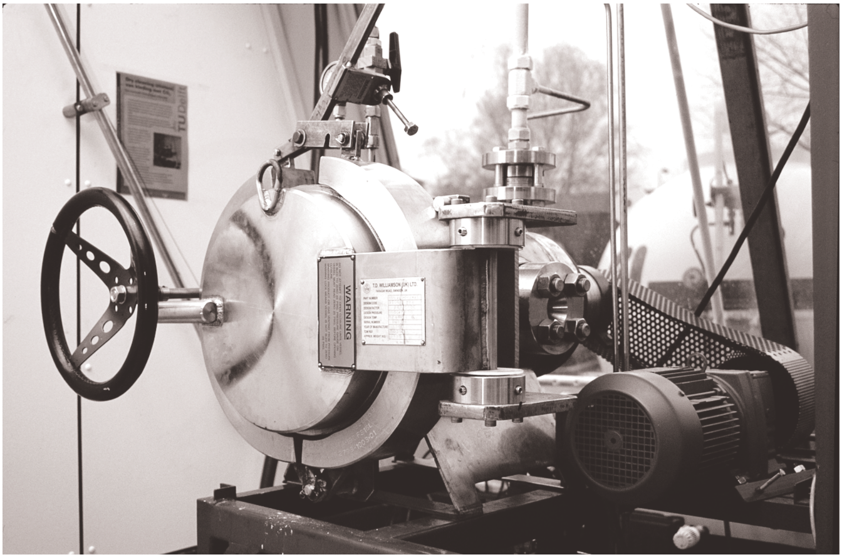

Photo: Piet Musters/ Delft Integraal

Figure 3: Cleaning-vessel (closed)

Photo: Piet Musters/ Delft Integraal

Figure 4: Cleaning-vessel (open)

The valves are supplied by Parker Hannifin plc (Barnstaple, United Kingdom). They are manually operated. The tubing consists of SS 316 with an outer diameter of ½ inch. The tubing is attached to the vessel, the pump, heat exchanger, filter and valves with A-lok tube fittings (Parker Hannifin plc, Barnstaple, United Kingdom).

2.2 Operation procedure

In a typical run, test fabrics are attached to cotton filling material. The test fabrics and the cotton filling material (approximately 400 gram) are placed in the drum. Additives can be added directly to the fabrics in the drum or can be added to the CO_2-circulation stream by means of a pump. The fabrics can also be pre-soaked in an additive solution before the test fabrics and the filling fabrics are placed in the drum.

The cleaning-vessel is closed and filled with a measured amount of CO_2 (using the totalizer of the mass flow meter). After the circulation pump is turned on, the CO_2 flows from the vessel through the filter, the pump, and the heat exchanger back into the vessel. After the washing step, the used CO_2 is replaced by fresh CO_2, which is circulated for another 10 minutes. After this rinsing step, the vessel is depressurized and the dry pieces of textile are removed.

2.3 Materials

To monitor the cleaning-results, soiled test fabrics have been used. In the experiments, test fabrics made of natural fibres as well as synthetic fibres are used. The natural fibres used are wool and cotton, the synthetic fibre used is polyester. A mix of natural and synthetic fibres is also used; this is polyester cotton. The size of the test fabrics is 6.5 cm x 7.5 cm.

From a detergency point of view, soils can be divided into five categories: oily and greasy soils, water-soluble soils, particulate soils, oxidizable or bleachable soils, and proteins and starchy soils [1].

Six different kinds of soils are used in the experiments described in this thesis:

- sebum (skin fat) coloured with carbon black (oily and greasy soils combined with particulate soils)
- clay particles (particulate soils)
- sand particles (particulate soils)
- butterfat with colorant (oily and greasy soils)
- egg yolk (proteins and starchy soils, oily and greasy soils)
- vegetable oil coloured with chlorophyll (oily and greasy soils, combined with oxidizable or bleachable soils)

Table 1: Used test fabrics and their abbreviations

	Wool	Polyester	Cotton	Polyester cotton
Sebum (skin fat) coloured with carbon black	SW	SP		
Clay particles	CW	CP		
Sand particles			SC	
Butterfat with colorant			BC	BPC
Egg yolk	EW	EP		
Vegetable oil coloured with chlorophyll			OC	OPC

All but the sand soiled test fabrics have been purchased from the Center for Testmaterials B.V. (Vlaardingen, The Netherlands). The sand has been purchased at Filcom B.V. (Papendrecht, the Netherlands) and the sand test fabrics were prepared at the Laboratory for Process Equipment. The used test fabrics and their abbreviations are shown in Table 1.

The chemicals used are specified in the chapters.

2.4 Measuring

To monitor the cleaning-results, the colour of the test fabrics was measured before and after cleaning. This was done with a spectrophotometer (Spectrocam 75 RE) using Standard Illuminant C as light source (average daylight, excluding ultraviolet light). The viewing angle used is the CIE 10º Supplementary Standard Observer. The test fabrics are measured using the $L^*a^*b^*$ colour space, where L^* indicates the lightness, and a^* and b^* are the chromaticity coordinates; $+a^*$ is the red direction, $-a^*$ the green direction, $+b^*$ the yellow direction, and $–b^*$ the blue direction. In this colour space, the colour difference ΔE is defined by the following equation:

$$\Delta E_{1-2} = \left((L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2\right)^{1/2} \tag{1}$$

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

$$\mathrm{CPI} = \left[1 - \frac{\Delta E_{\text{washed}-\text{unsoiled}}}{\Delta E_{\text{soiled}-\text{unsoiled}}}\right] \times 100\% \tag{2}$$

The cleaning-results of the sand soiled test fabrics are measured by weight difference. The percentage of sand removed (Wt%) is calculated using:

$$\mathrm{Wt\%} = \left[1 - \frac{\text{mass}_{\text{washed}} - \text{mass}_{\text{unsoiled}}}{\text{mass}_{\text{soiled}} - \text{mass}_{\text{unsoiled}}}\right] \times 100\% \tag{3}$$

References

[1] W.G. Cutler, R.C. Davis, Detergency; theory and test methods Part I, Dekker, New York 1972.

Chapter 3

The influence of mechanical action on cleaning-results

M.J.E. van Roosmalen, M. van Diggelen, G.F. Woerlee, G.J. Witkamp

Abstract

Previous studies indicate that the removal of non-polar soils in CO_2 is comparable to the level of dry-cleaning in perchloroethylene (PER). However, these studies show that the removal of particulate soil is insufficient in CO_2 compared to PER. Particle removal can be increased by the use of more mechanical action and/or the use of surfactants. From experiments, it is concluded that the removal of relatively large particles like sand increases with increasing mechanical action. However, the level of mechanical action has no influence on the removal of relatively small particulate and non-particulate soils (with the exception of clay on wool). Increasing the amount of mechanical action is therefore not the solution that will lead to the increase of the cleaning-results for relatively small particles (like carbon black and clay) up to the level of the cleaning-results using PER. The removal of relatively small particulate soils in CO_2 can be improved by the use of suitable surfactants that reduce adhesion forces.

A model for quantifying the amount of mechanical action has been developed. This model can be used to predict the optimal process conditions for relatively large particle removal. It is concluded (from the model and experiments) that the level of highest mechanical action in CO_2 is obtained in a two-phase environment at low pressure and temperature and that 75 RPM is the optimal number of revolutions in our system. At these conditions, however, the cleaning-results for small particles are not as good as the cleaning-results for these particles in PER.

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3.1 Introduction

Commercial dry-cleaning systems currently employ potentially toxic and environmentally harmful solvents. The most commonly used dry-cleaning solvent is perchloroethylene (PER), which is suspected to be carcinogenic. Other solvents used are chlorinated fluorocarbons and hydrocarbons, especially paraffins. There are increasing restrictions on the use of these dry-cleaning solvents.

Carbon dioxide (CO_2) is a viable alternative for these solvents. Carbon dioxide is non-toxic, non-flammable, ecologically sound, and available on a large scale. Therefore, it can serve as a permanent alternative for hydrocarbon solvents. An additional advantage of using CO_2 is that the fabrics will be dry after cleaning, because the carbon dioxide evaporates from the fabrics during depressurization of the cleaning-vessel. Therefore, no additional drying step is needed.

Previous studies by Gosolitis et al. [1] and Van Roosmalen et al. [2] indicate that the removal of non-polar soils in CO_2 is comparable to the level of cleaning in PER. However, these studies show that the removal of particulate soil is insufficient in CO_2 compared to PER. Particle removal can be increased by the use of more mechanical action and/or the use of surfactants. The prevailing mechanism of soiling by relatively large particles (like sand) is particle entrapment between the fibres in the yarn and between the yarns in the weave. For the removal of these soils, mechanical action is probably the most important factor. The adherence of small soil particles, like carbon black and clay, is primarily caused by Van der Waals forces [3, 4]. In certain cases, soil particles are not only held by molecular forces, but may also be occluded in microscopic holes or crevices. Investigations with a Scanning Electron Microscope (SEM) (Figures 1 and 2) show that in the case of carbon black the particles are primarily deposited at the surface of the fibres, whereas clay particles tend to agglomerate and collect in cracks and holes. The removal of relatively small particles is probably a combination of the use of surfactants and mechanical action.

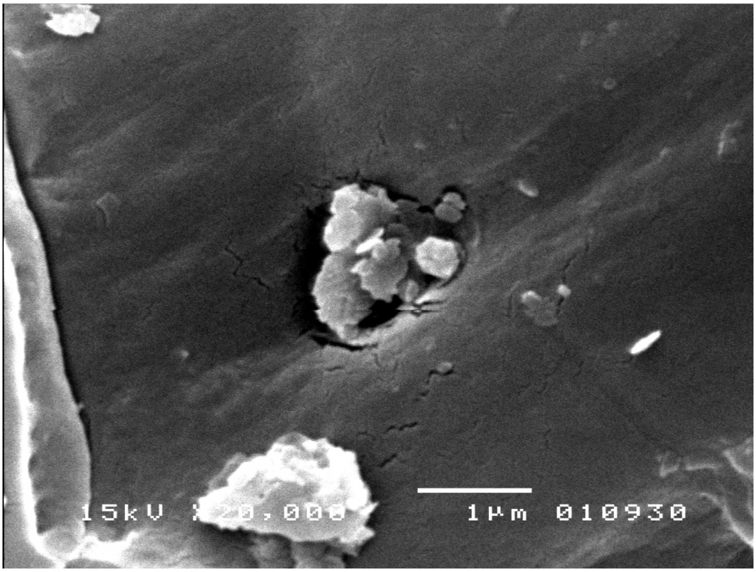

Figure 1: Agglomerated clay particles collected in cracks and holes

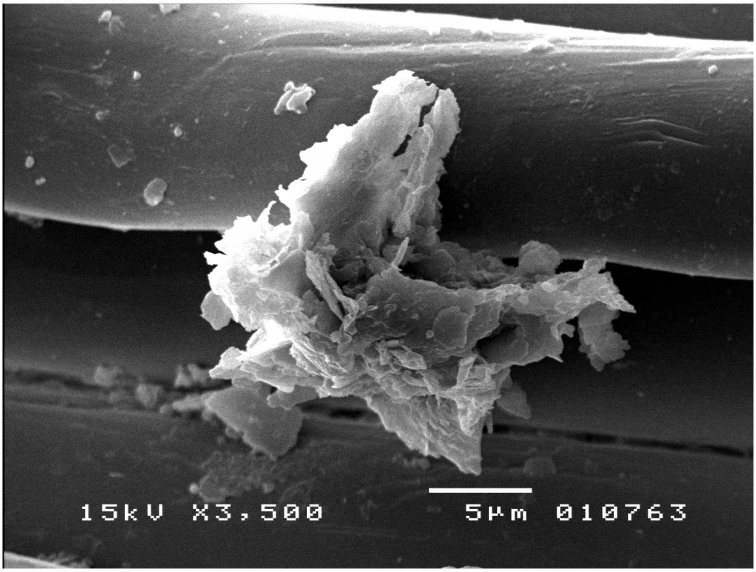

Figure 2: Carbon black particles deposited at fibre surface

In this chapter, the influence of mechanical action on the removal of particles is investigated.

Mechanical action can be brought into a washing machine by a rotating inner-drum. A model has been developed to describe the movement of the fabrics inside the pressurized vessel and to quantify the level of mechanical action as a function of the rotational speed of the inner-drum and process conditions. Furthermore, the model will be used to calculate the optimal inner-drum diameter.

3.2 Theory

This model is based on a study of the hydrodynamics in household washing machines by Van den Brekel [5]. In this study, four main movements of fabric are distinguished (Figure 3):

1. Pulling of the fabric through the liquid in the inner-drum.
2. Lifting the fabric out of the liquid.
3. Falling of the fabric through the drum.
4. Impact of fabric on the wall (or on the liquid) after falling.

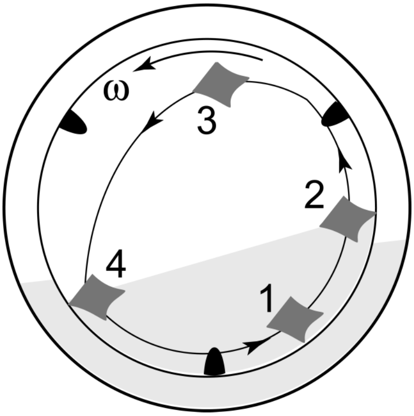

Figure 3: Path of a piece of fabric in a rotating drum

These four movements are all present in a drum partially filled with liquid and partially filled with gaseous carbon dioxide. In supercritical carbon dioxide, however, the second movement is not present. The movements create pressure drops across the fabric resulting in physical transport of the cleaning liquid and dirt through the fabric. Moreover, they also cause deformation of the fabric, which also contributes to soil removal.

The pressure drop across the fabric has been calculated for each movement in both CO_2 as well as in PER. The largest difference in pressure drop comparing the two solvents was seen for the impact (movement 4). Therefore, only the impact is considered in the model. After falling, the piece of textile will either hit the wall or the liquid surface depending on the liquid level. Here, the liquid level is assumed to be low enough for the piece of textile to hit the wall.

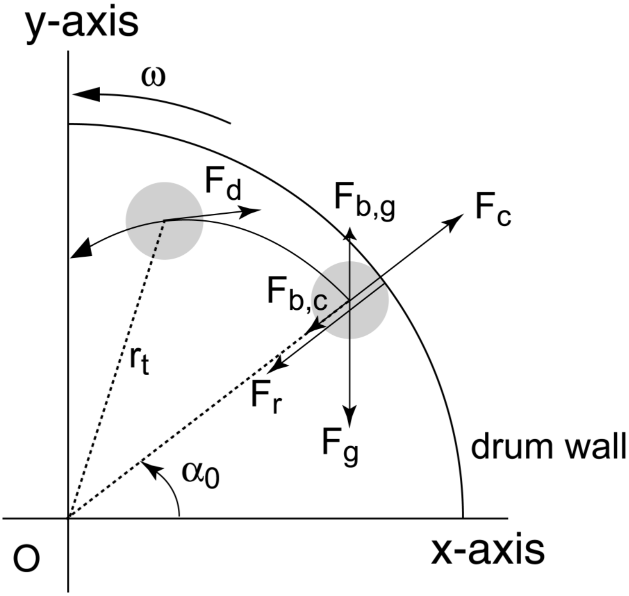

Figure 4: Free Body Diagram of a piece of textile in a rotating drum

The following simplifications of the process are made: the drum is regarded as a horizontally mounted cylinder rotating around its axis; the influence of the baffles, the perforation of the drum wall and the influence of both cylinder ends are neglected; the friction between the fabric and the wall is assumed to be high enough to prevent the fabric from sliding along the wall; the laundry is regarded as one small cylinder with a diameter and length of 0.05 m; the rotational motion of the fabric is neglected; and the inner-drum is rotating anti-clockwise. Based on these assumptions, the path of movement 4 is determined by the forces shown in Figure 4.

Using the force balance in radial direction, the point at which the piece of textile leaves the wall can be calculated with:

$$\vec{F}_{c,net} = \vec{F}_{g,net} \sin\alpha_0 \tag{1}$$

with $$\vec{F}_{c,net} = \vec{F}_c + \vec{F}_{b,c} = (m_{plug} - V_{plug}\rho_{gCO_2})\,\omega^2 \vec{r}_t \tag{2}$$

$$\vec{F}_{g,net} = \vec{F}_g + \vec{F}_{b,g} = (m_{plug} - V_{plug}\rho_{gCO_2})\,\vec{g} \tag{3}$$

where $\vec{F}_{c,net}$ [N] is the net centrifugal force; $\vec{F}_{g,net}$ [N] the net gravitational force; α_0 [rad] the angle at which the plug leaves the wall; $\vec{F}_{b,c}$ [N] the centrifugal buoyancy force; $\vec{F}_{b,g}$ [N] the gravitational buoyancy force; m_{plug} [kg] the mass of the textile plug, depending on the amount of fluid absorbed; V_{plug} [m^3] the volume of the textile plug; ρ_{gCO_2} [kg m^{-3}] the density of the gaseous CO_2; ω [rad s^{-1}] the angular velocity; $\vec{r}_t$ [m] the distance from the middle of the drum to the middle of the textile cylinder and $\vec{g}$ [m s^{-2}] the gravitational acceleration.

The drag forces are not mentioned in eq. (1), because up to the point where the plug leaves the wall, the reaction force of the drum ($\vec{F}_r$) compensates for the drag forces.

m_{plug} is given by:

$$m_{plug} = m_{textile} + m_{lCO_2} + m_{gCO_2} = V_{textile}\rho_{textile} + V_{lCO_2}\rho_{lCO_2} + V_{gCO_2}\rho_{gCO_2} \qquad (4)$$

Since there are no data available on liquid CO_2 absorption by textile, it is assumed that the amount of liquid carbon dioxide absorbed by textile is the same as the amount of water absorbed by textile. The volume fractions of textile, liquid CO_2 and gaseous CO_2 in the plug were, therefore, calculated from experiments using water. The calculated volume fractions are: volume fraction textile 0.1, volume fraction liquid CO_2 0.3 and volume fraction gaseous CO_2 0.6.

Equation (4) now becomes:

$$m_{plug} = \left(0.1\rho_{textile} + 0.3\rho_{lCO_2} + 0.6\rho_{gCO_2}\right) V_{plug} \qquad (5)$$

The density of the fibres used in the experiments described in this chapter is between 1100 kg/m^3 and 1500 kg/m^3, therefore we take a density of 1300 kg/m^3 for the textile.

Combining (1), (2) and (3) gives:

$$\sin\alpha_0 = \frac{\omega^2 r_t}{g} \qquad (6)$$

It is essential that the angular velocity does not exceed a critical value. Above this value, the textile plug will stick to the wall, depriving it from free fall and most of the mechanical action.

The initial velocity v_0 in x- and y- direction is given by:

$$v_{xo} = -r_t \omega \sin\alpha_0 \tag{7}$$

$$v_{yo} = r_t \omega \cos\alpha_0 \tag{8}$$

The path of the textile plug after leaving the wall is calculated using the following equations for each point of the path:

$$\vec{v}(t) = \vec{v}_0 + \int \vec{a}(t)dt \tag{9}$$

$$\vec{S}(t) = \vec{S}_0 + \int \vec{v}(t)dt \tag{10}$$

where $\vec{S}$ [m] is the position of the textile plug in the inner-drum, $\vec{a}$ [m s^{-2}] the acceleration, and t [s] the time.
Acceleration $\vec{a}$ is calculated using:

$$m_{plug}\vec{a} = \vec{F}_{g,net} + \vec{F}_d \tag{11}$$

Drag force $\vec{F}_d$ [N] is calculated using the following equation [6]:

$$\vec{F}_d = -\frac{1}{2} c_d \rho_{gCO_2} A_{plug} \vec{v}|v| \tag{12}$$

where c_d [-] is the drag coefficient; A_{plug} [m^2] the cross sectional area of the textile plug upon which the force $\vec{F}_d$ acts and v [m s^{-1}] the velocity of the textile plug. The textile plug is modelled as a cylinder at high Reynolds number, therefore we take c_d is 1 [6].

Combining (3), (11) and (12) gives:

$$m_{plug}\vec{a} = (m_{plug} - V_{plug}\rho_{gCO_2})\vec{g} - \frac{1}{2}\rho_{gCO_2}A_{plug}\vec{v}|v| \tag{13}$$

where $$A_{plug} = l_{plug}D_{plug} \tag{14}$$

$$V_{plug} = \frac{1}{4}\pi D_{plug}^2 l_{plug} \tag{15}$$

where l_{plug} [m] is the length of the textile plug and D_{plug} [m] the diameter of the textile plug.

The impact velocity and position can be calculated using equations (9) and (10). We assume that only the radial component of the velocity attributes to mechanical action, because the radial component will cause the direct deformation of the textile plug. Therefore, in the calculation of the impact velocity the tangential component is neglected.

3.3 Experimental

3.3.1 Apparatus

The experimental set-up is shown schematically in Figure 5. The cleaning-vessel has an inside diameter of 0.25 m and volume of 25 l. A rotating inner-drum is mounted inside the cleaning-vessel to provide the necessary mechanical action. This inner-drum, with a diameter of 0.21 m and a volume of 10 l, is perforated and connected to a rotating shaft. This shaft passes through the wall of the high-pressure vessel to the motor via a seal and bearings. The motor is PLC controlled and the machine can run complete washing programs. Before the fluid from the vessel enters the pump, it passes through a filter (pore size 11 µm), in order to remove particles, threads etc. During each cycle of circulation, the CO_2 passes through a heat exchanger contained in a cylinder with service fluid. The temperature of the service fluid can be regulated between 263 K and 333 K by a circulation heater/cooler, allowing the pressure in the closed CO_2 circulation to increase or decrease. The temperature, pressure, density and mass flow are monitored. Additives can be gradually added to the circulation stream by means of a pump.

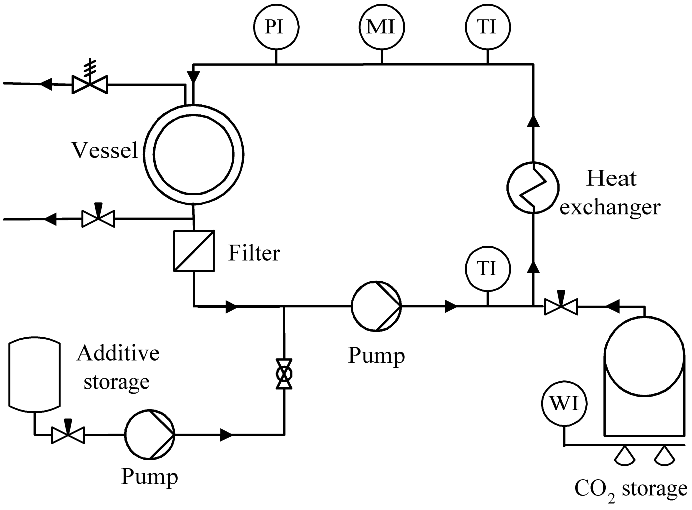

Figure 5: Experimental set-up

3.3.2 Operation procedure

In a typical run, test fabrics attached to filling material are placed in the drum. The cleaning-vessel is closed and filled with a measured amount of CO_2 After the circulation pump is turned on, the CO_2 flows from the vessel through the filter, the pump, and the heat exchanger back into the vessel. Additives can be added to the circulation stream by means of a pump.

Preliminary experiments have shown that most of the cleaning is done in the first 30 minutes. Therefore, the CO_2 is circulated for 30 minutes after which the used CO_2 is replaced by fresh CO_2, which is circulated for another 10 minutes. After this rinsing step, the vessel is depressurized and the dry pieces of textile are removed.

3.3.3 Materials

Carbon dioxide grade 3.7 is obtained from Hoek Loos B.V. (Schiedam, The Netherlands). A disadvantage of CO_2 is its limited ability to dissolve polar molecules. However, this can partly be overcome by the addition of polar compounds as co-solvents. Here, three additives are used: tap water to counteract the extraction of water from the fabric by CO_2, 1-tert-butoxy-2-propanol (TBP) from Sigma-Aldrich Chemie B.V (Zwijndrecht, The Netherlands) with a purity of 98 %+ as a co-solvent and 2-propanol (IPA) from J.T. Baker (Deventer, The Netherlands) with a stated purity of 99 %+ also as co-solvent. The used standard solution of additives consists of 77 wt% IPA, 15 wt% TBP and 8 wt% water.

To monitor the cleaning-results, soiled test fabrics have been used. These test fabrics are made of wool, polyester, cotton or a combination of cotton and polyester. The test fabrics are attached to cotton filling material.

From a detergency point of view, soils can be divided into five categories: oily and greasy soils, water-soluble soils, particulate soils, oxidizable or bleachable soils, and proteins and starchy soils [4]. Four different kinds of soils are used in the experiments described in this chapter:

- sebum coloured with carbon black (oily and greasy soils combined with particulate soils)
- butterfat with colorant (oily and greasy soils)
- clay particles (particulate soils)
- sand particles (particulate soils)

All but the sand soiled test fabrics have been purchased from the Center for Testmaterials B.V. (Vlaardingen, The Netherlands). The sand has been purchased at Filcom B.V. (Papendrecht, the Netherlands) and the sand test fabrics were prepared at the Laboratory for Process Equipment. The used test fabrics and their abbreviations are shown in Table 1.

Table 1: Used test fabrics and their abbreviations

	Wool	Polyester	Cotton	Polyester cotton
Sebum (skin fat) coloured with carbon black	SW	SP		
Butterfat with colorant			BC	BPC
Clay particles	CW	CP		
Sand particles			SC	

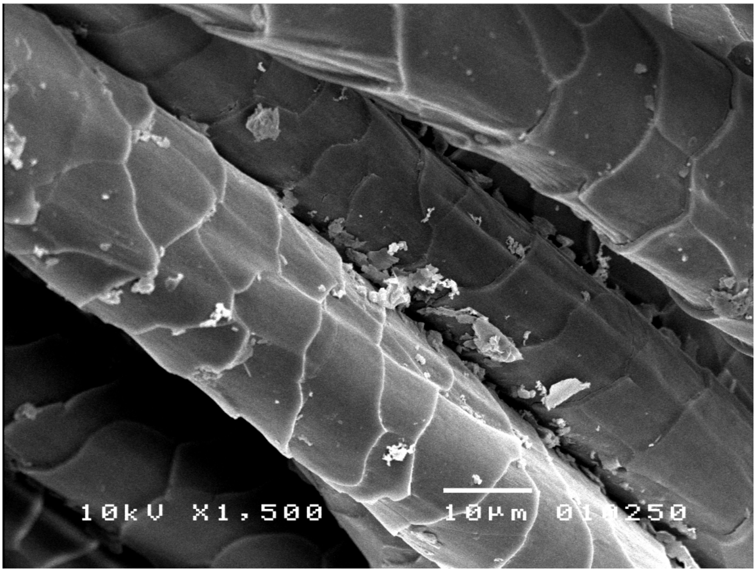

Figure 6: Sebum with carbon black on wool

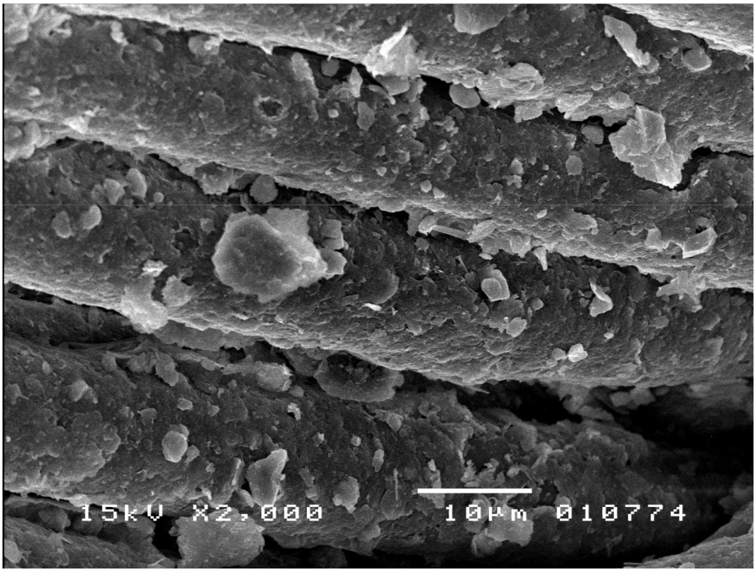

Figure 7: Clay on wool

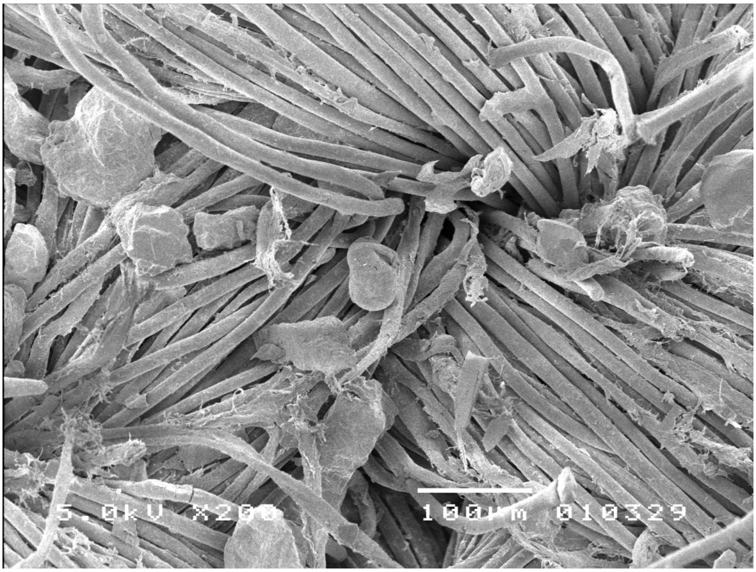

Figure 8: Sand on cotton

Studies with a SEM (see Figures 1, 2, 6, 7 and 8) give insight into the particle size of the three particulate soils used (Table 2).

Table 2: Size of particles

Soil	Particle Size [μm]
Sand	20 – 100
Carbon black	0 – 20
Clay	0 – 10

3.3.4 Measuring

To monitor the cleaning-results, the colour of the test fabrics was measured before and after cleaning. This was done with a spectrophotometer (Spectrocam 75 RE) using Standard Illuminant C as light source (average daylight, excluding ultraviolet light). The viewing angle used is the CIE 10º Supplementary Standard Observer. The test fabrics are measured using the $L^*a^*b^*$ colour space, where L^* indicates the lightness, and a^* and b^* are the chromaticity coordinates; $+a^*$ is the red direction, $-a^*$ the green direction, $+b^*$ the yellow direction, and $-b^*$ the blue direction. In this colour space, the colour difference ΔE is defined by the following equation:

$$\Delta E_{1-2} = \left((L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2\right)^{1/2} \qquad (16)$$

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

$$\mathrm{CPI} = \left[1 - \frac{\Delta E_{\mathrm{washed-unsoiled}}}{\Delta E_{\mathrm{soiled-unsoiled}}}\right] \times 100\% \qquad (17)$$

The cleaning-results of the sand soiled test fabrics are measured by weight difference. The percentage of sand removed (Wt%) is calculated using:

$$\mathrm{Wt\%} = \left[1 - \frac{\mathrm{mass}_{\mathrm{washed}} - \mathrm{mass}_{\mathrm{unsoiled}}}{\mathrm{mass}_{\mathrm{soiled}} - \mathrm{mass}_{\mathrm{unsoiled}}}\right] \times 100\% \qquad (18)$$

3.3.5 Experiments with PER

The soiled fabrics have also been washed in PER. This was done at a local dry cleaner's using a standard dry-cleaning procedure and no spotting. Spotting is a pre-treatment in which the detergent is physically brought into contact with the fabric. Spotting is a common method in the dry-cleaning industry for dealing with difficult stains.

3.4 Results and discussion

In a previous publication [2], first cleaning-results have been presented. Here, new test fabrics are introduced (CP, CW, SC) to study the removal of particles. Figure 9 shows the results of CO_2 dry-cleaning without additives, with additives gradually added to the circulation stream, and with the textile spotted with additives, all at 4.5 MPa and 283 K. Furthermore, the results with supercritical CO_2 (7.5 MPa, 311 K) as cleaning fluid are shown. In the experiments, the standard additive solution was used. The cleaning-results for PER are also given.

As can be seen in Figure 9, under all conditions butterfat (BC, BPC) was removed well. This is because of the high solubility of the butterfat in the non-polar carbon dioxide. Sebum coloured with carbon black (SW, SP) is much more difficult to remove with CO_2 than with PER. Studies on the removal of pure sebum and pure carbon black particles indicated that the removal of the pure sebum does not pose a problem using liquid CO_2 whereas pure carbon black does. Therefore, it is assumed that the carbon black particles are responsible for the poor cleaning-results of the fabrics soiled with sebum and carbon black. The poor results with clay particles (CW, CP) confirm the difficulty of removing particulate soils with CO_2. Figure 9 shows that supercritical carbon dioxide gives worse cleaning-results than liquid carbon dioxide for sebum coloured with carbon black and for clay.

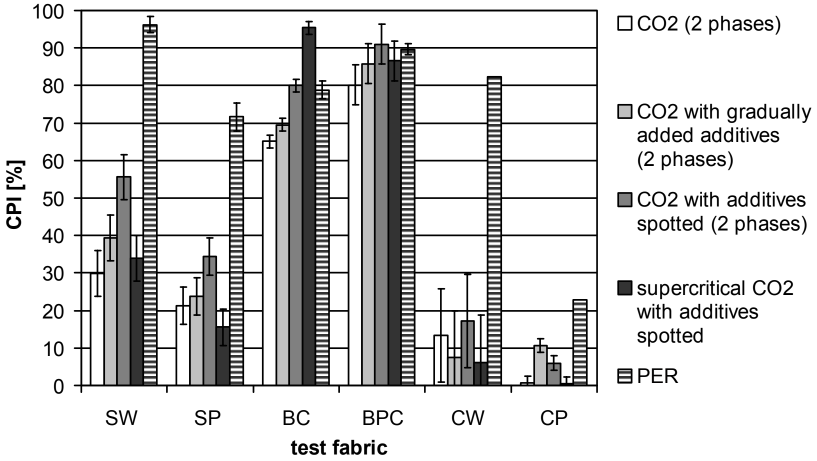

Figure 9: Cleaning Performance Index using carbon dioxide, additives and PER

Particle removal may be increased by the use of more mechanical action. The influence of three different levels of mechanical action on the removal of the described soils was investigated. The results of these experiments are shown in Figure 10 and Table 3. In series A, the inner-drum did not rotate, thus minimizing mechanical action. In series B and C, the drum rotated at 75 RPM. Furthermore, in series C heavy metal balls (diameter 28 mm) were added to the rotating drum, causing a high degree of mechanical action. The other operating conditions were kept constant during these series; the pressure was 4.5 MPa and the temperature 283 K. During the washing cycle, the standard additive solution was gradually added.

From these experiments, it is concluded that the cleaning-results of most of the test fabrics are not influenced much by increased mechanical action. The increase in mechanical action does not lead to an increase in the removal of carbon black particles from wool and polyester, and clay particles from polyester. It is interesting to note the substantial improvement of the clay particle removal from wool in series C (at highest level of mechanical action).

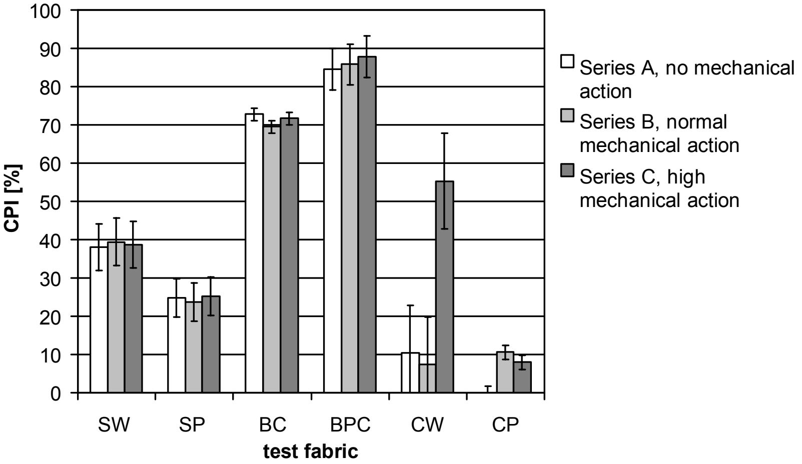

Figure 10: Influence of mechanical action on soil removal

Table 3: Influence of mechanical action on sand removal

Series		Wt. %	Standard deviation
A	No mechanical interaction	46	13
B	Normal mechanical interaction	77	20
C	High mechanical interaction	95	4
	PER	97	2

The results in Table 3 show that at a higher level of mechanical action more sand is removed. However, the mechanical action at normal conditions was not sufficient to remove all sand and high mechanical action is required to obtain good results. These results reflect the relatively low mechanical action in the CO_2-system.

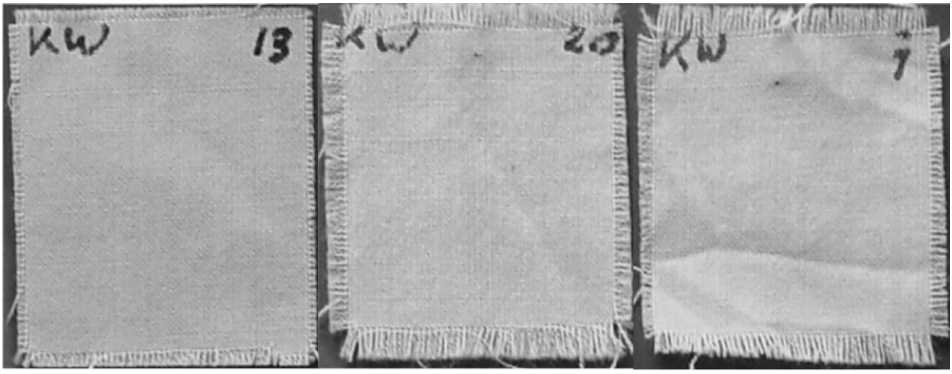

Figure 11: Woollen test fabrics washed in (from left to right):
CO_2, CO_2 with added metal balls, PER

Assuming that the visible damage of the test fabrics is a good indication of the amount of mechanical action exerted in a washing process, it can be concluded that fabrics during washing in CO_2 with added metal balls (series C) are subjected to approximately the same amount of mechanical action as during a wash cycle in PER (see Figure 11). This is in agreement with the results in Table 3; the amount of sand removed in series C is almost the same as the amount removed using PER.

It is concluded that the removal of relatively large (>20 μm) particles like sand increases with increasing mechanical action. However, the level of mechanical action has no influence on the removal of relatively small (<20 μm) particulate and non-particulate soils (with the exception of clay on wool). Increasing the amount of mechanical action is therefore not the solution that will lead to the increase of the cleaning-results for relatively small particles (like carbon black and clay) up to the level of the cleaning-results using PER.

The conclusions from the previous paragraph indicate that the surfactants used in the PER process reduce the adhesion forces of small particles to such an extent as to allow removal of relatively small particulate soil from the substrate. The main influence of mechanical action would then be restricted to mass transfer. Mass transfer in the washing process is understood to be the process by which fresh detergent is conveyed from the bath to the cloth, and by which the soil materials are transported away into the detergent bath. It is concluded that the removal of relatively small particulate soils in CO_2 cannot be improved significantly unless suitable surfactants are developed to reduce adhesion forces.

Figure 9 shows that clay and sebum with carbon black are better removed from wool (CW, SW) than from polyester (CP, SP). The type of fibre seems to have a significant effect on the removal of certain types of soil and it could be due to the bending and stretching of the more flexible wool fibre that detergency increases [4]. These deformations can cause local changes in pore velocity and loosening of particles captured in or between the yarns [5]. This explanation agrees with observations of the fabrics soiled with clay, where clean spots appeared at the location of folds (this is where most deformation takes place).

Furthermore, the chemical composition of polyester and wool can be of influence on the nature of the molecular forces binding the relatively small particles to the substrate. At molecular scale, with increasing distance between the particle and the contact surface, a diffuse double layer arises, which assists in the separation process by establishing an element of repulsion. This repulsion occurs because of the negative surface potentials of both particle and substrate; double layer interaction occurs. As surface potentials cannot be measured directly, the zeta-potential is used as a measure of surface charge. In the washing system with carbon dioxide water is present, the largest part of which originates from the fabrics and a smaller amount having been added to the system. Because of this water content, the pH of the CO_2-water system is approximately 3 [7]. At pH=3, wool has a zeta-potential of –10 mV [8], whereas polyester has a zeta-potential of approximately -5 mV [9]. Carbon black and clay have a negative potential at pH=3 [3]. Therefore, the repulsive forces between the particles and the wool will be higher than the forces between the particles and the polyester. This qualitatively explains the experimental result of better particle removal from the wool fibres than from polyester.

Validation of Model

A parameter that can be used to quantify the amount of mechanical action on a given piece of textile during a washing cycle is the impact velocity v_{imp}. Since v_{imp} is calculated with the model as a function of pressure, temperature, rotational speed and drum radius, the model can be used to predict the optimal values of these parameters.

Table 4 shows the calculated v_{imp} at varying pressures and rotational speeds in CO_2 and PER. It also shows the terminal velocity v_{ter}; this is the maximum velocity a falling piece of textile reaches at infinite drum size. The inner-drum radius of the experimental set-up (0.105 m) was used for the calculation of v_{imp}.

Pressure and temperature

Table 4 shows that the process conditions have a distinct influence on the impact and terminal velocity of the fabric. The model indicates a higher mechanical action at lower pressures and temperatures because of higher impact velocities. At 4.5 MPa and 283 K, the terminal velocity is almost twice as high as at 7.1 MPa and 302 K. This can be explained by considering the forces working on the textile plug. The drag force is lower at 4.5 MPa than at 7.1 MPa, because of the lower density of the gaseous CO_2 at decreasing temperatures and pressures. The gravitational buoyancy force is for the same reason also lower at 4.5 MPa. The gravitational force at 4.5 MPa is almost the same as at 7.1 MPa (because of the lower density of the gaseous CO_2 and the higher density of the liquid CO_2 at 4.5 MPa). This results in a higher net gravitational force at 4.5 MPa. Since the net gravitational force is higher and the drag force is lower at 4.5 MPa than at 7.1 MPa, the terminal velocity is higher at 4.5 MPa than at 7.1 MPa.

When we compare the forces in supercritical CO_2 (at 7.5 MPa) to the forces working in two-phase CO_2 at 4.5 MPa, we see that the drag force is higher in supercritical CO_2 and that the net gravitational force is lower. Therefore, the impact velocity in supercritical CO_2 is lower than in two-phase CO_2.

In PER, however, the net gravitational force is higher and the drag force is lower than in two-phase carbon dioxide. Therefore, v_{imp} will be higher in PER and, hence, mechanical action. This agrees with the experiments, shown in Table 3, where more sand is removed in PER than in CO_2.

Table 4: Results of calculations of the impact velocity as calculated for a drum diameter of 0.21 m. The terminal velocity is also indicated.

	65 RPM V_{imp} [m/s]	75 RPM V_{imp} [m/s]	85 RPM V_{imp} [m/s]	V_{ter} [m/s]
CO_2 at 4.5 MPa and 283 K, two phases ρ_{gCO_2} = 135 kg/m^3, ρ_{lCO_2} = 861 kg/m^3	0.99	1.16	1.11	1.47
CO_2 at 7.1 MPa and 302 K, two phases ρ_{gCO_2} = 312 kg/m^3, ρ_{lCO_2} = 629 kg/m^3	0.67	0.71	0.62	0.74
CO_2 at 7.5 MPa and 311 K, supercritical ρ_{CO_2} = 245 kg/m^3	0.61	0.62	0.51	0.64
PER at 0.1 MPa and 298 K ρ_{PER} = 1623 kg/m^3	1.30	1.62	1.63	22.8

The trend in mechanical action predicted by the above calculations was verified with experiments in which fabrics soiled with sand and clay were used. The influence of pressure and temperature on particle removal was tested at 75 RPM, the results are shown in Figure 12.

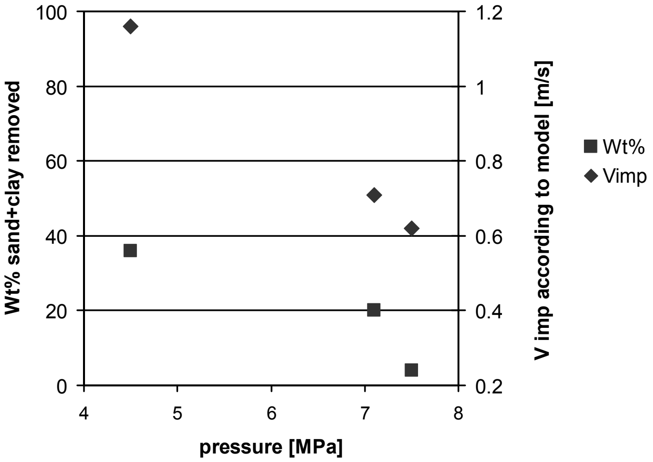

Figure 12: Influence of pressure on particle removal and calculated v_{imp} (at 75 RPM)

Rotational speed

To test the influence of rotational speed on particle removal, experiments were performed at 4.5 MPa and three different rotational speeds (see Figure 13).

From these two figures (Figures 12 and 13), we can conclude that the predicted v_{imp} follows the same trend as the amount of sand and clay removed. Therefore, the model can be used to predict the optimal process conditions for relatively large particle removal. It is concluded from the model and experiments, that the level of highest mechanical action in CO_2 is obtained in a two-phase environment at low pressure and temperature and that 75 RPM is the optimal number of revolutions.

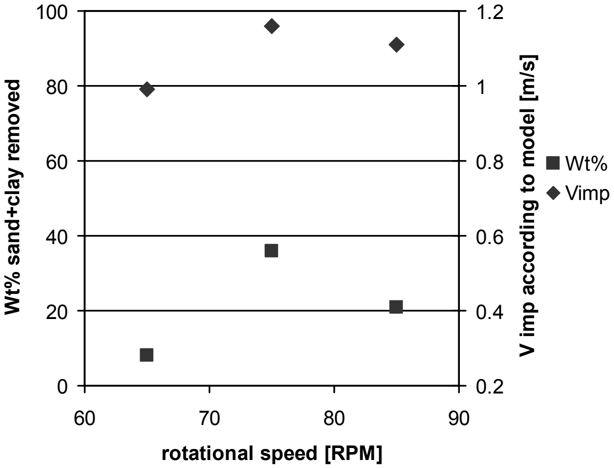

Figure 13: Influence of rotational speed on particle removal and calculated v_{imp} (at 4.5 MPa)

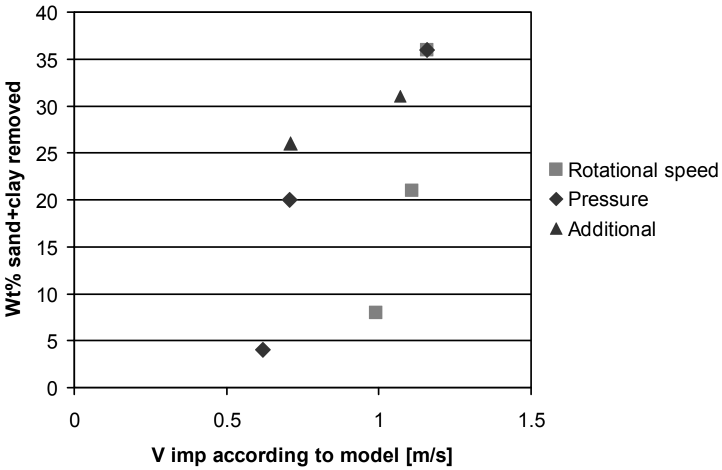

Figure 14: The amount of particles removed as function of the calculated v_{imp}

A larger drum radius will give the piece of textile more time to increase its impact velocity. According to the model, the radius at which the terminal velocity will be reached in CO_2 at 4.5 MPa and 283 K is 0.6 m.

When the removal of sand and clay particles is plot as a function of the impact velocity (Figure 14), a tendency in mechanical action as function of impact velocity becomes present. The impact velocity shows a threshold for particle removal, after this threshold the particle removal is increasing with increasing impact velocity. When the impact energy is consumed for particle removal only, the removal is expected to be a second order function of impact velocity.

3.5 Conclusions

The model can be used to predict the optimal process conditions for relatively large particle removal. It is concluded (from the model and experiments), that the level of highest mechanical action in CO_2 is obtained in a two-phase environment at low pressure and temperature and that 75 RPM is the optimal number of revolutions in our system.

The removal of relatively large particles like sand increases with increasing mechanical action. Different levels of mechanical action, however, do not influence the removal of relatively small particulate and non-particulate soils (with the exception of clay on wool). Increasing the amount of mechanical action is therefore not the solution that will lead to the increase of the cleaning-results for relatively small particles (like carbon black and clay) up to the level of the cleaning-results using PER. Unfortunately, the removal of relatively small particulate soils in CO_2 can be improved only by the use of suitable surfactants that reduce adhesion forces.

Acknowledgements

We would like to thank Friso Koopmans for providing preliminary studies.

References

[1] B. Gosolitis, J. Kurz, M. Sverev, Textile dry cleaning in liquefied CO_2, in: G. Brunner (Ed.), Proceedings 2nd International Meeting on High Pressure Chemical Engineering, Hamburg, Germany, 2001.

[2] M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide, experimental set-up and washing-results, in: G. Brunner (Ed.), Proceedings 2nd International Meeting on High Pressure Chemical Engineering, Hamburg, Germany, 2001.

[3] G. Jakobi, A. Löhr, M.J. Schwuger, D. Jung, W.K. Fischer, P. Gerike, K. Künstler, Detergents - Theory of washing process, in: Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 2000 Electronic release, Wiley-VCH Verlag GmbH, Weinheim 2000.

[4] W.G. Cutler, R.C. Davis, Detergency; theory and test methods Part I, Dekker, New York 1972.

[5] L.D.M. van den Brekel, Hydrodynamics and Mass Transfer in Domestic Drum-Type Fabric Washing Machines, Dissertation, Delft University of Technology, Delft 1987.

[6] R.H. Perry, D.W. Green, J.O. Maloney, Perry's chemical engineers' handbook; seventh edition, McGraw-Hill, New York 1997.

[7] K.H. Toews, R.M. Shroll, C.M. Wai, pH-defining equilibrium between water and supercritical CO_2. Influence on SFE of organics and metal chelates, Anal. Chem., 67 (1995) 4040.

[8] E. Hageböke, Über die Säureabsorption und das elektrokinetische Potential an Wolle, Dissertation, University of Bonn, Bonn 1956.

[9] H.-J. Jacobasch, I. Grosse, Anwendung der Zeta-potential-Messung in der Textilforschung und -praxis, Textiltechnik, 37 (1987) 266.

.

Chapter 4

The influence of process conditions and various co-solvents (alcohols) on cleaning-results

M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp

Abstract

The influence of the process conditions time and temperature on dry-cleaning results with CO_2 *has been examined in a 25-litre vessel. The optimal cleaning-time lay between 5 and 20 minutes. There was not one optimal cleaning temperature; therefore it is considered to perform the process at room temperature (without use of heating or cooling during the process).*

For most soils, the use of a co-solvent caused a substantial increase in their removal. Of the co-solvents investigated, 2-propanol was the most suitable.

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4.1 Introduction

Carbon dioxide can be used as substitute for the dry-cleaning solvents currently used. These solvents are potentially toxic and environmentally harmful. The most commonly used dry-cleaning solvent, perchloroethylene (PER), is suspected to be carcinogenic. Advantages of using carbon dioxide are that it is non-toxic, non-flammable, ecologically sound, and available on a large scale. A disadvantage of CO_2 is its limited ability to dissolve polar molecules. However, the characteristics of CO_2 can be modified by the addition of miscible, polar compounds; these are called co-solvents. In supercritical fluid extraction, short chain alcohols, for example methanol [1] and ethanol [2-4] are often used as co-solvent. In this chapter, the influence of the addition of various short chain alcohols on the cleaning-results is examined.

In Chapter 3 [5], the influence of mechanical action on cleaning-results has been presented. In this chapter, the influence of the process conditions time and temperature on the cleaning-results is examined.

4.2 Experimental

4.2.1 Apparatus

The experimental set-up is shown schematically in Figure 1. The experimental set-up was designed and constructed at the Laboratory for Process Equipment, Delft University of Technology (Delft, The Netherlands). The cleaning-vessel has an inside diameter of 0.25 m and volume of 25 l. This vessel was constructed at Van Steen Apparatenbouw B.V. (Pijnacker, The Netherlands). A rotating inner-drum is mounted inside the cleaning-vessel to provide the necessary mechanical action. This inner-drum, with a diameter of 0.21 m and a volume of 10 l, is perforated and connected to a rotating shaft. This shaft passes through the wall of the high-pressure vessel to the motor via a seal and bearings. The motor is PLC controlled and the machine can run complete washing programs. Before the fluid from the vessel enters the pump, it passes through a filter (pore size 11 μm), in order to remove particles, threads etc. During each cycle of circulation, the CO_2 passes through a heat exchanger contained in a cylinder with service fluid. The temperature of the service fluid can be regulated between 263 K and 333 K by a circulation heater/cooler, allowing the pressure in the closed CO_2 circulation to increase or decrease. The temperature, pressure, density, and mass flow are monitored.

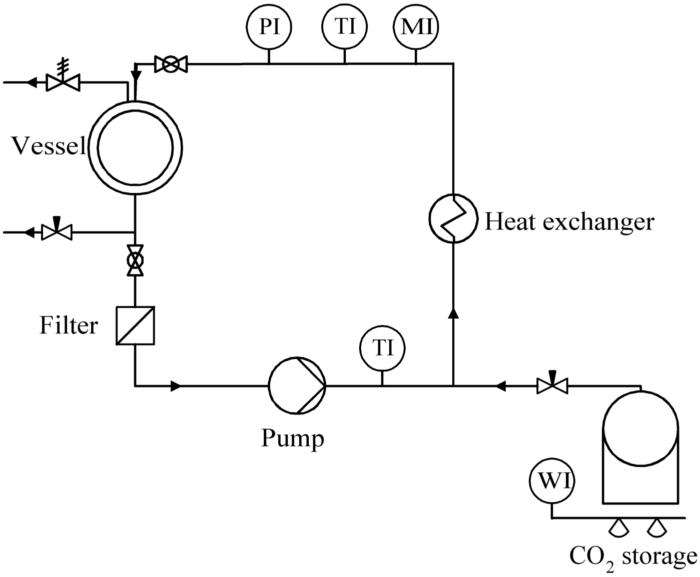

Figure 1: Experimental set-up

4.2.2 Materials

Carbon dioxide grade 3.7 is obtained from Hoek Loos B.V. (Schiedam, The Netherlands). The following co-solvents were used: methanol, ethanol, 1-propanol, 2-propanol and acetone from J.T. Baker (Deventer, The Netherlands) with a stated purity of 99 %+; 1-butanol from Janssen Chimica (Geel, Belgium) with a stated purity of 99 %+; 2-butanol from Merck Eurolab B.V. (Amsterdam, The Netherlands) with a stated purity of 99 %+;

1-pentanol and 1-hexanol from Merck-Schuchardt (Hohenbrunn, Germany) with a stated purity of 98 %+ and 1-tert-butoxy-2-propanol (TBP) from Sigma-Aldrich Chemie B.V (Zwijndrecht, The Netherlands) with a stated purity of 98 %+. Furthermore, tap water was used to counteract the extraction of water from the fabric.

Soiled test fabrics have been used to monitor the cleaning-results. All test fabrics have been purchased from the Center for Testmaterials B.V. (Vlaardingen, The Netherlands). Five different kinds of soils are used in the experiments described in this chapter:

- sebum (skin fat) coloured with carbon black (oily and greasy soils combined with particulate soils)
- clay particles (particulate soils)
- butterfat with colorant (oily and greasy soils)
- egg yolk (proteins and starchy soils, oily and greasy soils)
- vegetable oil coloured with chlorophyll (oily and greasy soils, combined with oxidizable or bleachable soils)

The used test fabrics and their abbreviations are shown in Table 1.

Table 1: Used test fabrics and their abbreviations

	Wool	Polyester	Cotton	Polyester cotton
Sebum (skin fat) coloured with carbon black	SW	SP		
Clay particles	CW	CP		
Butterfat with colorant			BC	BPC
Egg yolk	EW	EP		
Vegetable oil coloured with chlorophyll			OC	OPC

In a typical run, the test fabrics are attached to cotton filling material. The test fabrics and the cotton filling material (400 gram) are placed in the drum. Before the test fabrics and the filling fabrics are placed in the drum, the fabrics are pre-soaked in an additive solution. The standard solution of additives consists of 77 wt% 2-propanol, 15 wt% TBP and 8 wt% water.

4.2.3 Measuring

To monitor the cleaning-results, the colour of the test fabrics was measured before and after cleaning. The way of measuring is described in more detail in Chapter 2.
The Cleaning Performance Index (CPI) is calculated to determine the cleaning-results. Here, the CPI is defined as:

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

where ΔE is the measured colour difference in the $L^*a^*b^*$ colour space [6].

4.2.4 Experiments with PER

The soiled fabrics have also been cleaned in PER. This was done at a local dry cleaner's using a standard dry-cleaning procedure and no spotting. Spotting is a pre-treatment in which the detergent is physically brought into contact with the fabric. Spotting is a common method in the dry-cleaning industry for dealing with difficult stains.

4.3 Results and discussion

4.3.1 Cleaning-time

Figures 2 and 3 show the cleaning-results at 4.5 MPa and 283 K as a function of the cleaning-time. In Figure 3, the average CPI of the used test fabrics is also given. In the experiments, 12 kg CO_2 and 325 grams of the standard additive solution were used.

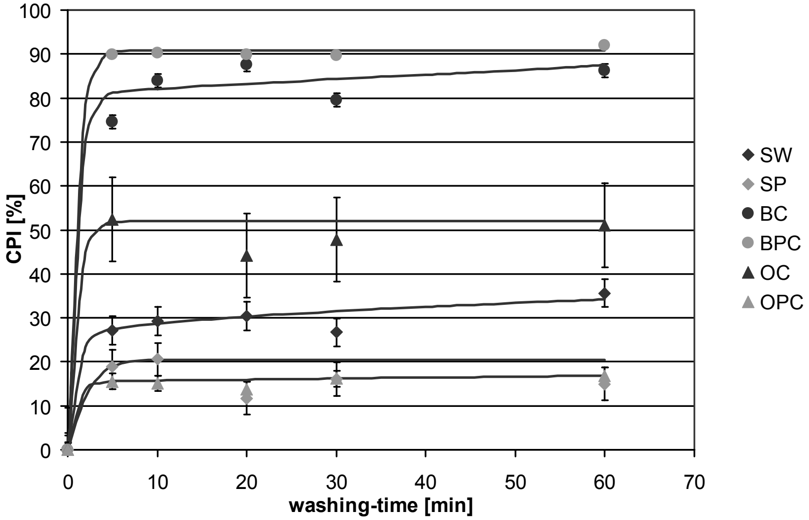

Figure 2: CPI at 4.5 MPa and 283 K as function of the cleaning-time for SW, SP, BC, BPC, OC and OPC test fabrics

From the figures, we can conclude that the maximum soil removal is already obtained in the first five minutes, except for the EP test fabric (20 minutes). Therefore, the optimal cleaning-time lies between 5 and 20 minutes. The cleaning-time in CO_2 is comparable to the cleaning-time in PER, where the cleaning-time is 5 minutes. In the PER process, one hour is needed to dry the fabrics after cleaning. In dry-cleaning with carbon dioxide, however, no drying is needed, because the fabrics are dry after cleaning (carbon dioxide evaporates from the fabrics during depressurization of the cleaning-vessel). Therefore, dry-cleaning with carbon dioxide is a faster process than dry-cleaning with PER.

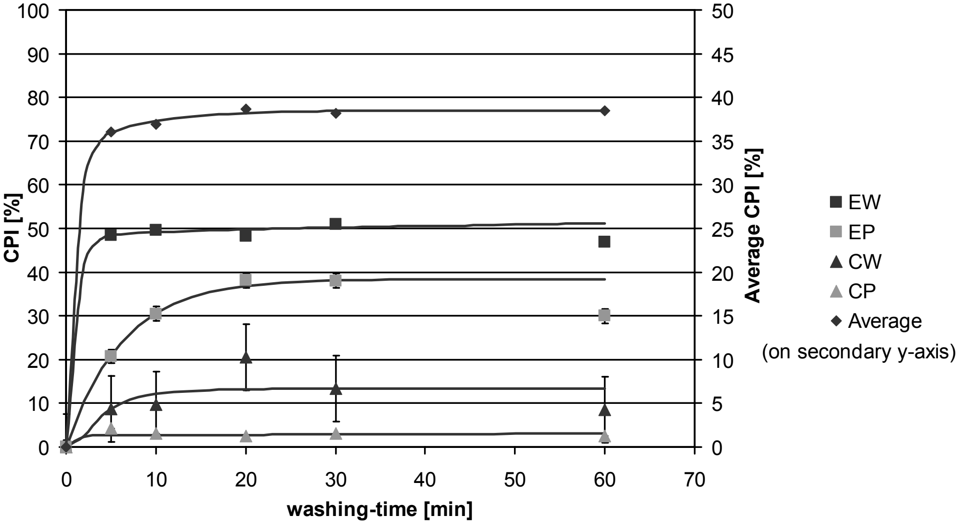

Figure 3: CPI at 4.5 MPa and 283 K as function of the cleaning-time for EW, EP, CW and CP test fabrics. Average CPI of all test fabrics is shown on secondary y-axis

4.3.2 Temperature

Experiments were performed at 278 K (4.0 MPA), 283 K (4.5 MPa), 293 K (5.7 MPa), 303 K (7.2 MPa) and 309 K (8.0 MPa). All these points (except for 309 K, 8.0 MPa) lie on the two-phase line. A two-phase system is preferred in dry-cleaning, because the amount of mechanical action is higher in a two-phase system than in a one-phase system [5]. In these experiments, 12 kg CO_2 and 325 grams of the standard additive solution were used. Figures 4 and 5 show the cleaning-results as function of temperature at a cleaning-time of 30 minutes. The average CPI of the used test fabrics is shown in Figure 5.

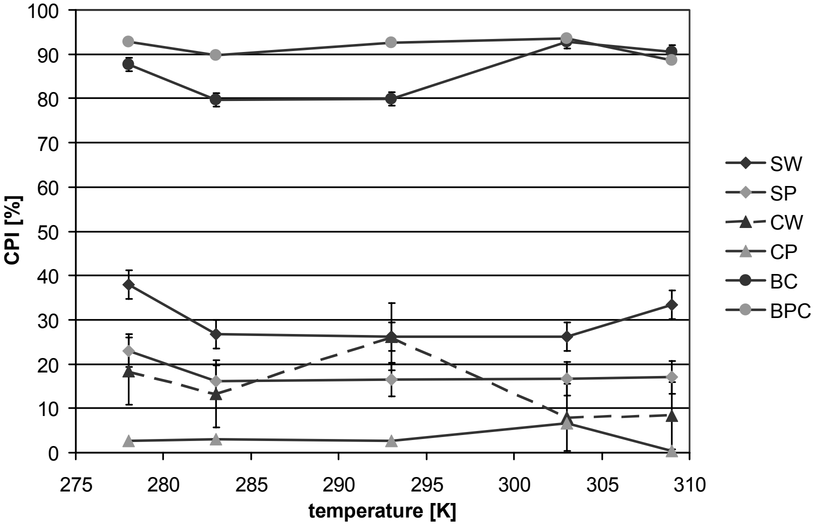

Figure 4: CPI as function of temperature for SW, SP, CW, CP, BC and BPC test fabrics (cleaning-time is 30 minutes)

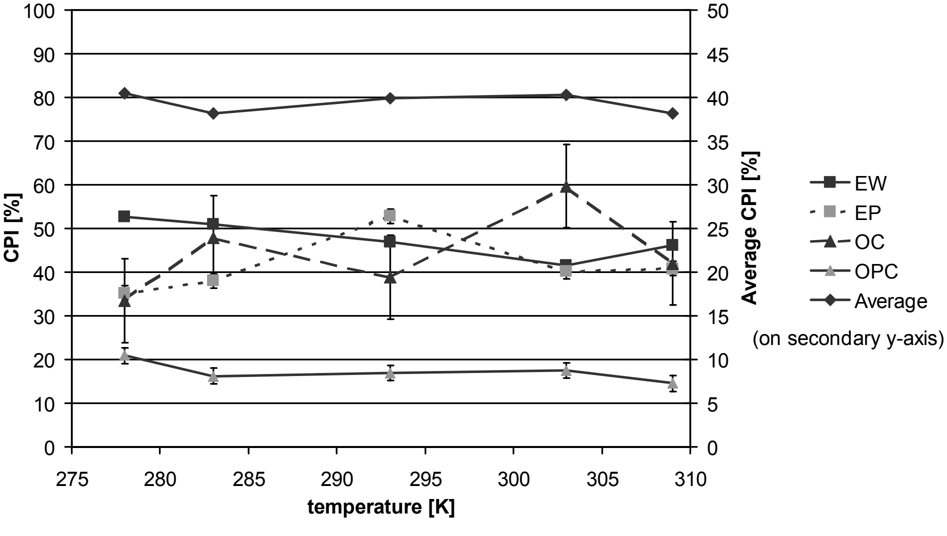

Figure 5: CPI as function of temperature for EW, EP, OC and OPC test fabrics (cleaning-time is 30 minutes). Average CPI of all test fabrics is shown on secondary y-axis

The optimal cleaning-temperature differs from test fabric to test fabric. When we look at the average CPI, we see that there is not one optimal overall cleaning-temperature in the investigated temperature range. Supercritical CO_2 gives the same average CPI as liquid CO_2. From a practical point of view, room temperature (without use of heating or cooling during the process) would be the optimal temperature.

4.3.3 Co-solvent

Cleaning-experiments were performed using nine different co-solvents. Figures 6 and 7 show the cleaning-results as function of the used co-solvent. The experiments were performed at 4.5 MPa and 283 K with a cleaning-time of 30 minutes. In each experiment, 6 kg CO_2, 25 g water and 250 g co-solvent were used. In Table 2 the results for dry-cleaning with PER are shown.

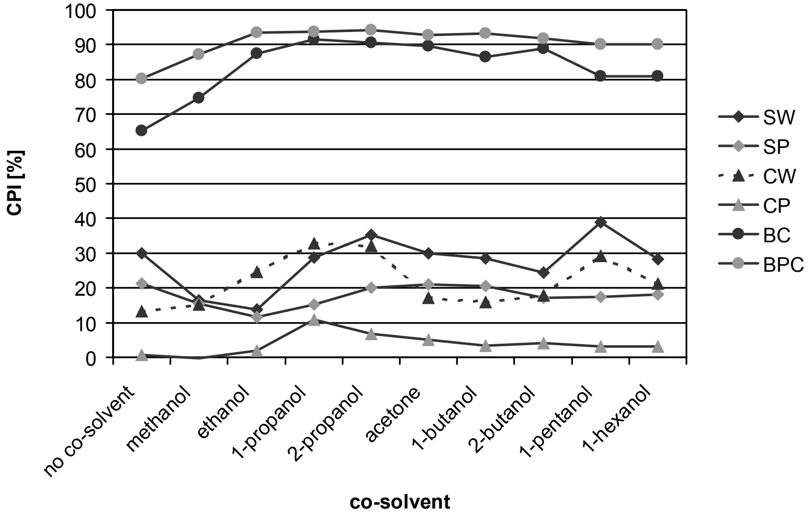

Figure 6: CPI as function of co-solvent for SW, SP, CW, CP, BC and BPC test fabrics

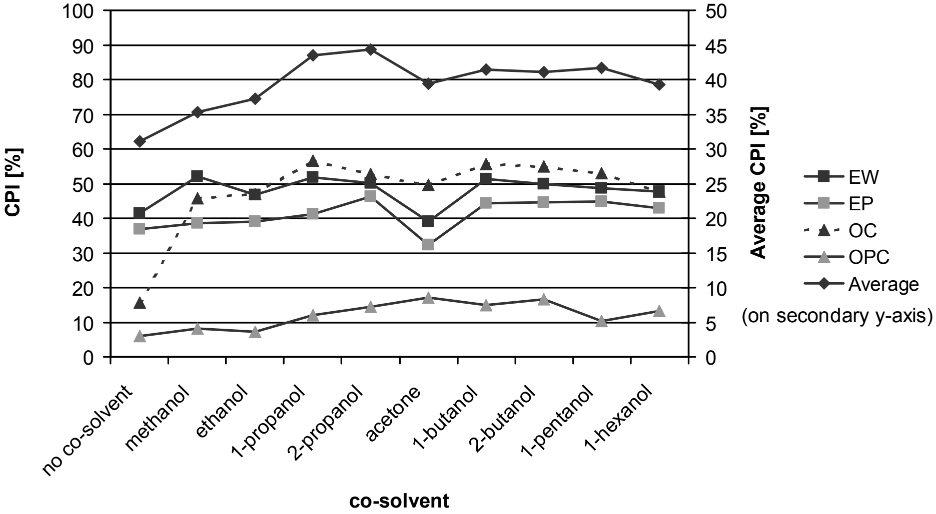

Figure 7: CPI as function of co-solvent for EW, EP, OC and OPC test fabrics.
Average CPI of all test fabrics is shown on secondary y-axis

When the data in Figures 6 and 7 are compared with the data in Table 2, it can be concluded that for most soils the use of a co-solvent causes a substantial increase in cleaning-result. In these figures, it is also shown that, for most stains, there are little differences in cleaning-results using different co-solvents. However, the average CPI shows that the optimal co-solvent lies between 1-propanol and 1-pentanol (with the exception of acetone). However, 1-butanol and 1-pentanol are harmful, and 1- and 2-butanol have a strong odour, and are, therefore, not suitable for dry-cleaning. Furthermore, 2-propanol is cheaper than 1-propanol and when we compare the Material Safety Data Sheets we see that 2-propanol is safer to use than 1-propanol. Therefore, 2-propanol is the most suitable co-solvent of the alcohols tested in this chapter.

Table 2: Cleaning Performance Index [CPI] for dry-cleaning with PER

Test fabric	CPI [%]	Test fabric	CPI [%]
SW	96	BPC	90
SP	72	EW	62
CW	82	EP	52
CP	23	OC	52
BC	79	OPC	27
		Average	63

The dielectric constant is a bulk property of importance in solvation. Addition of polar co-solvents increases the polarity and the dielectric constant. The dielectric constants are calculated for the mixtures of carbon dioxide, water and co-solvent used in the above-mentioned experiments. In these calculations, it is assumed that there are no interactions between the mixture components. Therefore, the following mixing-rule was used:

$$\varepsilon = \sum_i \nu_i \varepsilon_i \qquad (2)$$

where ε [-] is the dielectric constant of the mixture, ν_i [-] the volume fraction of species i in the mixture and ε_i [-] is the dielectric constant of species i. In Figure 8, the average CPI of all test fabrics is given as function of the dielectric constant. In this figure, the dielectric constant varies over a pretty small range. A larger range might be obtained by the addition of a larger amount of co-solvent. This is, however, unwanted from a practical and economical point of view.

From Figure 8, it is concluded that the optimal dielectric constant will lie around 2.6, which is surprisingly close to the dielectric constant of PER, which is 2.5 at 294 K.

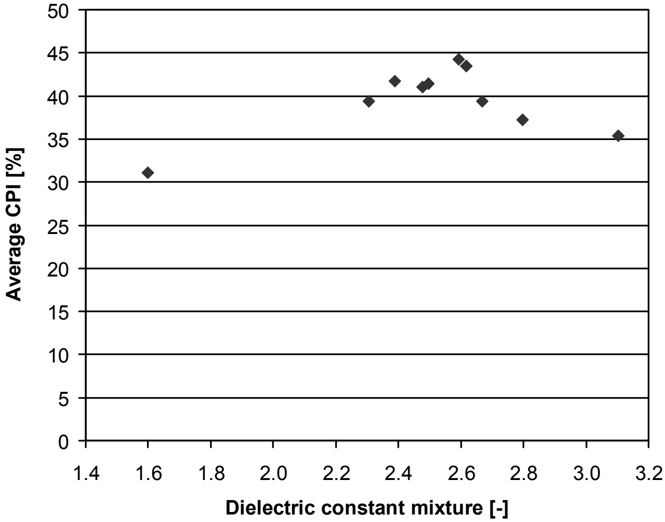

Figure 8: Average CPI of all test fabrics as function of the dielectric constant of the mixture

Next to the dielectric constant, other important properties for dry-cleaning will also change with the addition of co-solvent. When a co-solvent is added, density will increase and, hence, the solvating power of the carbon dioxide. The experiments with varying temperature (where the density of the pure CO_2 varies from 289 kg/m^3 to 896 kg/m^3) show, however, that this effect may play a minor role in the increase of the cleaning-results. Local composition enhancements around the soil in the CO_2/co-solvent mixture may also play a role in the solubility increase of the soil when a co-solvent is added [7]. Furthermore, interaction between soil and co-solvent via hydrogen bonding can also play an important role in solubility enhancement [8]. Surface tensions between the CO_2-phase and the fibre and between the CO_2-phase and the soil might also be reduced. In addition, the viscosity of the CO_2-phase may also increase, having a positive effect on soil-removal (increasing momentum transfer, drag force).

To make a good description of the influence of the addition of co-solvents on these properties and their influence on the dry-cleaning process, a more extensive study is needed. For example, the solubility of different soil components can be investigated as function of the added co-solvent.

4.3 Conclusions

The optimal cleaning-time lay between 5 and 20 minutes.
There was not one optimal cleaning-temperature in the investigated temperature range (278-309 K). From a practical point of view, room temperature (without use of heating or cooling during the process) would be the optimal temperature.
It was shown that for most soils the use of a co-solvent caused a substantial increase in the cleaning-result. Of the alcohols tested in this chapter, 2-propanol was the most suitable as co-solvent.

Acknowledgements

We would like to thank Alex Breijer, Jan Willem van Ganswijk and Maarten Wichhart for their assistance in the experimental work.

References

[1] C. Kersch, M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Extraction of heavy metals from fly ash and sand with ligands and supercritical carbon dioxide, Ind. Eng. Chem. Res., 39 (2000) 4670.

[2] L. Teberikler, S. Koseoglu, A. Akgerman, Selective extraction of phosphatidylcholine from lecithin by supercritical carbon dioxide/ethanol mixture, J. Am. Oil Chem. Soc., 78 (2001) 115.

[3] A. Pasquel, M.A.A. Meireles, M.O.M. Marques, A.J. Petenate, Extraction of stevia glycosides with CO_2 + water, CO_2 + ethanol, and CO_2 + water + ethanol, Braz. J. Chem. Eng., 17 (2000) 271.

[4] M.J. Cocero, L. Calvo, Supercritical fluid extraction of sunflower seed oil with CO_2-ethanol mixtures, J. Am. Oil Chem. Soc., 73 (1996) 1573.

[5] Chapter 3 of this thesis; M.J.E. van Roosmalen, M. van Diggelen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide; The influence of mechanical action on washing-results, J. Supercrit. Fluids, 27 (2003) 97.

[6] ASTM Standards on Color and Appearance Measurement 5th ed., ASTM, Philadelphia 1996.

[7] E.J. Roggeman, A.M. Scurto, J.F. Brennecke, Spectroscopy, solubility, and modeling of cosolvent effects on metal chelate complexes in supercritical carbon dioxide solutions, Ind. Eng. Chem. Res., 40 (2001) 980.

[8] S.S.T. Ting, S.J. Macnaughton, D.L. Tomasko, N.R. Foster, Solubility of naproxen in supercritical carbon dioxide with and without cosolvents, Ind. Eng. Chem. Res., 32 (1993) 1471.

Chapter 5

Surfactants for particulate soil removal in dry-cleaning with high-pressure carbon dioxide

M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp

Abstract

The removal of particulate soils from textile in dry-cleaning with CO_2 is insufficient compared to perchloroethylene (PER). Especially the removal of relatively small particles (<20 μm) poses a problem. Various anionic and amine based surfactants have been investigated to enhance the removal of particulate, but also of non-particulate soils in dry-cleaning with high-pressure CO_2.

The cleaning performance index for relatively small particulate soil (CPI_{part}) increased from 24 % (when no surfactants were used) to a maximum of 51 % (when surfactants were used), which shows that particle removal is possible in CO_2 dry-cleaning. The use of these surfactants, however, does not bring particle removal up to the level of PER (CPI_{part} of 68 %). The removal of non-particulate soils in CO_2 with water, surfactant and co-solvent is better than in PER. The overall results using the investigated surfactants are promising; the overall result increases from 70 % (when no surfactants are used) to 87 % (when surfactants are used) compared to the level when using PER.

Surfactant particles were formed in all experiments. In the case of the amines, these particles may be formed by reaction. The formed surfactant particles are probably responsible for the removal of the soil particles from the textile. The presence of surfactant particles creates more mechanical action and may cause an abrasive effect. The charged surfactant may also adhere to the soil particles and/or fabric, thereby establishing an element of repulsion and/or a steric barrier.

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The use of a co-solvent (2-propanol) had a positive effect on the removal of particulate and non-particulate soils when using amines. However, when anionic surfactants were used, the addition of a co-solvent had a pronounced negative effect on particulate soil removal.

5.1 Introduction

There is increasing interest in carbon dioxide as replacement for the currently used dry-cleaning solvents. The most commonly used dry-cleaning solvent is PER (perchloroethylene), which is suspected to be carcinogenic and is environmentally harmful. Previous studies [1, 2] indicate that the removal of non-polar soils in CO_2 is comparable to the level of cleaning in PER. These studies, however, show that the removal of particulate soils is insufficient in CO_2 compared to PER. Particulate soil removal can be increased by the use of more mechanical action and/or the use of surfactants. The removal of relatively large (>20 µm) soil particles, like sand, can be increased up to the level of removal in PER by increasing the amount of mechanical action [3]. Increasing the amount of mechanical action has, however, no influence on the removal of relatively small (<20 µm) soil particles, like carbon black [3]. To increase the removal of small soil particles, surfactants are needed. Various commercially available non-ionic surfactants have been investigated [4]. The investigated commercially available non-ionic surfactants give in CO_2 worse or only slightly better results than carbon dioxide with water. Ionic surfactant adsorption onto the fibre and particle surface can significantly change the surface charge and can, hence, establish an element of repulsion between the fibre and the soil particle [5]. The adsorption of a layer of surfactants can also cause a cleaning-effect. By adsorption of surfactants, a wedge is formed between the fibre and the particle and they are pried apart, with the aid of hydrodynamic shear forces [6]. In this chapter, various anionic and amine based surfactants are investigated.

The use of a co-solvent can have a positive effect on cleaning-results. In Chapter 4 [7], various alcohols were used as co-solvent. 2-Propanol (IPA) turned out to be the most suitable co-solvent for dry-cleaning with CO_2 (when no surfactants are used). The influence of the use of IPA together with the above-mentioned surfactants is investigated.

5.2 Experimental

5.2.1 Apparatus

The experimental set-up is shown schematically in Figure 1. The experimental set-up was designed and constructed at the Laboratory for Process Equipment, Delft University of Technology (Delft, The Netherlands). The cleaning-vessel has an inside diameter of 0.25 m and volume of 25 l. This vessel was constructed at Van Steen Apparatenbouw B.V. (Pijnacker, The Netherlands). A rotating inner-drum is mounted inside the cleaning-vessel to provide the necessary mechanical action. Metal balls (diameter 28 mm) were added to the inner drum to increase mechanical action. The inner-drum, with a diameter of 0.21 m and a volume of 10 l, is perforated and connected to a rotating shaft. This shaft passes through the wall of the high-pressure vessel to the motor via a seal and bearings. The motor is PLC controlled and the machine can run complete washing programs. Before the fluid from the vessel enters the pump, it passes through a filter (pore size 11 μm), in order to remove particles, threads etc. During each cycle of circulation, the CO_2 passes through a heat exchanger contained in a cylinder with service fluid. The temperature of the service fluid can be regulated between 263 K and 333 K by a circulation heater/cooler, allowing the pressure in the closed CO_2 circulation to increase or decrease. The temperature, pressure, density, and mass flow are monitored.

In all experiments, the pressure was 4.5 MPa and the temperature was 283 K. At this temperature and pressure, CO_2 forms a two-phase system with a relatively high liquid density and a relatively low vapour density, which causes a relatively high amount of mechanical action [3]. The dry-cleaning time is 30 minutes. After cleaning, the wash load is rinsed with pure carbon dioxide for 10 minutes. The dry-cleaning vessel has two viewing glasses through which the contents of the vessel can be observed.

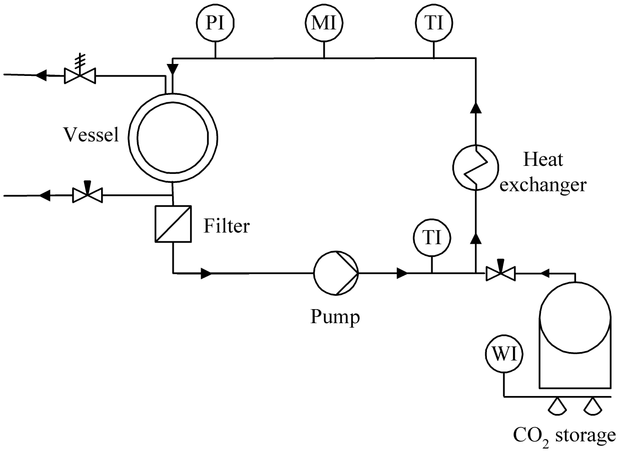


Figure 1: Experimental set-up

5.2.2 Materials

Carbon dioxide grade 3.7 is obtained from Hoek Loos B.V. (Schiedam, The Netherlands). The following surfactants were used: dioctyl sulfosuccinate, sodium salt (DOSS) with a stated purity of 96 % from Acros Organics (Geel, Belgium), 1-naphthyl phosphate monosodium salt, monohydrate (NSH) with a stated purity of 98 %+ from Avocado (Heysham, Great Britain), trisodium phosphate hexahydrate (SPH) with a stated purity of 97 %+ from Fluka (Zwijndrecht, The Netherlands), stearic acid, sodium salt (SAS) with a stated purity of 96 % from Acros Organics (Geel, Belgium), dodecyl sulfate, sodium salt (DSS) with a stated purity of 97 %+ from Merck Eurolab B.V. (Amsterdam, The Netherlands), 1-dodecylamine (DDA) (stated purity 98 %+), 1-hexadecylamine (HDA) (stated purity 90 %+), 1-octadecylamine (ODA) (stated purity 95 %), di-n-propylamine (DPA) (stated purity 98 %+), di-n-butylamine (DBA) (stated purity 98 %+), di-n-hexylamine (DHA) (stated purity 97 %+) and tribenzylamine (TBA) (stated purity 99 %+) from Fluka (Zwijndrecht, The Netherlands), di-n-octylamine (DOA) with a stated purity of 98 % from Aldrich (Zwijndrecht, The Netherlands), and tributylammonium iodide (TBAI) with a stated purity of 98 %+ from Merck-Schuchardt (Hohenbrunn, Germany). 2-Propanol (IPA) from J.T. Baker (Deventer, The Netherlands) (stated purity 99 %+) was used as co-solvent. Furthermore, tap water was used to counteract the extraction of water from the fabric.

To monitor the cleaning-results, soiled test fabrics have been used. Test fabrics made of natural fibres as well as synthetic fibres are used. The natural fibres used are wool and cotton, the synthetic fibre used is polyester. A mix of natural and synthetic fibres is also used; this is polyester cotton.

From a detergency point of view, soils can be divided into five categories: oily and greasy soils, water-soluble soils, particulate soils, oxidizable or bleachable soils, and proteins and starchy soils [6].

Five different kinds of soils are used in the experiments described in this chapter:

- sebum (skin fat) coloured with carbon black (particle size: 0-20 µm [3]) (oily and greasy soils combined with particulate soils)
- clay particles (particle size: 0-10 µm [3]) (particulate soils)
- egg yolk (proteins and starchy soils, oily and greasy soils)
- butterfat with colorant (oily and greasy soils)
- vegetable oil coloured with chlorophyll (oily and greasy soils combined with oxidizable or bleachable soils)

All test fabrics have been purchased from the Center for Testmaterials B.V. (Vlaardingen, The Netherlands). The used test fabrics and their abbreviations are shown in Table 1. The test cloths are divided into two different types: cloths soiled with non-particulate soil (EW, EP, BC, BPC, OC, OPC) and cloths 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 cloths 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_2, whereas pure carbon black does.

Table 1: Used test fabrics and their abbreviations

	Wool	Polyester	Cotton	Polyester cotton
Sebum (skin fat) coloured with carbon black	SW	SP		
Clay particles	CW	CP		
Egg yolk	EW	EP		
Butterfat with colorant			BC	BPC
Vegetable oil coloured with chlorophyll			OC	OPC

In a typical run, the test fabrics are attached to cotton filling material. The test fabrics and the cotton filling material (400 gram) are placed in the drum. Before the test-fabrics and the filling fabrics are placed in the drum, the fabrics are pre-soaked in an additive solution. This additive solution consists of water, co-solvent and/or surfactant. The composition of the solution is given for each experiment in the section Results and discussion.

5.2.3 Measuring

To monitor the cleaning-results, the colour of the test fabrics was measured before and after cleaning. This was done with a spectrophotometer (Spectrocam 75 RE) using Standard Illuminant C as light source (average daylight, excluding ultraviolet light). The viewing angle used is the CIE 10º Supplementary Standard Observer. The test fabrics are measured using the $L^*a^*b^*$ colour space, where L^* indicates the lightness, and a^* and b^* are the chromaticity coordinates; $+a^*$ is the red direction, $-a^*$ the green direction, $+b^*$ the yellow direction, and $–b^*$ the blue direction.

In this colour space, the colour difference ΔE is defined by the following equation:

$$\Delta E_{1-2} = \left((L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2\right)^{1/2} \qquad (1)$$

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

$$\mathrm{CPI} = \left[1 - \frac{\Delta E_{\mathrm{washed-unsoiled}}}{\Delta E_{\mathrm{soiled-unsoiled}}}\right] \times 100\% \qquad (2)$$

5.2.4 Experiments with PER

The soiled fabrics have also been cleaned in PER. This was done at a local dry cleaner's using a standard dry-cleaning procedure and no spotting. Spotting is a pre-treatment in which the detergent is physically brought into contact with the fabric. Spotting is a common method in the dry-cleaning industry for dealing with difficult stains.

5.3 Results and discussion

The average deviation per test fabric in CO_2 and in PER is shown in Table 2 in the appendix.

5.3.1 Anionic surfactants

The cleaning-results for the experiments with anionic surfactants are shown in Figure 2. The results per test fabric are shown in Table 3 in the appendix. In these experiments, 6 kg CO_2, 25 g water and 10 g surfactant were used, except for the experiment with NSH (1-naphthyl phosphate monosodium salt, monohydrate) where 5 g surfactant was used. During these series, the pressure was 4.5 MPa and the temperature was 283 K. In

Figure 2, 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, $CPI_{n\text{-}p}$ (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), are shown.

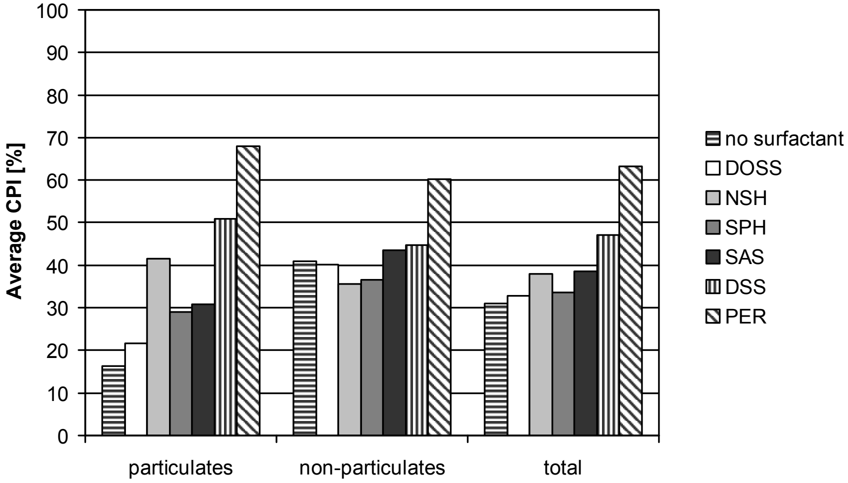


Figure 2: Average CPIs using anionic surfactants

During all experiments, the anionic surfactants were not completely solubilized in the liquid CO_2; small surfactant particles were visible. From Figure 2, we conclude that the addition of anionic surfactant has a distinct positive influence on the removal of particulate soil, especially when using NSH or DSS (dodecyl sulfate, sodium salt). The use of surfactants has, however, almost no influence on the results of the non-particulate soils. This was to be expected, because the anionic surfactants were selected to enhance particulate soil removal.

To increase the cleaning-results of non-particulate soils, IPA (2-propanol) was added as co-solvent. The results of the experiments with the addition of an anionic surfactant and a co-solvent are shown in Figure 3. The result for each separate test fabric is shown in

Table 4 in the appendix. In these experiments, 6 kg CO_2, 25 g water, 250 g IPA, and no surfactant, 50 g DOSS (dioctyl sulfosuccinate, sodium salt), 10 g NSH, 10 g SPH (trisodium phosphate hexahydrate), 50 g SAS (stearic acid, sodium salt) or 10 g DSS were used. The process conditions were the same as during the experiments without co-solvent. In all experiments, a part of the surfactant was present in the form of solid surfactant particles.

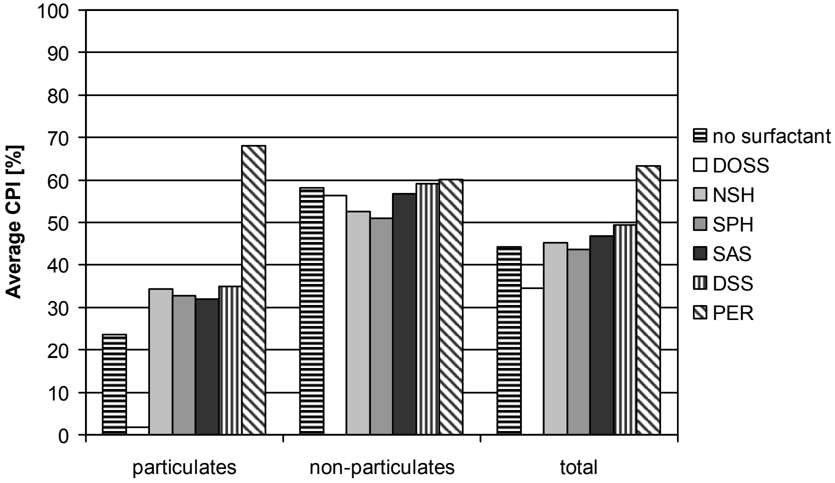


Figure 3: Average CPIs using anionic surfactants and IPA

Figures 2 and 3 show that the addition of a co-solvent has a positive effect on the cleaning-results for non-particulate soils for all surfactants (absolute increase in $CPI_{n\text{-}p}$ 13-17 %). IPA also has a positive effect on the removal of particulate soils when there is no surfactant added (absolute increase in CPI_{part} 8 %). For most anionic surfactants (except for SAS and SPH), however, the use of a co-solvent has a pronounced negative influence on the cleaning-results for particulate soil (decrease in absolute CPI_{part} 7-21 %). When IPA is used, four (NSH, SPH, SAS, DSS) of the five investigated surfactants give almost the same CPI_{part} (32-35 %). DOSS gives a significantly lower result (CPI_{part} 2 %). Although IPA has a negative influence on the effect of the surfactants, the removal of particulate soil is still higher with surfactants (32-35 %, except for DOSS) than without surfactants ($\mathrm{CPI}_{\mathrm{part}}$ 24 %).

It is difficult to explain the behaviour of the anionic surfactants in the presence of a co-solvent. When we consider the results for all surfactants that we have tested, we see that the anionic surfactants are the only surfactants that show this behaviour. In literature, no evidence could be found of the negative influence of alcohols on cleaning-results in dry-cleaning. The addition of a co-solvent may change the adsorption or adherence of the surfactants at the textile or soil surface. The structure of the anionic surfactants (small cationic ion and large anionic ion) differs clearly from the other tested surfactants. This might be a reason why the co-solvent only has a negative influence on the adsorption of the anionic surfactants. In apolar solvents, the large ions have a stronger preference for the solvent than the smaller ones; the trend is that the smaller one adsorbs on the surface of particles and fibres [8]. This would give the particles and the fibres a positive charge, which causes repulsion between the particle and the fibre. When the solvent is made more polar (by the addition of IPA), however, the larger ions may tend to be adsorbed by the surface. Adsorption of one layer of these ions will probably give the fibre and the particle no charge. Therefore, cleaning might then not be based on repulsion but on the formation of a wedge formed between the fibre and the particle by adsorption of surfactants. The difference in cleaning mechanism may cause the difference in cleaning-result.

The influence of co-solvents on the cleaning-results for anionic surfactants may be a caused by the above-mentioned effect, but other effects may also play a role (e.g. influence of co-solvent on solubility).

5.3.2 Amines

As well as the experiments with anionic surfactants, cleaning-tests were also performed using amines as surfactants. The results of these tests are shown in Figures 4 and 5. The results for the separate test fabrics are shown in Table 5 in the appendix. In these experiments, 6 kg CO_2, 25 g water and 10 g surfactant were used, except for the experiment with DPA (di-n-propylamine), where 5 g surfactant was used.

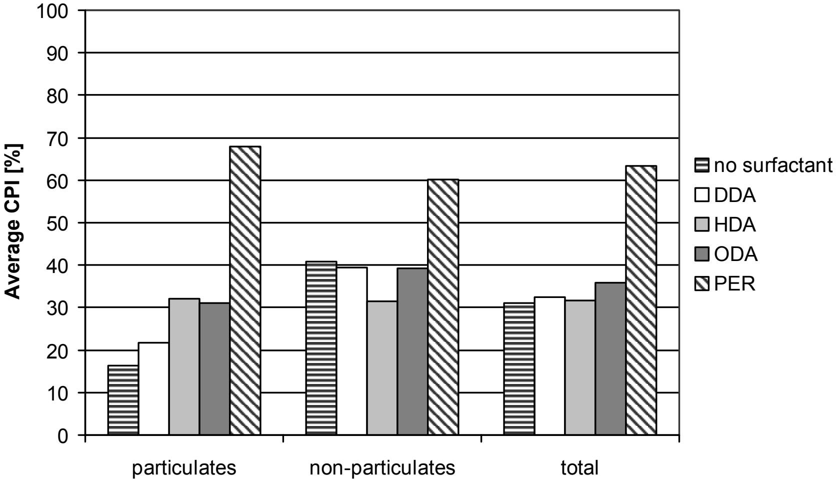


Figure 4: Average CPIs using primary amines

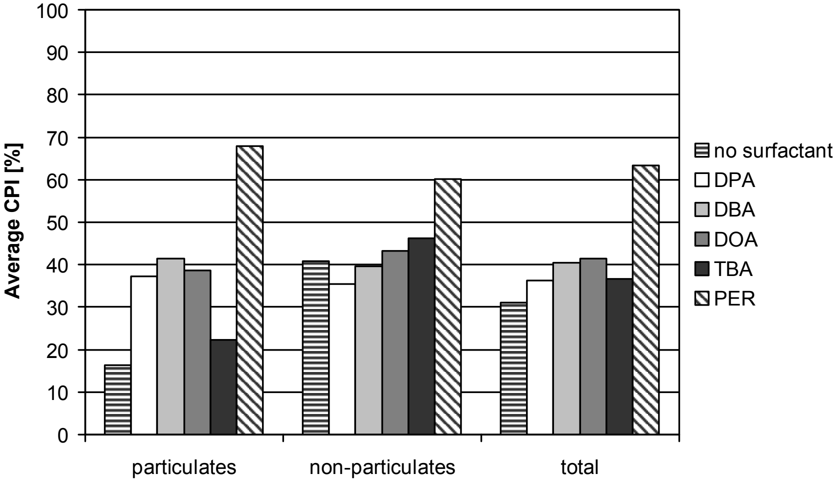


Figure 5: Average CPIs using secondary or tertiary amines

During the experiments, the pressure was 4.5 MPa and the temperature was 283 K.

From Figures 4 and 5, it is concluded that the use of amines has almost no influence on the removal of non-particulate soils. There is, however, a distinct influence on the removal of particulate soil. For the primary amines DDA (1-dodecylamine), HDA (1-hexadecylamine) and ODA (1-octadecylamine), there is an absolute increase in CPI_{part} of 5-16 %. The absolute increase in CPI_{part} for the secondary amines is larger (21-25 %). For the tertiary amine TBA (tribenzylamine), the absolute increase in CPI_{part} is 6 %. These figures show that the secondary amines are the most suitable amines for particulate soil removal when no co-solvent is used.

During all experiments with amines, solid surfactant particles were present. The primary amines were added as solids. The observed surfactant particles are, however, not only primary amines but also reaction products. Solid ODA can react with both liquid and vapour carbon dioxide to form solid product [9]. For the surfactant particles formed in CO_2 using DDA and ODA, the melting point was determined. The difference in melting point between the formed surfactant particles and the unreacted DDA and ODA was 20-35 K. This indicates that the primary amines might have reacted to form a solid product. The secondary amines DPA, DBA (di-n-butylamine) and DHA (di-n-hexylamine) are liquid at room temperature and atmospheric pressure. When they are added to carbon dioxide, however, surfactant particles are formed. This indicates that the secondary amines may also react with carbon dioxide to form solid product. According to [10], highly basic primary and secondary aliphatic amines can react with supercritical CO_2 thereby forming insoluble products. Tertiary amine TBA is solid at room temperature and atmospheric pressure. Solid particles were present during the experiments using this tertiary amine.

When the amines are used, various reactions may occur. The amines can be protonated according to the following reactions:

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \qquad (3)$$

$$H_2CO_3 + H_2O \longleftrightarrow H_3O^+ + HCO_3^- \qquad (4)$$

$$RN + H_3O^+ \longleftrightarrow RNH^+ + H_2O \qquad (5)$$

in which RN is a primary, secondary or tertiary amine.

In the dry-cleaning system with carbon dioxide water is present, which originates from the fabrics and from having been added to the system. Because of this water content, the pH of the CO_2-water system is approximately 3 [11]. The pKa of the amines used in this chapter lies between 10 and 11. Therefore, the amines can be protonated (eq. 5).

Primary and secondary amines can also react with carbon dioxide to form a carbamate [12-20]:

$$CO_2 + R_1R_2NH \longleftrightarrow R_1R_2NH^+COO^- \qquad (6)$$

in which R_1R_2NH is a primary or a secondary amine. The formed zwitterion is found in the isoelectric area. Above the isoelectric area, the zwitterion can be deprotonated by a base (eq. 7-9) [12-19]:

$$R_1R_2NH^+COO^- + R_1R_2NH \longleftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \qquad (7)$$

$$R_1R_2NH^+COO^- + H_2O \longleftrightarrow R_1R_2NCOO^- + H_3O^+ \qquad (8)$$

$$R_1R_2NH^+COO^- + HCO_3^- \longleftrightarrow R_1R_2NCOO^- + H_2CO_3 \qquad (9)$$

The formed anion (eq. 7-9) can react as follows [18, 19]:

$$R_1R_2NCOO^- + H_2O \longleftrightarrow R_1R_2NH + HCO_3^- \qquad (10)$$

Below the isoelectric area of the zwitterion, the zwitterion can be protonated according to the following reaction [20]:

$$R_1R_2NH^+COO^- + H_3O^+ \longleftrightarrow R_1R_2NH^+COOH + H_2O \qquad (11)$$

Since different reactions can take place using primary and secondary amines in CO_2 and since the reaction constants are not known under the process conditions used, we do not exactly know which compounds are formed. We, however, do know that a reaction has taken place forming a solid compound.

Tertiary amines cannot directly react with carbon dioxide, because tertiary amines lack the N-H bond required to form the carbamate ion [21-26].

The formation of zwitterions may play an important role in the cleaning process: TBA, which cannot react with CO_2 to form zwitterions, gives significantly lower results for particle removal. Furthermore, reactions (4) and (6) can be considered as competing reactions. When no water is present, it can be expected that more amines will react with CO_2 to form zwitterions compared to the situation where water is present. Experiments without the addition of water were performed. In these experiments, the results for particle removal increased significantly. These results confirm the hypothesis that the zwitterions play an important role in particle removal. However, the low cleaning-results using TBA may also be caused by the fact that TBA is not able to adsorb at the surface of the fibre and the soil particle because of steric hindrance.

To increase the cleaning-results for the non-particulate soils, IPA was also used as co-solvent during dry-cleaning with amines. In these experiments, 6 kg CO_2, 25 g water, 250 g IPA and 10 g amine were used, except for the experiment with DDA, in which 15 g amine was used. The process conditions were the same as during the experiments without IPA. The results of these experiments are shown in Figures 6 and 7. The results for the separate test fabrics are shown in Table 6 in the appendix.

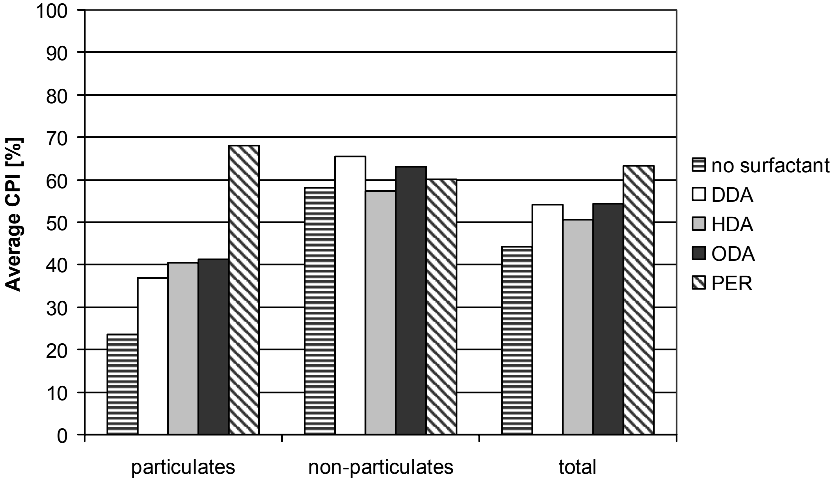


Figure 6: Average CPIs using primary amines and IPA

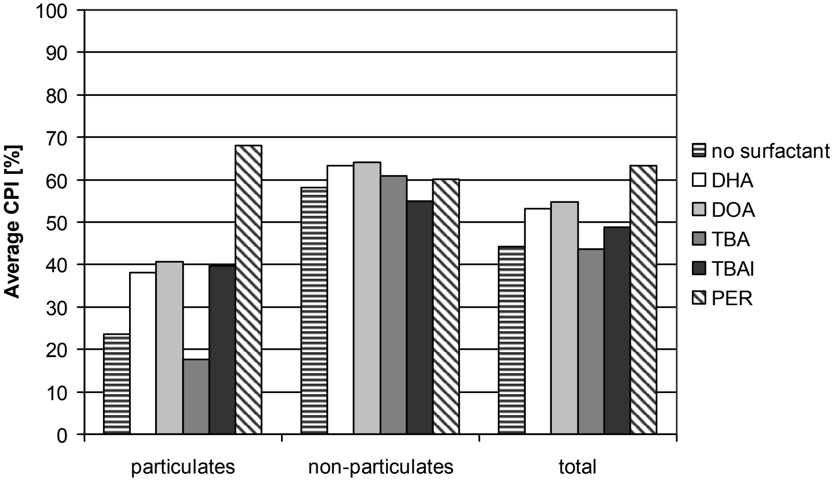


Figure 7: Average CPIs using a secondary amine, tertiary amine or quaternary ammonium salt, and IPA

From Figures 4, 5, 6 and 7, it can be concluded that the use of a co-solvent has a positive influence on the removal of non-particulate soils, which was to be expected. The use of

IPA has, however, in some cases also a positive influence on the removal of particulate soil, especially when using a primary amine. Using primary amines, CPI_{part} increases with an absolute percentage of 8-15 % when using IPA. For secondary and tertiary amines, the use of IPA has almost no or negative influence on the removal of particulate soil.

When we compare the results with and without amines (when using IPA), we conclude that the amines have a positive influence on the removal of particulate soils when IPA is used (except for TBA). Next to a positive influence on the removal of particulate soils, the use of amines also has a positive influence on the removal of non-particulate soils when using IPA (maximum increase in absolute CPI_{n-p} 8 %).

When IPA is used, the primary amines and the secondary amines give approximately the same results. Tertiary amines give worse results for the removal of particulate soil, but approximately the same for non-particulate soils. For the quaternary ammonium salt, the removal of particulate soil is approximately the same as for primary and secondary amines, but the removal of non-particulate soils is less than when using primary or secondary amines.

5.3.3 Discussion

When the results of all surfactants (amines and anionic surfactants) are compared, it is shown that DSS (without the use of IPA) gives the best results for particulate soil removal (CPI_{part} 51 %). NSH, DBA (both without IPA) and HDA, ODA, DOA (di-n-octylamine) and TBAI (tributylammonium iodide) (all with IPA) give good results for particulate soil removal (CPI_{part} between 40 and 41 %). The use of surfactants causes an increase in the cleaning performance index for relatively small particulate soil (CPI_{part}) from 24 % (when no surfactants are used) to a maximum of 51 % (when surfactants are used). The results are, however, still lower than when using PER (CPI_{part} 68 %), but the difference in cleaning performance between CO_2 and PER has become less.

The best surfactant for removal of non-particulate soils is DDA (with IPA), which gives a CPI_{n-p} of 66 %. Good results are obtained when using ODA, DHA and DOA (with IPA), these surfactants give a $CPI_{n\text{-}p}$ of 63-64 %, which is slightly higher than the $CPI_{n\text{-}p}$ obtained without surfactant, but with IPA (58 %). The removal of non-particulate soils in CO_2 with water, surfactant and co-solvent is better than in PER ($CPI_{n\text{-}p}$ 60 %). Without IPA, the best surfactant for the removal of non-particulate soils is TBA ($CPI_{n\text{-}p}$ 46 %) (For CO_2 and water: $CPI_{n\text{-}p}$ 41 %).

Best overall results without using IPA are achieved when using DSS (CPI_{total} 47 %). Best result with IPA is obtained when using DOA, which gives a CPI_{total} of 55 %. Good results are obtained using DDA, HDA, ODA and DHA (CPI_{total} 51-54 %). The CPI_{total} using CO_2, IPA and water is 44 %. The overall results in CO_2 are still lower than in PER (when PER is used, the result is 63 %), but the difference in cleaning performance between CO_2 and PER has decreased significantly. Using full-scale machines will give more mechanical action [3] and will probably bring the results in CO_2 up to the level of PER.

The removal of soil particles using amines or anionic surfactants may be based on the repulsion of the soil particles and textile. Charged compounds can be adsorbed by soil particles and/or fibres; thereby charging the soil particles and/or textile. This will establish an element of repulsion. This repulsion, together with mechanical action, may lead to the removal of small soil particles. Sorption of the used surfactants and the formation of a layer of surfactants on the particle and/or the fibre may also lead to the removal of particles. A wedge is then formed between the fibre and the particle and they are pried apart. Furthermore, the presence of surfactant particles may create more mechanical action and/or an abrasive effect.

To study the influence of the amount of surfactant particles present, different amounts of ODA were used. In the experiments, 6 kg CO_2, 25 g water, 250 g IPA and 1, 10 or 40 gram ODA were used. Experiments were performed at 4.5 MPa and 283 K. The results of the experiments are shown in Figure 8. Observation of the cleaning fluid through the viewing glasses showed that the amount of surfactant particles clearly increased with the amount of surfactant used. The results in Figure 8 show that with increasing amount of surfactant the CPI_{part} increases. From these data, the conclusion may be drawn that the surfactant particles formed by the reaction of the amine surfactants may (partly) be responsible for the removal of the soil particles from the textile.

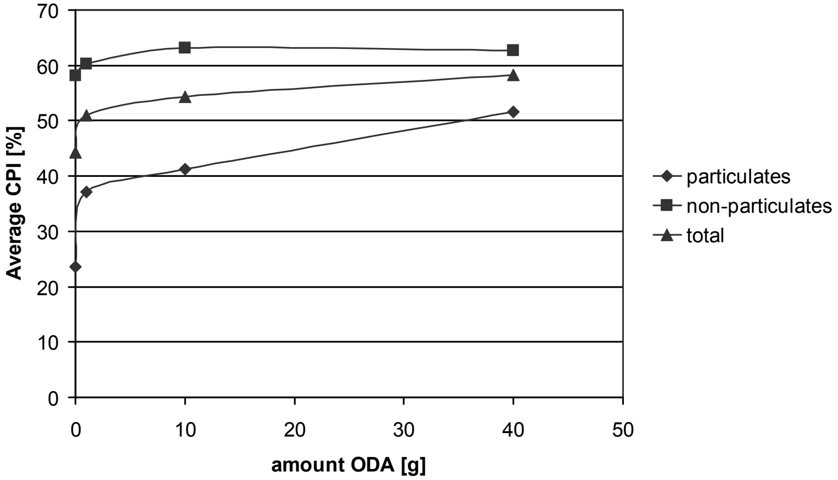


Figure 8: Average CPIs using ODA in various concentrations

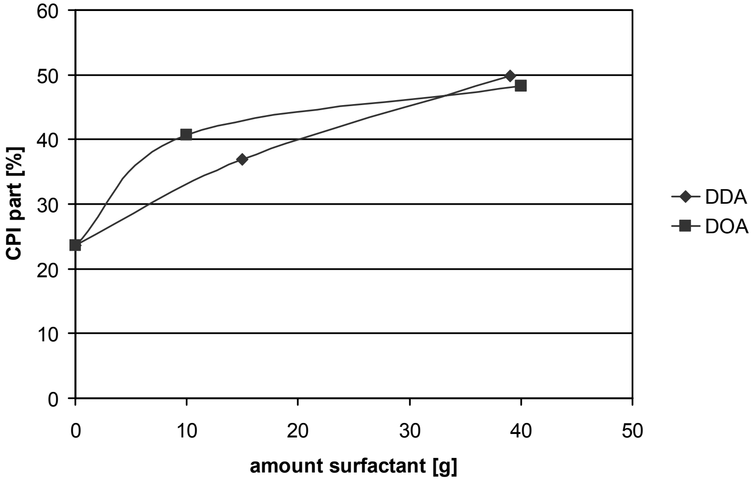
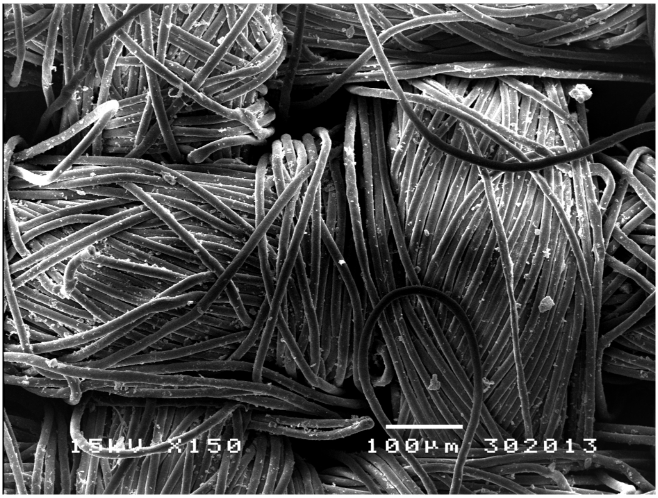
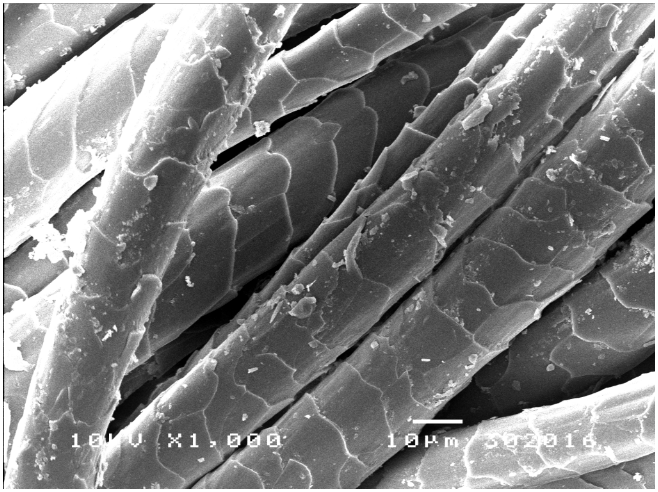


Figure 9: Average CPI_{part} as function as the amount of surfactant used for DDA and DOA



a) SP, 150 x



b) SW, 1000 x

Figure 10: SEM pictures of SW and SP fabrics after cleaning using DDA

The influence of the amount of surfactant on particulate soil removal was also investigated for DDA and DOA. The amounts used were 15 and 39 g DDA, 10 and 40 g

DOA. In these experiments, 6 kg CO_2, 25 g H_2O and 250 g IPA were used. Experiments were performed at 4.5 MPa and 283 K. In Figure 9, the CPI_{part} is shown for the two surfactants. Observation of the cleaning fluid during the experiments showed that more surfactant particles were formed when more surfactant was used. In Figure 9, it is shown that for these surfactants particulate soil removal also increases with increasing surfactant (and surfactant particle) concentration. These results support the hypothesis that the surfactant particles formed may be (partly) responsible for the removal of the soil particles from the textile.

After the cleaning-process, no white surfactants stains were visible on the fabrics. SEM (Scanning Electron Microscope) pictures were taken of the SW and SP fabric after cleaning with DDA to see if the solid surfactant was removed from the fabric. These pictures are shown in Figure 10. From Figure 10, it can be concluded that few surfactant particles remain on the fabric. The particles that remain on the fabric are small; the diameter is between 0-20 µm.

5.4 Conclusions

The overall results of the investigated surfactants are promising; the result increased from 70 %, when no surfactants are used, to 87 %, when surfactants are used, compared to the level when using PER. DOA gave the best results, DDA, HDA, ODA and DHA also gave good results.

Surfactant particles were formed in all experiments. In the case of the amines, these particles may be formed by reaction. The formed surfactant particles are probably partly responsible for the removal of the soil particles from the textile. The presence of surfactant particles may create more mechanical action and/or an abrasive effect. The charged surfactant may also adhere to the soil particles and/or fabric, thereby establishing an element of repulsion and/or a steric barrier.

Acknowledgements

We wish to thank the Ministry of Economic Affairs; The Ministry of Housing, Spatial Planning and Environment; and the Ministry of Education, Culture and Science for the financial support of the project EET K98044.

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Appendix

The results for the individual test cloths are given in Tables 2-6.

Table 2: Average relative deviation [%] in CPI per test fabric in CO_2 and PER

Test fabric	Average deviation in CO_2 [%]	Average deviation in PER [%]	Test fabric	Average deviation in CO_2 [%]	Average deviation in PER [%]
SW	10	2	BPC	5	2
SP	11	5	OC	5	5
EW	16	1	OPC	8	5
EP	15	2	KW	25	
BC	2	3	KP	22	

Table 3: CPI [%] for individual test cloths using anionic surfactants

	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
No surfactant	30	21	13	1	41	37	65	80	16	6
DOSS	42	29	18	0	33	26	69	82	22	8
NSH	70	41	46	9	37	26	57	74	16	4
SPH	53	29	31	3	37	30	59	74	17	3
SAS	44	26	47	7	45	38	65	82	25	6
DSS	58	40	66	39	47	38	62	76	27	19
PER	96	72	82	22	62	52	79	90	52	27

Table 4: CPI [%] for individual test cloths using anionic surfactants and IPA

	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
No surfactant	35	20	32	7	50	46	91	94	53	14
DOSS	7	0	0	0	47	46	88	92	56	9
NSH	67	28	40	2	50	43	83	84	40	15
SPH	55	28	44	4	45	39	82	87	44	9
SAS	54	32	33	9	63	43	86	92	35	22
DSS	52	40	34	14	59	41	89	94	55	18

Table 5: CPI [%] for individual test cloths using amines

	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
No surfactant	30	21	13	1	41	37	65	80	16	6
DDA	30	23	25	9	41	28	66	80	19	3
HDA	66	38	30	0	18	18	52	74	22	5
ODA	45	25	48	6	41	34	56	77	24	4
DPA	51	32	58	8	33	21	64	75	19	0
DBA	71	51	33	11	36	28	61	76	20	18
DOA	63	41	38	13	44	36	61	80	32	7
TBA	5	5	60	19	53	42	68	80	28	8
PER	96	72	82	22	62	52	79	90	52	27

Table 6: CPI [%] for individual test cloths using amines and IPA

	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
No surfactant	35	20	32	7	50	46	91	94	53	14
DDA	48	38	55	7	69	54	88	91	64	27
HDA	71	39	41	11	51	50	78	83	59	22
ODA	63	46	43	12	62	48	89	92	62	27
DHA	69	31	41	11	56	55	82	87	71	29
DOA	61	44	49	9	61	55	91	93	61	24
TBA	25	10	31	5	54	49	86	89	65	21
TBAI	60	42	39	17	54	40	82	84	48	20
PER	96	72	82	22	62	52	79	90	52	27

References

[1] B. Gosolitis, J. Kurz, M. Sverev, Textile dry cleaning in liquefied CO_2, in: G. Brunner (Ed.), Proceedings 2nd International Meeting on High Pressure Chemical Engineering, Hamburg, Germany, 2001.

[2] M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide, experimental set-up and washing-results, in: G. Brunner (Ed.), Proceedings 2nd International Meeting on High Pressure Chemical Engineering, Hamburg, Germany, 2001.

[3] Chapter 3 of this thesis; M.J.E. van Roosmalen, M. van Diggelen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide; The influence of mechanical action on washing-results, J. Supercrit. Fluids, 27 (2003) 97.

[4] M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, The influence of mechanical action and commercially available surfactants on particle removal in dry-cleaning with high-pressure carbon dioxide, in: A. Bertucco (Ed.), Chemical Engineering Transactions, Volume 2, 2002. Proceedings of 4th International Symposium on High Pressure Process Technology and Chemical Engineering, High Pressure in Venice, September 22-25, 2002, Venice, Italy, 2002, p.885.

[5] G. Jakobi, A. Löhr, M.J. Schwuger, D. Jung, W.K. Fischer, P. Gerike, K. Künstler, Detergents - Theory of washing process, in: Ullmann’s Encyclopedia of Industrial Chemistry, Sixth Edition, 2000 Electronic release, Wiley-VCH Verlag GmbH, Weinheim 2000.

[6] W.G. Cutler, R.C. Davis, Detergency; theory and test methods Part I, Dekker, New York 1972.

[7] Chapter 4 of this thesis; M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide- the influence of process conditions and various co-solvents (alcohols) on washing-results, J. Supercrit. Fluids, 27 (2003) 337.

[8] J. Lyklema, Fundamentals of interface and colloid science; Volume II Solid-liquid interfaces, Academic Press, London 1995.

[9] W.J. Schmitt, R.C. Reid, The solubility of paraffinic hydrocarbons and their derivatives in supercritical carbon dioxide, Chem. Eng. Commun., 64 (1988) 155.

[10] M. Ashraf-Khorassani, L.T. Taylor, Nitrous oxide versus carbon dioxide for supercritical fluid extraction and chromatography of amines, Anal. Chem., 62 (1990) 1177.

[11] K.H. Toews, R.M. Shroll, C.M. Wai, pH-defining equilibrium between water and supercritical CO_2. Influence on SFE of organics and metal chelates, Anal. Chem., 67 (1995) 4040.

[12] M. Caplow, Kinetics of carbamate formation and breakdown, J. Am. Chem. Soc., 90 (1968) 6795.

[13] P.V. Danckwerts, The reaction of CO_2 with ethanolamines, Chem. Eng. Sci., 34 (1979) 443.

[14] P.M.M. Blauwhoff, G.F. Versteeg, W.P.M. van Swaaij, A study on the reaction between CO_2 and alkanolamines in aqueous solutions, Chem. Eng. Sci., 39 (1984) 207.

[15] G.F. Versteeg, W.P.M. van Swaaij, On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions-I. Primary and secondary amines, Chem. Eng. Sci., 43 (1988) 573.

[16] D.A. Glasscock, J.E. Critchfield, G.T. Rochelle, CO_2 absorption/desorption in mixtures of methyldiethanolamine with monoethanolamine or diethanolamine, Chem. Eng. Sci., 46 (1991) 2829.

[17] R.J. Littel, G.F. Versteeg, W.P.M. van Swaaij, Kinetics of CO_2 with primary and secondary amines in aqueous solutions-I. Zwitterions deprotonation kinetics for DEA and DIPA in aqueous blends of alkanolamines, Chem. Eng. Sci., 47 (1992) 2027.

[18] E.B. Rinker, S.S. Ashour, O.C. Sandall, Kinetics and modelling of carbon dioxide absorption into aqueous solutions of diethanolamine, Ind. Eng. Chem. Res., 35 (1996) 1107.

[19] W. Bouhamra, O. Bavbek, E. Alper, Reaction mechanism and kinetics of aqueous solutions of 2-amino-2-methyl-1,3-propandiol and carbon dioxide, Chem. Eng. J., 73 (1999) 67.

[20] W. Rosenblatt, Amino Acid Amphoterics, in: E.G. Lomax (Ed.), Amphoteric Surfactants, Second Edition, Marcel Dekker, Inc., New York, 1996, p.49.

[21] E.B. Rinker, S.S. Ashour, O.C. Sandall, Absorption of carbon dioxide into aqueous blends of diethanolamine and methyldiethanolamine, Ind. Eng. Chem. Res., 39 (2000) 4346.

[22] T.L. Donaldson, Y.N. Nguyen, Carbon dioxide kinetics and transport in aqueous amine membranes, Ind. Eng. Chem. Fundam., 19 (1980) 260.

[23] N. Haimour, A. Bidarian, O.C. Sandall, Kinetices of the reaction between carbon dioxide and methyldiethanolamine, Chem Eng. Sci., 42 (1987) 1393.

[24] G.F. Versteeg, W.P.M. van Swaaij, On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions-II. Tertiary amines, Chem. Eng. Sci., 43 (1988) 587.

[25] R.J. Littel, W.P.M. van Swaaij, G.F. Versteeg, Kinetics of carbon dioxide with tertiary amines in aqueous solution, AIChE J., 36 (1990) 1633.

[26] E.B. Rinker, S.S. Ashour, O.C. Sandall, Kinetics and modelling of carbon dioxide absorption into aqueous solutions of N-methyldiethanolamine, Chem. Eng. Sci., 50 (1995) 755.

Chapter 6

Amino acid based surfactants for dry-cleaning with high-pressure carbon dioxide

M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp

Abstract

The currently most used dry-cleaning solvent is perchloroethylene (PER). Carbon dioxide could be an ideal solvent to replace PER. Amino acid based surfactants have been studied 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 irritating to the skin. 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_2*. The surfactant Amihope LL (N-lauroyl-L-lysine) gives the best cleaning-results. An important process parameter using this surfactant is the addition of water. The addition of water is required for sufficient removal of non-particulate soils. However, when no water is added to the system, there is a large increase in particulate soil removal. Therefore, a 2-bath process is proposed. The first bath is for particulate soil removal and has optimal conditions for particulate soil removal; the second bath has optimal conditions for non-particulate soil removal. The 2-bath process using Amihope LL gives excellent results: the result for particulate soil removal is 84 % compared to the results for PER, the result for non-particulate soil removal is 98 % compared to PER and the overall result is 92 % compared to PER.*

Contents are submitted to The Journal of Supercritical Fluids

6.1 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. The removal of non-polar soils in CO_2 is comparable to the level of cleaning in PER [1]. A disadvantage of CO_2, however, is its limited ability to dissolve polar molecules. The characteristics of CO_2 can be modified by the addition of a co-solvent. For dry-cleaning with CO_2, various co-solvents have been investigated of which 2-propanol (IPA) was the most suitable [2]. For most non-particulate soils, the results using CO_2 and IPA were comparable to the results using PER. Removal of particulate soils is difficult in CO_2 [3-5]. The removal of particulate soils from textile can be increased by increasing the mechanical action and/or the addition of surfactants. Relatively large particles (>20 μm) can be removed in CO_2 by increasing the mechanical action [6]. Increasing the mechanical action will, however, increase textile damage. Therefore, the amount of mechanical action should be a balance between large particle removal and textile damage.

Increasing the mechanical action has no positive influence on the removal of small particles (<20 μm) [6]. In order to remove small particles in CO_2, surfactants have to be used. Several non-ionic surfactants have been investigated [7, 8]; the addition of some of these surfactants had a positive effect on small particle removal, but did not increase the results in CO_2 up to the level of the results in PER. Anionic surfactants have also been studied [9]; the addition of some anionic surfactant had a distinct positive influence on the removal of particulate soil. For most anionic surfactants, however, the use of a co-solvent (which is required to remove non-particulate soils sufficiently) had a pronounced negative influence on the cleaning-results for particulate soil. It was shown [9] that amines as surfactants have a positive influence on the removal of particulate soils and also on the removal of non-particulate soils. For most amines, the use of co-solvent IPA hardly influenced the removal of particulate soil. The best overall result using CO_2 and an amine in the experimental set-up was 87 % compared to the PER bench mark. Unfortunately, amines are skin irritants which makes them less suitable for dry-cleaning. It is for this reason that we searched for alternatives.

There is increasing interest in the use of amino acid based surfactants [10]. For the production of amino acid based surfactants, renewable, low-cost raw materials are used [11]. Furthermore, the surfactants have a low toxicity, are biodegradable and not irritating to the skin. These characteristics make the amino acid based surfactants attractive for dry-cleaning with carbon dioxide.

In this chapter, various amino acid based surfactants based have been studied. To optimize the dry-cleaning process with carbon dioxide and the surfactants, the influence of various process parameters on the cleaning-results is investigated. The studied parameters are temperature (and, hence, since the system is closed, pressure and density), cleaning-time and amount of mechanical action. Furthermore, the influence of the amount of each substance used (CO_2, IPA, surfactant and water) was explored.

6.2 Experimental

6.2.1 Apparatus

The experimental set-up is shown schematically in Figure 1. The set-up was designed and constructed at the Laboratory for Process Equipment, Delft University of Technology (Delft, The Netherlands). The cleaning-vessel has an inside diameter of 0.25 m and volume of 25 l. This vessel was constructed at Van Steen Apparatenbouw B.V. (Pijnacker, The Netherlands). A rotating drum is mounted inside the cleaning-vessel to provide mechanical action. This inner-drum, with a diameter of 0.21 m and a volume of 10 l, is perforated and connected to a rotating shaft. The shaft passes through the wall of the high-pressure vessel to the motor via a seal and bearings. The motor is PLC controlled and the machine can run complete washing programs. The dry-cleaning vessel has two viewing glasses through which the contents of the vessel can be observed.

Before the fluid from the vessel enters the pump, it passes through a filter (pore size 11 µm), in order to remove particles, threads etc. During each cycle of circulation, the CO_2 passes through a heat exchanger contained in a cylinder with service fluid. The temperature of the service fluid can be regulated between 263 K and 333 K by a circulation heater/cooler, allowing the pressure in the closed CO_2 circulation to increase or decrease. The temperature, pressure, density, and mass flow are monitored. Additives can be gradually added to the circulation stream by means of a pump. After cleaning, the wash load is rinsed with pure carbon dioxide for 10 minutes.

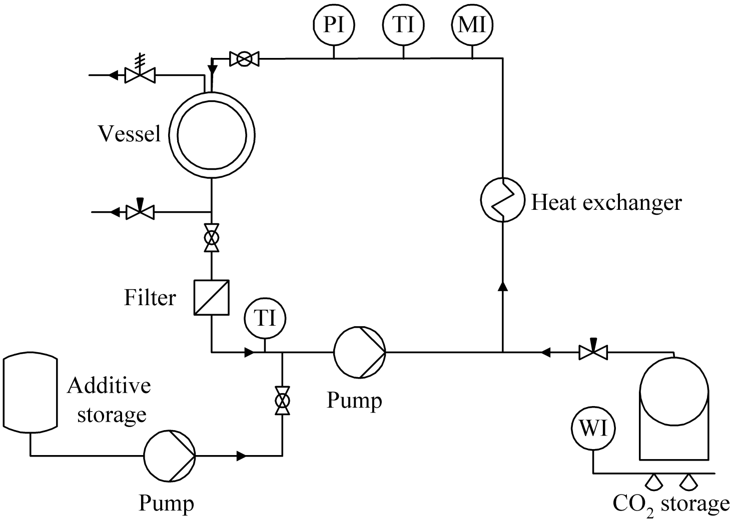


Figure 1: Experimental set-up

6.2.2 Materials

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 %+ was used as co-solvent. Furthermore, tap water was used. The following surfactants from Ajinomoto Co., Inc. (Tokyo, Japan) were used: Amifat P-30 (pyrrolidone carboxylic acid glyceryl oleate), CAE (DL-Pyrrolidone carboxylic acid salt of *N*-cocoyl-L-arginine ethyl ester), Amisoft LS-11 (*N*-(1-oxododecyl)-L-glutamic acid, monosodium salt), Amisoft MS-11 (*N*-(1-oxotetradecyll)-L-glutamic acid, monosodium salt), Amisoft HS-11 (*N*-(1-oxooctadecyl)-L-glutamic acid, monosodium salt), Amisoft CS-11 (L-glutamic acid, *N*-cocoacyl derivs., mono sodium 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).

Soiled test fabrics have been used to monitor the cleaning-results. The test fabrics have been purchased from the Center for Testmaterials B.V. (Vlaardingen, The Netherlands). Five different kinds of soils are used in the experiments described in this chapter:

- sebum (skin fat) coloured with carbon black particles (particle size 0-20 μm [6])
- clay particles (particle size 0-10 μm [6])
- egg yolk
- butterfat with colorant
- vegetable oil coloured with chlorophyll

The used test fabrics and their abbreviations are shown in Table 1. The test cloths are divided into two different types: cloths soiled with non-particulate soil (EW, EP, BC, BPC, OC, OPC) and cloths 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 cloths 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_2, whereas pure carbon black does.

In a typical run, the test fabrics are attached to cotton filling material. The test fabrics and the cotton filling material (400 gram) are placed in the drum. Before the test fabrics and the filling fabrics are placed in the drum, the fabrics are pre-soaked in an additive solution. This additive solution consists of water and/or co-solvent and/or surfactant. The composition of the solution is given for each experiment in the section Results and discussion.

Table 1: Used test fabrics and their abbreviations

	Wool	Polyester	Cotton	Polyester cotton
Sebum (skin fat) coloured with carbon black	SW	SP		
Clay particles	CW	CP		
Egg yolk	EW	EP		
Butterfat with colorant			BC	BPC
Vegetable oil coloured with chlorophyll			OC	OPC

6.2.3 Measuring

To monitor the cleaning-results, the colour of the test fabrics was measured before and after cleaning. The way of measuring is described in more detail in Chapter 2.

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

$$\mathrm{CPI} = \left[1 - \frac{\Delta \mathrm{E}_{\mathrm{washed-unsoiled}}}{\Delta \mathrm{E}_{\mathrm{soiled-unsoiled}}} \right] \times 100\% \tag{1}$$

where $\Delta \mathrm{E}$ is the measured colour difference in the $L^*a^*b^*$ colour space [12].

6.2.4 Experiments with PER

The soiled fabrics have also been cleaned in PER. This was done at a local dry cleaner's using a standard dry-cleaning procedure and no spotting. Spotting is a pre-treatment in which the pure detergent is physically brought into contact with the stain on the fabric. Spotting is a common method in the dry-cleaning industry for dealing with difficult stains.

6.3 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, $CPI_{n\text{-}p}$ (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. From duplicate experiments, we can calculate the absolute deviations. For CPI_{part} the absolute deviation is between 3 and 4 %, for $CPI_{n\text{-}p}$ the absolute deviation is between 2 and 3 %, for CPI_{total} the absolute deviation is about 2 %.

6.3.1 Amino acid based surfactants

The cleaning-results for the experiments with the amino acid based surfactants are shown in Figures 2 and 3. In Figure 2, the results are shown for the solid anionic surfactants Amisoft LS-11, MS-11, HS-11, CS-11 and the liquid anionic surfactant LT-12. In Figure 3, the results are shown for the liquid non-ionic surfactant Amifat P-30, the solid cationic surfactant CAE and the solid amphoteric surfactant Amihope LL. The results per test fabric are shown in Table 2 in the appendix. In the experiments, 6 kg CO_2, 25 g water and 10 g surfactant was used, except for the experiment with CAE in which 4 g surfactant was used. Cleaning-tests with these surfactants were performed at 5.7 MPa and 293 K. The cleaning-time was 30 minutes.

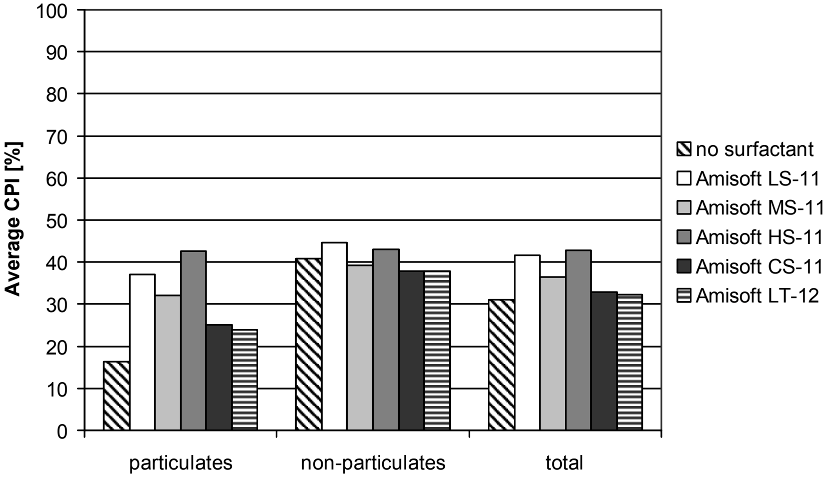


Figure 2: Average CPIs using the anionic surfactants Amisoft LS-11, MS-11, HS-11, CS-11 and LT-12

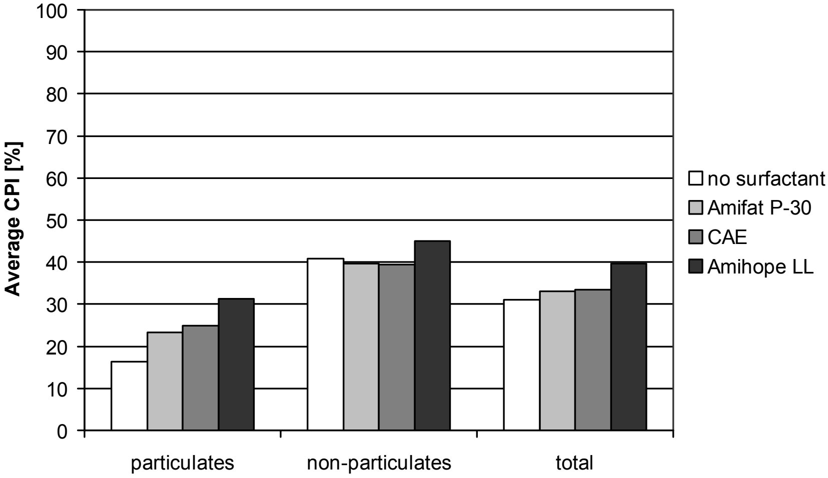
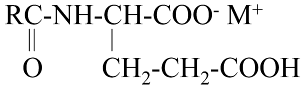


Figure 3: Average CPIs using the nonionic surfactant Amifat P-30, the cationic surfactant CAE and the amphoteric surfactant Amihope LL

During all experiments with solid surfactants, the surfactants were not completely solubilized in the liquid CO_2; small surfactant particles were visible. The liquid surfactants Amisoft LT-12 and Amifat P-30 were also not completely solubilized in the CO_2: after cleaning and rinsing, fatty surfactant stains remain on the fabrics.

In Figures 2 and 3, it is shown that all amino acid based surfactants had a positive influence on the cleaning-results for particulate soil; the absolute increase in CPI_{part} is 7-21 %. Despite the use of surfactants, the results for particulate soil removal are still lower than in PER; the CPI_{part} for PER is 68 %.

The general structure of the Amisoft surfactants is given in Figure 4. For Amisoft LS-11, MS-11, HS-11 and CS-11, M^+ is Na^+. For Amisoft LT-12, M^+ is triethanolamine. RCO is lauroyl for Amisoft LS-11 and Amisoft LT-12, myristoyl for Amisoft MS-11, stearoyl for Amisoft HS-11 and cocoyl for Amisoft CS-11. Figure 2 shows that for the anionic surfactants the length of the hydrophobic group and the type of hydrophilic group can make a difference in particulate soil removal, e.g. sodium as hydrophilic group (Amisoft LS-11) gives better cleaning-results than triethanolamine (Amisoft LT-12).



$$\underset{\underset{\mathrm{O}}{\|}}{\mathrm{RC}}\text{-NH-}\underset{\underset{\mathrm{CH_2\text{-}CH_2\text{-}COOH}}{|}}{\mathrm{CH}}\text{-COO}^-\ \mathrm{M}^+$$

Figure 4: General structure of Amisoft surfactants

Most surfactants have little influence (maximum decrease in absolute CPI 3 %, maximum increase 4 %) on the removal of non-particulate soils. The results for non-particulate soil removal using a surfactant and CO_2 are lower than in PER (max. 45 % vs. 60 %).

The liquid surfactants Amifat P-30 and Amisoft LT-12 give hardly any improvement on the cleaning performance. This is probably because these surfactants remain as fatty stains on the fabric. The anionic surfactants Amisoft LS-11, Amisoft HS-11 and the amphoteric surfactant Amihope LL give the best overall results.

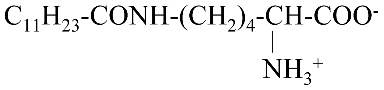
Anionic surfactants may be adsorbed by the soil particles and/or the fibres; thereby charging the soil particles and/or the textile. If this leads to negative charging of the soil particles as well as the fabric, then this may establish an element of repulsion. This repulsion may lead to the removal of the soil particles. The positive influence of charged solid surfactants on particulate soil removal was also found in Chapter 5 [9].

The amphoteric surfactant Amihope LL (Figure 5) has a structure that is similar to the zwitterion that forms when an amine reacts with CO_2. Primary and secondary amines can react with carbon dioxide according to the following reaction [13]:

$$CO_2 + R_1R_2NH \longleftrightarrow R_1R_2NH^+COO^- \qquad (2)$$

In Chapter 5 [9], we have already suggested that the formation of a zwitterion plays a role in the cleaning-process with amines. The results with Amihope LL confirm this earlier finding.

Next to repulsion by charge, the formation of a wedge between the fibre and the soil particle (by adsorption of surfactant) may also lead to particulate soil removal. Furthermore, the presence of surfactant particles may create an abrasive effect and/or more mechanical action.



$$C_{11}H_{23}\text{-CONH-}(CH_2)_4\text{-}\underset{\displaystyle NH_3^+}{\underset{|}{C}}H\text{-COO}^-$$

Figure 5: Structure of Amihope LL

6.3.2 *Co-solvent influence*

To increase the cleaning-results of the non-particulate soils, IPA was added as co-solvent. The results of the experiments with the addition of a co-solvent are shown in Figure 6. The result for each separate test fabric is shown in Table 3 in the appendix. In the experiments, 6 kg CO_2, 25 g water, 250 g IPA and 10 g surfactant was used. The process conditions were the same as during the experiments without co-solvent. In all experiments, a part of the surfactant was present in the form of solid surfactant particles.

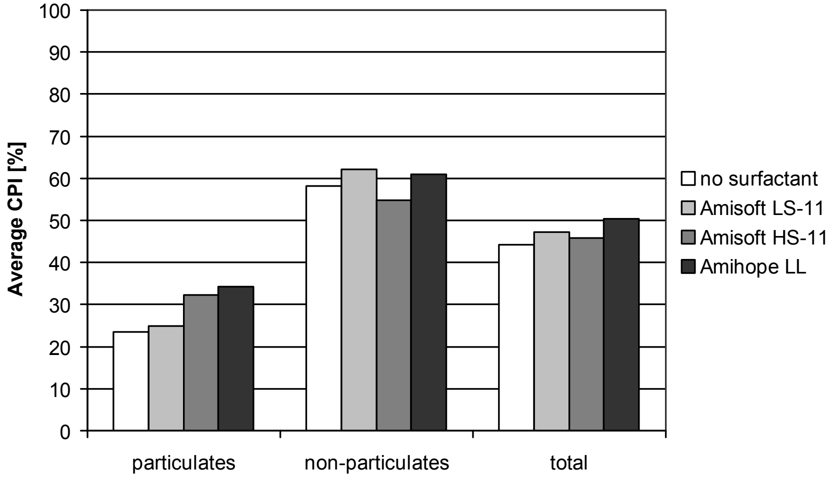


Figure 6: Average CPIs using amino acid based surfactants and IPA

Figures 2, 3 (no co-solvent) and 6 (with co-solvent) show that the addition of a co-solvent has a positive effect on the cleaning results for non-particulate soils for all surfactants (absolute increase in $CPI_{n\text{-}p}$ 16-21 %). The use of a co-solvent increases the results for the non-particulate soils up to the level in PER ($CPI_{n\text{-}p}$ 60 %). For the anionic surfactants Amisoft LS-11 and HS-11, however, the use of a co-solvent has a pronounced negative influence on the cleaning-results for particulate soil (decrease in absolute CPI_{part} 10-12 %). This effect was expected; it was also found when other anionic surfactants were applied with CO_2 [9]. The amphoteric surfactant Amihope LL gives the best result for particulate soil removal and the best overall result (CPI_{total} 50 %). The overall result using Amihope LL is, however, still lower than the result using PER (CPI_{total} 63 %). Optimization of the process may bring the results for Amihope LL closer to the results for PER.

6.3.3 Process analysis

To optimise the dry-cleaning process with carbon dioxide and the surfactant Amihope LL, the influence of various process parameters on the cleaning-results was investigated. The parameters studied are temperature (and, hence, since the system is closed, pressure and density), cleaning-time and amount of mechanical action. Furthermore, the influence of the amount of each substance used was also examined. In the previous paragraph, we already concluded that the use of a co-solvent (IPA) is required for sufficient removal of non-particulate soils. Here, the influence of the amount of CO_2, surfactant (Amihope LL) and water on the cleaning-results was investigated.

6.3.3.1 Mechanical action

Three different levels of mechanical action were investigated:

1. no mechanical action: no inner-drum rotation
2. normal mechanical action: inner-drum rotating at 75 rpm
3. high mechanical action: inner drum rotating at 75 rpm, heavy metal balls (diameter 28 mm) were added to the inner-drum

During the experiments, the temperature was 293 K and the pressure 5.7 MPa, the cleaning time was 30 minutes. 6 kg CO_2, 250 g IPA, 25 g water and 10 g Amihope LL was used. The result for each separate test fabric is shown in Table 4 in the appendix. The CPI_{part} for no mechanical action was 31 %, for normal mechanical action 32 % and for high mechanical action 34 %. Therefore, we conclude that the amount of mechanical action has almost no influence on the removal of relatively small soil particles when surfactants are used; increasing the rotational speed from 0 to 75 rpm has almost no influence and even the addition of balls has only a small influence on small particle removal. SP is the only test cloth for which the cleaning-results increase with mechanical action.

It was expected that at least normal mechanical action would be necessary for small particulate soil removal since the hydrodynamic forces on the soil particles and the transport of the loosened soil particles to the washing fluid play an important role in particulate soil removal. The experiments show that mechanical action may not be necessary for small particle removal. Mechanical action is, however, necessary for the removal of the surfactant from the fabrics; after cleaning without mechanical action, there were some white spots on the fabric, indicating that there was surfactant left on the fabric. Figure 7 shows an SEM (Scanning Electron Microscope) picture of the SW fabric cleaned without mechanical action. The surfactant left on the fabric is clearly visible.

Figure 7: Amihope LL particles deposited at the fibre surface using no mechanical action

6.3.3.2 Temperature

Experiments were performed at 282 K (4.4 MPa), 289 K (5.2 MPa), 296 K (6.1 MPa) and 303 K (7.2 MPa). All these points lie on the two-phase line. A two-phase system is preferred in dry-cleaning, because mechanical action is required to remove relatively large soil particles. The amount of mechanical action is higher in a two-phase system than in a one-phase system [6]. In the experiments, 6 kg CO_2, 250 g IPA, 25 g water and 5 g Amihope LL was used. Figure 8 shows the average CPIs as function of temperature at a cleaning-time of 30 minutes. The result for each separate test fabric is shown in Table 5 in the appendix.

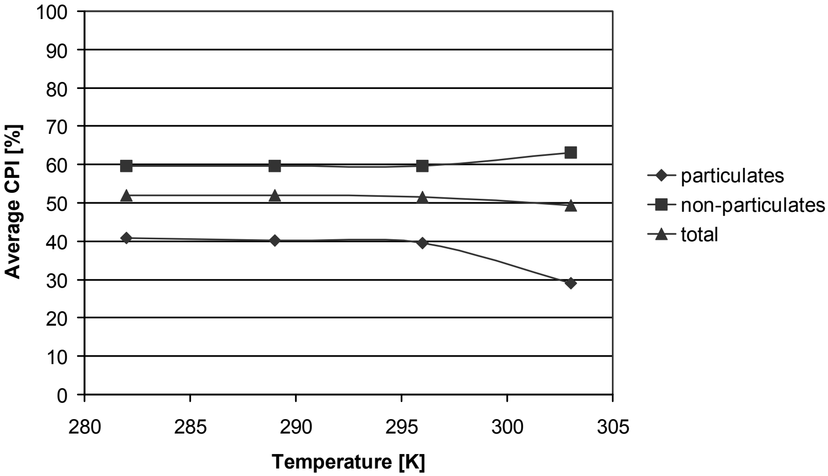


Figure 8: Average CPIs as function of temperature

From Figure 8, it can be concluded that the removal of particulate soil decreases with increasing temperature and that the removal of non-particulate soil slightly increases with increasing temperature. These effects are present between 296 K and 303 K. For non-particulate soil removal, this is in agreement with the solubility increase with temperature (although the density of the liquid phase decreases with increasing temperature). Furthermore, temperature increase may cause viscosity decrease of the soil and exceeding the melt temperature of fatty soils which also enhances non-particulate soil removal. It is difficult to explain the better particle removal at lower temperatures. At first, one would think of an influence via mechanical action (with decreasing temperature, the density of the gaseous phase decreases and the density of the liquid phase increases; and, therefore, the mechanical action increases [6]). The results using different levels of mechanical action, however, show that mechanical action has almost no influence on small particle removal. Since mechanical action is not responsible for better particle removal at lower temperatures, the surfactant is probably not working as well under higher temperatures (303 K) as under lower temperatures (lower than 296 K). A reason for this may be that temperature increase might cause a decrease in the efficiency and effectiveness of the adsorption of surfactants. The adsorption of anionic surfactants at solid-water interfaces is generally exothermic and hence more effective at lower temperatures [14]. This also might be the case for our amphoteric surfactant.

6.3.3.3 Cleaning-time

The fabrics were cleaned during 5, 10 or 30 minutes. During these experiments, 6 kg CO_2, 250 g IPA, 25 g water and 10 g Amihope LL was used and the pressure was 5.7 MPA, the temperature 293 K. In Figure 9, the results are given for these experiments. The result for each separate test fabric is shown in Table 6 in the appendix.

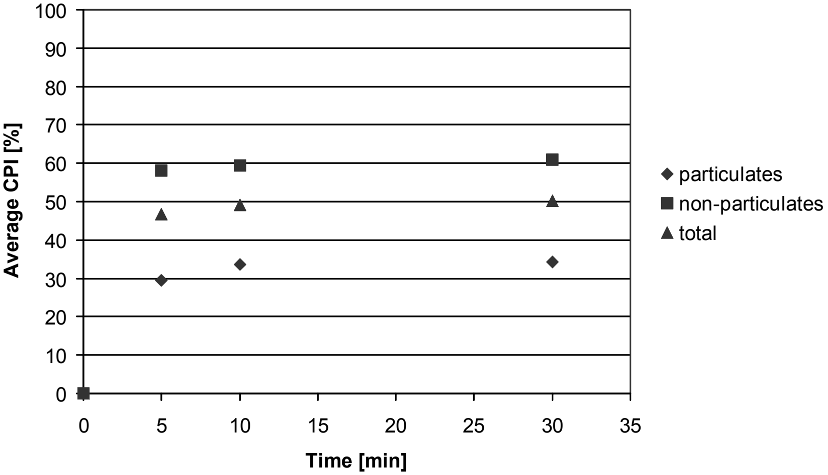


Figure 9: Average CPIs as function of time

From Figure 9, it can be concluded that the optimal cleaning-time will lie around 10 minutes. A longer cleaning-time would enhance the cleaning-results for SP and OPC, but would cost more and would increase the damage to the fabrics (although the observed damage in CO_2 is low). This optimal time (10 minutes) is similar to earlier findings using no surfactant [2]. The cleaning-time in CO_2 is comparable to the cleaning-time in PER, where the cleaning-time is 5 minutes. In the PER process, however, one hour is required to dry the fabrics after cleaning. In dry-cleaning with carbon dioxide, no drying is required, because the fabrics are dry after cleaning (even when IPA and water are added).

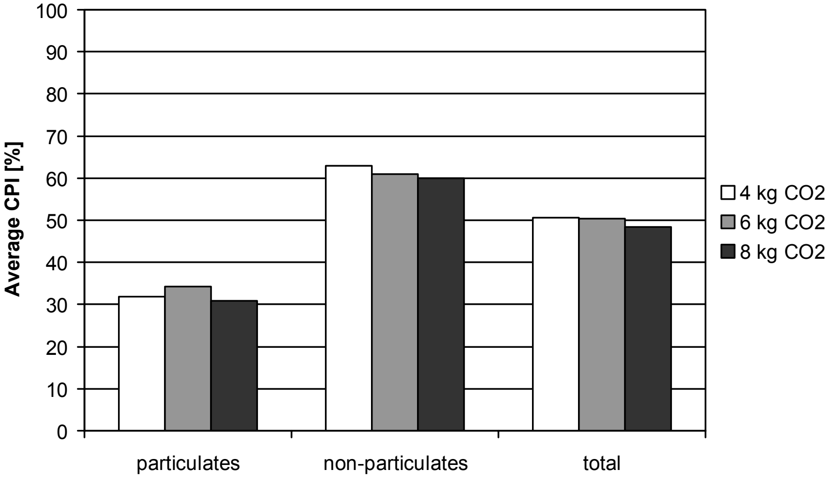


Figure 10: Average CPIs as function of the amount of CO_2

6.3.3.4 Amount of CO_2

The amount of CO_2 used in the experiments was 4, 6 or 8 kg CO_2. During these experiments, 250 g IPA, 25 g water and 10 g Amihope LL was used, the pressure was 5.7 MPA, the temperature 293 K and the cleaning-time was 30 minutes. The influence of the amount of CO_2 on the cleaning-results is shown in Figure 10. The result for each separate test fabric is shown in Table 7 in the appendix. Figure 10 shows that the amount of CO_2 has little influence on the cleaning-results (difference in absolute CPI max. 3 %). Best overall cleaning-results will be obtained using 4-6 kg CO_2.

6.3.3.5 Amount of surfactant (Amihope LL)

Five different amounts of surfactant were used to investigate the influence of the amount of surfactant on the cleaning-results; these amounts are 0, 1, 5, 10 and 20 g Amihope LL. During these experiments, 6 kg CO_2, 250 g IPA, and 25 g water was used, the pressure was 5.7 MPA, the temperature 293 K and the cleaning-time was 30 minutes. The results using different amounts of surfactant are given in Figure 11, the result for each separate test fabric is shown in Table 8 in the appendix.

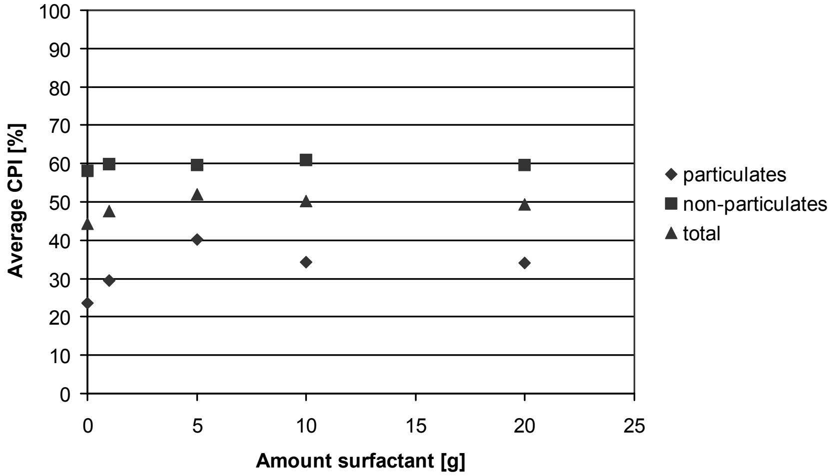


Figure 11: Average CPIs as function of the amount of surfactant (Amihope LL) used

Figure 11 shows that the amount of surfactant has no influence on the results for non-particulate soil removal, which was already concluded earlier in this chapter. The amount of surfactant, however, has a pronounced effect on particulate soil removal; there is, surprisingly, an optimum at 5 g. This optimum in particle removal is caused by the optimal removal of clay particles using 5 g surfactant, the removal of carbon black particles is almost constant between 5 and 20 g surfactant.

6.3.3.6 Amount of water

In a previous article concerning amines [9], it was mentioned that the amount of water added to the system can have a large influence on the cleaning-results for particulate soils. Therefore, the influence of the addition of water on the cleaning-results was also investigated for Amihope LL. The amount of water added during the experiments was 0, 25 or 50 gram. 6 kg CO_2, 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. The result for each separate test fabric is shown in Table 9 in the appendix.

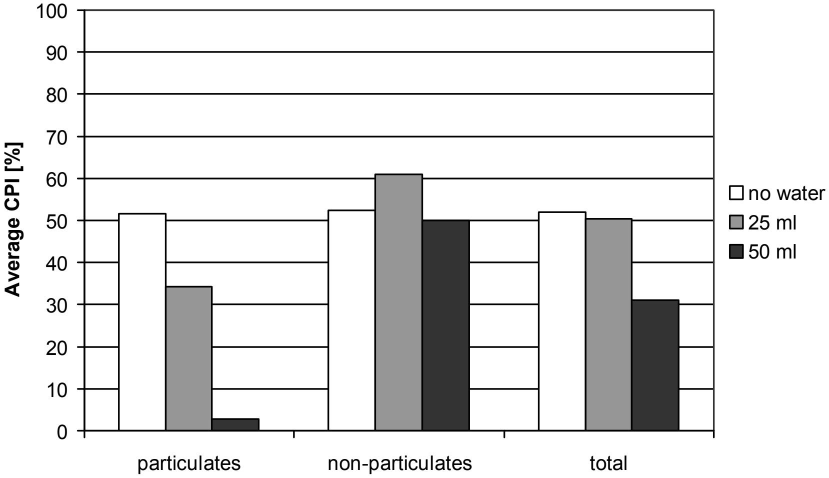


Figure 12: Average CPIs as function of the amount of water

As shown in Figure 12, the addition of water has a drastic influence on particulate soil removal; the CPI_{part} 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 required: the CPI_{n-p} 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_{n-p} decreases from 61 % to 50 %).

The addition of free water to the system may cause a pH change in the CO_2 phase. Free water is water that is separately added to the system, not the water that is inherently present in textile (e.g. the regain of wool is around 16 % at room temperature). It is, however, expected that this pH change is small near and in the textile, because the water that was already present in the textile may act as a buffer. Although the pH change might be small, this still might influence the charge of the surfactant, textile and soil particles. These three charge changes may cause a decrease in repulsion between the fabric and the particulate soil which may cause the decrease in particulate soil removal.

The addition of water may have a positive influence on the removal of some polar soils (e.g. water soluble soils). This may cause an increase in the results for the removal of non-particulate soils. Furthermore, the addition of water may cause swelling of the fibres, which may even out surface rugosities [14]. Furthermore, it allows diffusion of bath components to the interior of the fibre [15]. This can make the soil more accessible for the CO_2, which may cause an increase in the removal of non-particulate soils. This hypothesis is confirmed by the fact that the removal of egg yolk from polyester (a fibre that does not swell much and is already smooth) does not increase with the addition of water. The swelling of the fibre might cause a decrease in particulate soil removal: particles may get trapped.

The removal of all soils decreases when 50 g water is added. This amount of water may wet the textile and the soil too much, whereby the soil becomes less accessible for the CO_2.

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 the best for dry-cleaning with CO_2. The first bath is for particulate soil removal and has optimal conditions for particulate soil removal: no addition of water and temperature lower than or equal to 297 K. The second bath has optimal conditions for non-particulate soil removal: some water is added and the temperature will be around 303 K. 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_2, 5 g Amihope LL and 250 g IPA was used; the cleaning-time was 30 minutes. The use of IPA in the first bath is not necessary for the removal of particulate soil, but is added to this bath to remove already some non-particulate soil. In the second bath, the temperature was 298 K, the pressure 6.4 MPa; 6 kg CO_2, 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 13, which also shows the result for 1-bath dry-cleaning with and without water (already shown in Figure 12) and the results for dry-cleaning with PER in a commercial dry-cleaning apparatus. The result for each separate test fabric is shown in Table 10 in the appendix.

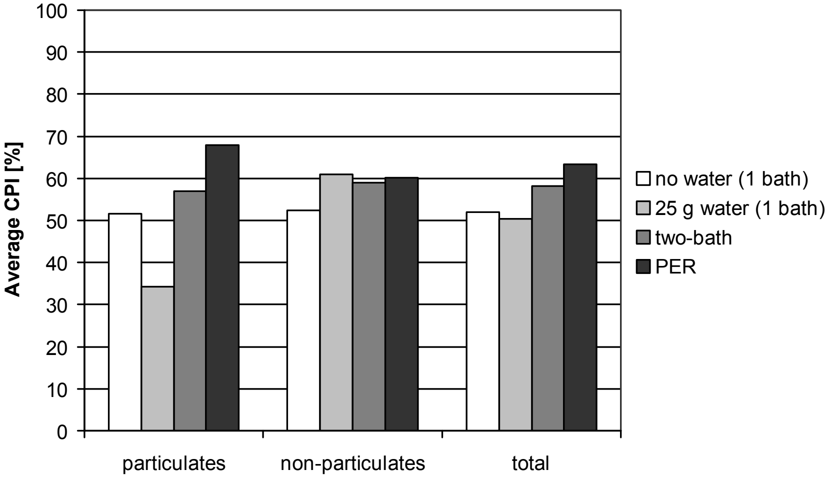


Figure 13: Average CPIs for 1-bath CO_2 dry-cleaning (with/without water), 2-bath CO_2 dry-cleaning and dry-cleaning with PER

Figure 13 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 when using PER (in a commercial dry-cleaning apparatus), non-particulate soil removal is 98 % compared to when using PER. This results in an overall result which is 92 % compared to when using PER.

After this two-bath process, no white surfactants stains were visible on the fabrics. An SEM picture (Figure 14) was taken of the SW fabric to see if the solid surfactant was removed from the fabric. From Figure 14 it can be concluded that few surfactant particles remain on the fabric and that the remaining surfactant particles are smaller than the particles shown in Figure 7. Since Amihope LL can be used in make-up products, skin care products and hair care products, it is not to be expected that remaining surfactant particles will cause any problems (e.g. skin irritation).

Figure 14: SW fabric after two-bath process

6.4 Conclusions

The 2-bath process using the amino acid based surfactant Amihope LL (*N*-lauroyl-L-lysine) gives excellent results: particulate soil removal is 84 % compared to PER (in a commercial dry-cleaning apparatus), non-particulate soil removal is 98 % compared to PER and the overall result is 92 % compared to PER.

An important process parameter is water addition. Water is required for sufficient removal of non-particulate soils. The addition of water has, however, a negative influence on particle removal. A two-bath process was proposed in which the first bath has optimal conditions for particulate soil removal (no addition of water) and the second bath has optimal conditions for non-particulate soil removal.

The surfactant Amihope LL gives the best cleaning-results. Using this surfactant, the optimal cleaning time will lie around 10 minutes. For non-particulate soil removal, the addition of a co-solvent is required to get sufficient results and a temperature above 296 K gives the best results.

The amount of mechanical action and the amount of CO_2 had no noticeable influence on particle removal. Furthermore, particle removal was best at temperatures below 296 K and when 5 g surfactant was used.

Acknowledgements

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Appendix

The results for the individual test cloths are given in Tables 2-10.

Table 2: CPI [%] for individual test cloths using amino acid based surfactants

	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
No surfactant	30	21	13	1	41	37	65	80	16	6
Amisoft LS-11	55	31	51	11	48	34	67	83	22	14
Amisoft MS-11	42	26	54	7	43	23	65	78	18	8
Amisoft HS-11	67	38	50	16	45	27	63	80	26	17
Amisoft CS-11	37	21	36	7	37	18	65	76	22	9
Amisoft LT-12	44	21	28	2	34	21	67	80	19	6
Amifat P-30	32	15	36	10	32	17	77	85	22	5
CAE	37	25	35	3	36	22	69	84	19	7
Amihope LL	47	35	37	6	48	29	71	84	25	14
PER	96	72	82	22	62	52	79	90	52	27

Table 3: CPI [%] for individual test cloths using amino acid based surfactants and IPA

	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
No surfactant	35	20	32	7	50	46	91	94	53	14
Amisoft LS-11	39	20	33	8	59	41	92	95	62	24
Amisoft HS-11	58	18	46	8	51	31	89	94	48	15
Amihope LL	53	40	38	6	60	41	92	95	52	26
PER	96	72	82	22	62	52	79	90	52	27

Table 4: CPI [%] for individual test cloths soiled with relatively small particles as function of amount of mechanical action

	SW	SP	CW	CP
No mechanical action	44	29	35	18
Normal	49	35	36	10
High	53	40	38	6

Table 5: CPI [%] for individual test cloths as function of temperature

Temperature [K]	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
282	59	32	59	13	55	38	90	94	58	23
289	51	40	58	12	54	38	92	96	52	26
296	55	42	51	9	56	41	93	96	53	20
303	45	33	32	6	62	44	94	97	57	24

Table 6: CPI [%] for individual test cloths as function of cleaning-time

Cleaning-time [min]	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
5	44	35	35	5	58	38	89	94	53	17
10	55	34	34	11	58	41	89	94	55	20
30	53	40	38	6	60	41	92	95	52	26

Table 7: CPI [%] for individual test cloths as function of amount of CO_2

Amount CO_2 [kg]	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
4	50	35	32	10	63	49	94	96	56	21
6	53	40	38	6	60	41	92	95	52	26
8	44	37	33	10	56	45	90	93	55	21

Table 8: CPI [%] for individual test cloths as function of amount surfactant (Amihope LL)

Amount surfactant [g]	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
0	35	20	32	7	50	46	91	94	53	14
1	41	31	38	8	58	38	91	95	53	26
5	51	40	58	12	54	38	92	96	52	26
10	53	40	38	6	60	41	92	95	52	26
20	54	37	37	8	58	39	90	92	53	25

Table 9: CPI [%] for individual test cloths as function of amount of water

Amount water [g]	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
0	71	49	71	16	44	40	75	83	49	21
25	53	40	38	6	60	41	92	95	52	26
50	15	1	0	0	27	42	86	89	48	8

Table 10: CPI [%] for individual test cloths for 1-bath CO_2 dry-cleaning (with/without water), 2-bath CO_2 dry-cleaning and dry-cleaning with PER

	SW	SP	CW	CP	EW	EP	BC	BPC	OC	OPC
No water (1 bath)	71	49	71	16	44	40	75	83	49	21
25 g water (1 bath)	53	40	38	6	60	41	92	95	52	26
2-bath	72	57	83	17	56	39	91	94	54	20
PER	96	72	82	22	62	52	79	90	52	27

References

[1] B. Gosolitis, J. Kurz, M. Swerev, Present situation of research and technology of textile cleaning in liquefied CO_2, in: M. Perrut, E. Reverchon (Ed.), Proceedings of the 7th meeting on supercritical fluids, Particules design, Materials and natural products processing, Antibes, France, 2002, p. 389.

[2] Chapter 4 of this thesis; M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide- the influence of process conditions and various co-solvents (alcohols) on washing-results, J. Supercrit. Fluids, 27 (2003) 337.

[3] J. Kurz, A. Hilbink, B. Gosolitis, Present situation of research and technology of textile cleaning in compressed CO_2, in: GVC-Fachausschuss “High-Pressure Chemical Engineering”, Karslruhe, Germany, 1999, p. 267.

[4] K. D. Hasenclever, Textilecleaning with solvents – is there a future?, in: Proceedings of the 41st wfk international detergency conference, Düsseldorf, Germany, 2003, p. 236.

[5] M. Seiter, Textile cleaning in liquid carbondioxide, in: Proceedings of the 41st wfk international detergency conference, Düsseldorf, Germany, 2003, p. 253.

[6] Chapter 3 of this thesis; M.J.E. van Roosmalen, M. van Diggelen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide; The influence of mechanical action on washing-results, J. Supercrit. Fluids, 27 (2003) 97.

[7] M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, The influence of mechanical action and commercially available surfactants on particle removal in dry-cleaning with high-pressure carbon dioxide, in: A. Bertucco (Ed.), Chemical Engineering Transactions, Volume 2, 2002. Proceedings of 4th International Symposium on High Pressure Process Technology and Chemical Engineering, High Pressure in Venice, September 22-25, 2002, Venice, Italy, 2002, p.885.

[8] M.P. Garate, G. Frens, Detergent performance in dry-cleaning with liquid CO_2, in: A. Bertucco (Ed.), Chemical Engineering Transactions, Volume 2, 2002. Proceedings of 4th International Symposium on High Pressure Process Technology and Chemical Engineering, High Pressure in Venice, September 22-25, 2002, Venice, Italy, 2002, p.873.

[9] Chapter 5 of this thesis; M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Surfactants for particulate soil removal in dry-cleaning with high-pressure carbon dioxide, The Journal of Supercritical Fluids, in press.

[10] J.L. Torres, E. Piera, M.R. Infante, P. Clapés, Purification of non-toxic, biodegradable arginine-based gemini surfactants, bis(args), by ion exchange chromatography, Prep. Biochem. & Biotechnol., 31 (2001) 259.

[11] M.R. Infante, A. Pinazo, J. Seguer, Non-conventional surfactants from amino acids and glycolipids: structure, preparation and properties, Colloids Surfaces A: Physicochem. Eng. Aspects, 123-124 (1997) 49.

[12] ASTM standards on color and appearance measurement 5th ed., ASTM, Philadelphia 1996.

[13] E.B. Rinker, S.S. Ashour, O.C. Sandall, Absorption of carbon dioxide into aqueous blends of diethanolamine and methyldiethanolamine, Ind. Eng. Chem. Res., 39 (2000) 4346.

[14] W.G. Cutler, R.C. Davis, Detergency; theory and test methods Part I, Dekker, New York 1972.

[15] A.M. Schwartz, The physical chemistry of detergency, in: Surface and Colloid Science Vol. 5, Ed. E. Matijević, John Wiley & Sons Inc., New York 1972.

Chapter 7

The cleaning-mechanisms in dry-cleaning with CO_2 and the solid surfactant Amihope LL

Abstract

In this chapter, the mechanisms that may play a role in particulate soil removal using the surfactant Amihope LL were investigated. The cleaning action of the surfactant is probably a combination of adsorption and mechanical action. Adsorption of surfactant may cause a wedge between the fibre and the particles. Furthermore, adsorption of surfactants may reduce the Van der Waals attraction between the fibre and the soil. The presence of surfactant particles creates more mechanical action and may cause an abrasive effect by impact of the surfactant particles with the soil particles.

7.1 Introduction

In this chapter, we investigate which mechanisms may play a role in particulate soil removal using the surfactant Amihope LL.

According to Cutler [1], a surfactant must be adsorbed by the fibre and/or the particle (preferably by both) to have a positive influence on the cleaning-results. By adsorption of a layer of surfactants, a wedge is formed between the fibre and the particle [1], which may cause the release of the particle from the fibre with the aid of hydrodynamic forces. Adsorption of surfactants may also reduce the Van der Waals attraction between the fibre and the soil. Furthermore, adsorption may lead to charge increase of the fibre and particle and, hence, mutual repulsion of the soil and the textile.

Based on this charge increase, Batra et al. [2] propose a two stage mechanism for particle removal in an aqueous system using ionic surfactants. In the first stage there is transportation of the surfactant to the surface of the fibre and/or particulate soil followed by surfactant adsorption, the second stage consists of removal of particles by fluid action. In the first stage, the surfactant must penetrate through the capillary systems of the fibre or the soil or through the slit between the surface of the fibre and the soil. The height of the slit (around 1 nm) between the surface of the fibre and the soil is characterized initially by Van der Waals-London attractive forces and Born repulsion forces [3]. The penetration of surfactant is followed by adsorption of surfactant. Usually, the transport of the surfactant to the surface (driven by concentration gradients or hydrodynamic forces) determines the adsorption rate.

In stage 2 of the model of Batra et al., a zeta-potential develops on the surfaces after ionic surfactants are adsorbed onto these surfaces (for explanation of zeta-potential, see Appendix). This leads to a repulsive double layer interaction between the surfaces. Also, the Van der Waals attraction between the fibre and the particle decreases. Thus, the adherence of the particle to the surface is considerably weakened. Hydrodynamic forces (drag force and lift force) cause the removal of the adhering particle. In the model of Batra et al., the magnitude of the critical hydrodynamic force (the force beyond which the particle can be detached) is dependent on the zeta-potential (which is a function of the bulk concentration of surfactant), particle size, and on surface roughness.

Timmerman [4] developed a dynamic model for detergency, see Figure 1. In this model, the top layer of the admicelle of surfactants formed at the textile surface moves over the surface. Fluid flow (caused by mechanical action in the liquid (by e.g. rotation of the vessel)) exerts periodical friction forces on the textile. These forces stretch the yarns and the fibres. The elongation and deformations cause flow of the liquid inside the fabric. Van der Donck [5] has demonstrated flow of the solution in the pores of the textiles created by mechanical action on the textile yarns. According to Timmerman, this liquid flow exerts a drag force on the adsorbed surfactant layers. The surfactant molecules in these layers have a degree of mobility, and will be dragged over the interface between the solid and the solution. The mobility of the surfactant could produce gradients in the surface coverage at obstructing particles. The Marangoni force in these gradients can roll and lift loosely adherent particles from the surface into the liquid. Subsequently, it could roll them into the liquid that flows by.

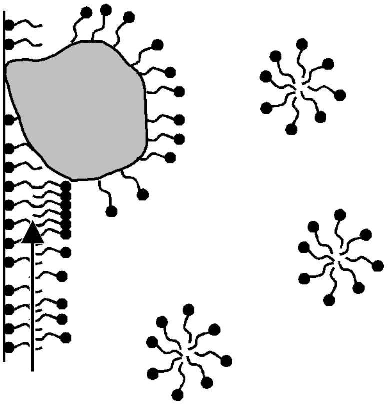


Figure 1: Dynamic model for detergency, redrawn from [4].
This Figure is based on the situation in water

This model requires slip of the liquid at the pore walls, instead of Poiseuille flow through the narrow pores in the textile material. According to Timmerman, for small capillary radii ($R < 4\eta/\mu$, in which η is the dynamic viscosity and μ is the friction coefficient) the preferred mode of response will be plug flow rather than a Poiseuille flow, because at this small radii plug flow will give the smallest energy dissipation. For a sodium dodecyl sulphate solution in water, Timmerman calculates the critical radius for plug flow ($2.6 \cdot 10^{-8}$ m) and concludes that this is of the same order as the radius of textile plugs. Furthermore, from experiments using nanomembranes, Timmerman concludes that there is conclusive evidence for the mobility of surfactant molecules in the adsorbed layers.

Elaborating on this, we think that the flow along the surface might also cause the particle to move but not enough to detach it from the surface. Surfactants may adsorb to the extra free particle and textile surface exposed by the particle movement. The adsorbed surfactants may form an obstruction between the textile and the particle, inhibiting the particle surface from reattaching to the textile. This may finally cause detachment of the particle from the textile surface. Important parameters in this mechanism are particle size, particle shape, interaction between the particle and the solid, properties of the fluid etc.

The surfactant Amihope LL is solid and has a very low solubility in CO_2; in all performed experiments with Amihope LL, surfactant particles were present. According to [6], Amihope LL is soluble in solutions with a pH less than 2 or more than 13. To determine the order of magnitude of the solubility of Amihope LL, experiments were performed. The solubility in a mixture of water (86.1 wt%) and acetic acid (13.9 wt%) with a pH of 2.1 was lower than $1 \cdot 10^{-3}$ wt%. To simulate the system CO_2-IPA (2-propanol)-water, the solubility was also measured in hexane (95.0 wt%)-IPA (4.0 wt%)-acetic acid (0.8 wt%). The solubility in this system was lower than $2 \cdot 10^{-3}$ wt%.

The present surfactant particles may also be partly responsible for the cleaning-effect of Amihope LL; they may cause more mechanical action and/or an abrasive effect.

From the previous paragraphs we can distinguish five different mechanisms that may play a role in particulate soil removal:

- By adsorption of a layer of surfactants, a wedge is formed between the fibre and the particle [1], which may cause the release of the particle from the fibre with the aid of hydrodynamic forces.
- Adsorption of surfactants may reduce the Van der Waals attraction between the fibre and the soil.
- Adsorption of ionic surfactants may lead to charge increase of the fibre and soil particle and, hence, mutual repulsion of the soil and the textile. Thus, the adherence of the soil particle to the surface is considerably weakened. Hydrodynamic forces (drag force and lift force) cause the removal of the adhering particle.
- Mobility of adsorbed surfactants could produce gradients in the surface coverage at obstructing particles. The Marangoni force in these gradients can roll and lift loosely adherent particles from the surface into the liquid. Subsequently, it could roll them into the liquid that flows by.
- The surfactant particles cause mechanical action and/or an abrasive effect that leads to the removal of soil particles from the fibre.

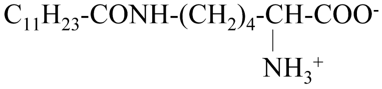
To find out what mechanisms can take place in dry-cleaning with CO_2 and Amihope LL, we first investigate the adsorption of surfactant on the used fibres and used particulate soils, after that the mechanical effects are examined. In our previous publications [7-9], the following test fabrics soiled with small particulate soils were used: sebum coloured with carbon black on wool (SW) and on polyester (SP), and clay on wool (CW) and on polyester (CP). To investigate adsorption, the chemical characteristics of the surfactant Amihope LL, used textile fibres (wool and polyester) and used particulate soils (carbon black and clay) have to be considered. Thereafter, the possibility of adsorption of surfactant by the fibres and the particulate soils is considered.

7.2 Adsorption

7.2.1 Chemical characteristics

7.2.1.1 Amihope LL

First, we take a look at the surfactant Amihope LL. The chemical structure of Amihope LL is given in Figure 2. The stereo representation is given in Figure 3.



$$C_{11}H_{23}\text{-CONH-}(CH_2)_4\text{-}\underset{\underset{\displaystyle NH_3^+}{|}}{CH}\text{-COO}^-$$

Figure 2: Amihope LL

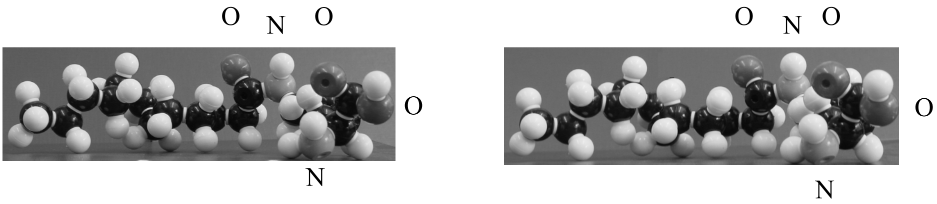


Figure 3: Stereo representation of Amihope LL

The tail of the surfactant is hydrophobic, the head group hydrophilic. It is not to be expected that the tail of the surfactant will shield the polar atoms from the apolar solvent, because this is entropically unfavourable. Hydrogen bonds between the surfactants molecules will probably be formed and therefore surfactant aggregates will be present.

The charge of this amphoteric surfactant is pH-dependent. The pK_a (negative logarithm of the acid dissociation constant) of the acidic site is 2.53 ± 0.24, the pK_b (negative logarithm of the base dissociation constant) of the basic site 4.23 ± 0.16 [10]. The pH of the point of zero charge (pH^0) can be calculated using these numbers according to the following formula [11]:

$$pH^0 = \log V_m + \frac{1}{2}\left(pK_a - pK_b + pK_w\right) - \frac{1}{2}\log\left(\frac{[AH]}{[B]}\right) \qquad (1)$$

where V_m is the molar volume of water
K_w is the dissociation constant of water
[AH] is the concentration of sites that can be negatively charged
[B] is the concentration of sites that can be positively charged

K_w was taken from [12]. The calculated pH^0 is 5. Below this pH, a part of the surfactant will be in a net cationic state, the rest of the surfactant will be in the net neutral state. In the net neutral state the surfactant may be seen as having distinct anionic and cationic charges (zwitterionic) or as semipolar nonionic surfactant [13]. According to Chaves et al. [14], however, it is necessary to consider individual charge-charge interactions for amphoteric surfactants; consideration of only the net charge does not lead to an accurate prediction of adsorption. The surfactant in the net neutral state should therefore be considered as a zwitterion and not as a nonionic.

7.2.1.2 Wool

Wool is largely based on keratin, which is a polyamino acid. The structure of amino acids is given in Figure 4. The structure of keratin is given in Figure 5.

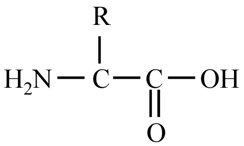


Figure 4: Amino acid

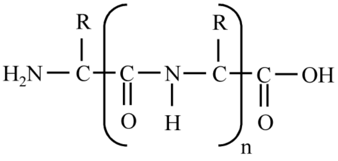


Figure 5: Keratin

As shown in Figure 5, the keratin fibres contain carboxyl groups and amino groups. Amino groups can chemisorb anionic surfactants, carboxyl groups chemisorb cationic surfactants.

There are about 21 amino acids in wool; group R varies from one amino acid to another. The 7 amino acids that occur most in wool [15] are listed in Table 1. In this Table, the pK_a of the acidic sites and the pK_b of the basic site are also given. Furthermore, for each amino acid the pH^0 was calculated using equation (1).

Table 1: Overview of most occurring amino acids in wool

Amino acid	pK_a acidic site [10]	pK_b basic site [10]	pH^0
Cystein	2.07	2.95	5.4
Cystine	1.70	5.28	4.0
Aspartic acid	2.28	4.05	4.9
Asparagine	2.3	5.66	4.1
Glutamic acid	2.17	4.24	4.8
Glutamine	2.27	4.48	4.7
Serine	2.16	4.6	4.6

The isoelectric point of keratin is approximately 4.9 [16]. Reported isoelectric points of wool vary between 3.4 and 4.5 [1]. It is assumed that in CO_2 the pH at the wool surface is approximately 3 [17], because of the water present in the wool (wool is hydrophilic). At a pH of 3, a part of the keratin will be in a net cationic state, the rest will be in the net neutral state.

7.2.1.3 Polyester

The most common polyester is the polymer of terephthalic acid (Figure 6) and ethylene glycol (Figure 7); polyethylene terephthalate (PET) (Figure 8). Polyester is hydrophobic.

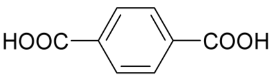


Figure 6: Terephthalic acid

$HO-C-C-OH$

Figure 7: Ethylene glycol

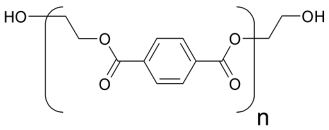


Figure 8: Polyester

7.2.1.4 Carbon black

In [18] a detailed description of the formation and the chemical properties of carbon black is given. Carbon black is formed by either pyrolysis or by partial combustion of vapours containing carbon. Depending on the production process and the raw materials, carbon black, next to carbon (80-99.5 wt%), also contains chemically bound hydrogen (0.3-1.3 wt%), oxygen (0.5-15.0 wt%), nitrogen (0.1-0.7 wt%), and sulfur (0.1-0.7 wt%). The hydrogen in carbon black is bound as CH groups at the edge of the carbon layers. Nitrogen seems to be primarily integrated into the aromatic layer system as heteroatoms. Oxygen is bound to the surface in the form of =O, -OH or -COOH groups. Carbon black is (overall) hydrophobic.

7.2.1.5 Clay

The structure of clay is described in detail in [11]. The structure of kaolinite (a clay mineral) is shown in Figure 9. The basic building bricks of clay minerals are tetrahedra with Si^{4+} atoms in the centre which are four coordinated by oxygens, and octahedrons with Al^{3+} or Mg^{2+} in the centres which are coordinated by oxygens and (especially with magnesium) hydroxyls. In the tetrahedral layer Si^{4+} may be partly substituted by Al^{3+} (this takes place during the genesis of the mineral) without altering the lattice (isomorphic substitution). Similarly, in the octahedral layers Al^{3+} may be replaced by Mg^{2+}, Fe^{2+} or other bivalent cations. As a result, a negative charge develops inside the solids. This negative charge gives rise to a constant charge residing on the plates. This is usually compensated with sodium and calcium ions in the interlayer space. The charge of the edges is variable, generated by the uptake or release of protons. The point of zero charge of the edges is probably near neutral. At low pH, the edge surface charge is positive. Clay is hydrophilic.

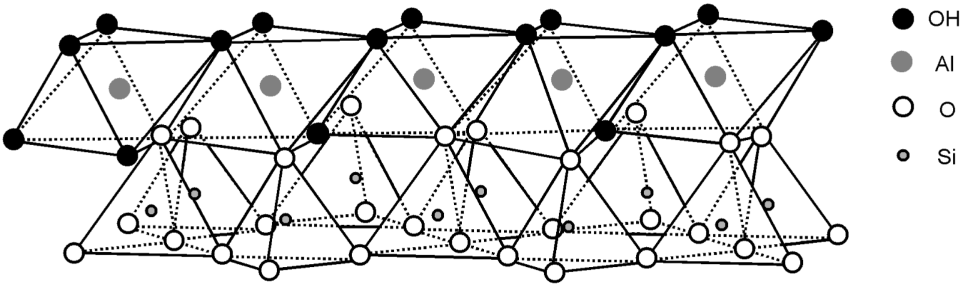


Figure 9: Structure of a kaolinite crystal, redrawn from [11]

7.2.2 Adsorption of surfactants on fibres and soil

There are two main ways of surfactant adsorption: chemisorption and physical adsorption. Ionic surfactants can be chemisorbed by fibres via ion exchange and ion pairing. On a hydrophilic surface, like wool and clay, the electrostatic interaction between a charged surface and an oppositely charged surfactant is often the driving force for adsorption from solution onto the solid surface. The amount adsorbed may be determined by this electrostatic interaction and the electrostatic repulsion within the adsorbed layer [19]. Chemisorption of the ionic surfactants can be followed by physical adsorption of these surfactants (multilayer adsorption).

The first layer of adsorption can also be formed by physical adsorption of nonionic or ionic surfactants, this can be followed by physical adsorption of another layer of surfactant. The attractive forces causing physical adsorption may have different origins, for example London-Van der Waals, hydrophobic and steric forces.

The adsorption of surfactants can change the hydrophilicity of the substrate; if a hydrophilic substrate adsorbs a surfactant with its head group, the hydrophobic surfactant tail points to the solvent and the surface becomes hydrophobic.

We will first consider chemisorption of Amihope LL on the fibres and particulate soils, followed by physical adsorption.

7.2.2.1 Chemisorption of Amihope LL

7.2.2.1.1 Wool

At a pH of 3, a part of the surfactant and a part of the wool will be in a net cationic state, the rest of the surfactant and the wool will be in the net neutral state. The surfactant Amihope LL may react with the COO^- groups of wool (with its NH_3^+ groups) and the NH_3^+ groups of wool (with its COO^- groups). A schematic representation of different types of chemisorption is shown in Figure 10. Drawing a shows the adsorption of a net positive surfactant by a COO^- group of wool, drawing b shows adsorption of the zwitterionic surfactant by the a positive and a negatively charged group of wool, drawing c shows adsorption of the zwitterionic surfactant by a positively charged group of wool, and drawing d shows adsorption of the zwitterionic surfactant by a negatively charged group of wool.

It is hard to say what the charge of the wool will become after chemisorption. The sorption of zwitterions by a positive and a negatively charged group of wool has no influence on the total charge. The adsorption of the zwitterionic surfactant by a positively or a negatively charged group of wool has also no influence on the total charge. The adsorption of the net positive surfactant by a COO^- group of wool, however, will result in a less negatively charged wool surface. All resulting charge is still concentrated at the wool surface, as demonstrated in Figure 10.

By adsorption of surfactant, the wool becomes hydrophobic.

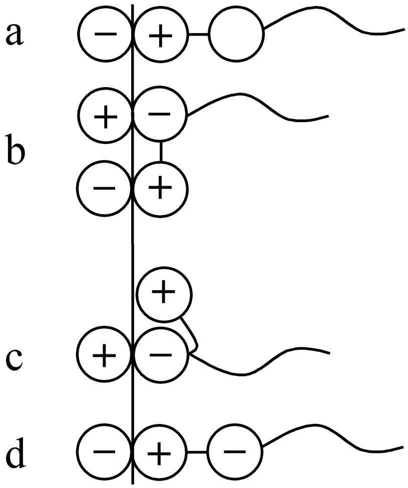


Figure 10: Adsorption of surfactant by wool

7.2.2.1.2 Polyester

Since polyester has no groups that can react with the surfactant, no chemisorption will take place.

7.2.2.1.3 Carbon black

Carbon black contains acidic oxides; it can chemisorb the surfactant (by the surfactant NH_3^+ group) with its COO^- group. Therefore, the net positively charged surfactants and the zwitterionic surfactants of Amihope LL can react with carbon black (see Figure 11, drawings a and b).

In water, the carbon black acquires a negative charge [3]. When the net cationic surfactant is adsorbed by the carbon black, the charge of the carbon black is reduced. Adsorption of the zwitterionic surfactant will not affect the charge. In total, the charge will probably be reduced by the adsorption of one layer of surfactant. The charge that is present is concentrated at the carbon black surface.

The carbon black stays hydrophobic.

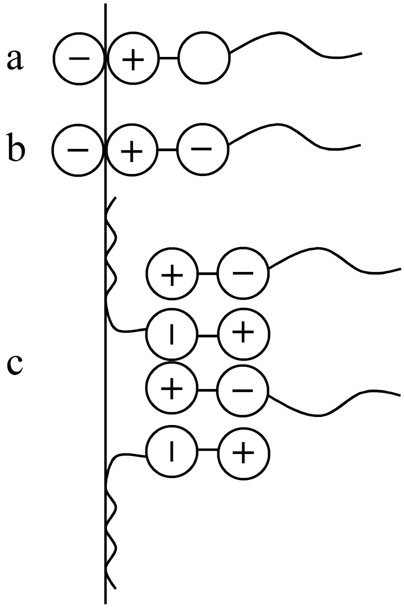


Figure 11: Adsorption of surfactant by carbon black

7.2.2.1.4 Clay

The surfactants can undergo cation exchange with the cations in the interlayer space of the clay [20]. This will not affect the charge of the clay. Furthermore, the surfactants can also react with the silicic acid groups and the basic alumina groups, it depends on the pH with which groups they will react. After chemisorption of one layer of surfactant, the charge of the clay will probably be reduced. Additionally, the charge that is still present is concentrated at the clay surface. The clay will become hydrophobic.

7.2.2.2 Physical adsorption of Amihope LL

7.2.2.2.1 Wool and clay

According to Somasundaran [21], the adsorption of ionic surfactants on hydrophilic substrates (like clay and wool) in non-aqueous solutions proceeds to a monolayer and there is no further evidence of lateral interactions or aggregation among the adsorbed molecules. Therefore, it is to be expected that only one layer of Amihope LL will be adsorbed on wool and clay.

7.2.2.2.2 Polyester

Polyester is hydrophobic. Therefore, it is not favourable for the surfactants to adsorb at the hydrophobic surface with their hydrophilic head group. However, the surfactants might adsorb at the polyester with their hydrophobic tail. The polar head group of the surfactant molecule is then exposed to a solvent (CO_2) with which it is not compatible. Therefore, adsorption of the first layer of surfactants will be followed by the formation of a second layer of surfactants by ion-pair interactions.

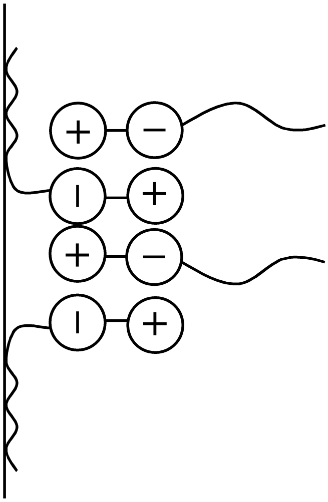


Figure 12: Adsorption of surfactant by polyester

The surfactant molecules may form aggregates (as shown in Figure 12) that would effectively create a polar microdomain to shield the head groups from the surface and the solution [21]. In this aggregate, the hydrophobic tails are on the outside, interacting with the CO_2 and the polyester fibre.

7.2.2.2.3 Carbon black

In carbon black, chemisorption and physical adsorption can take place simultaneously. Chemisorption will take place with the head group towards the surface (drawings a and b in Figure 11). Physical adsorption may take place with the hydrophobic tail towards the hydrophobic carbon black surface (drawing c in Figure 11), followed by the formation of a second layer of surfactants by ion-pair interactions.

7.2.3 Discussion of adsorption

We can conclude that one layer of surfactant will be chemisorbed on wool and clay. On carbon black also one layer of surfactants will be chemisorbed, two or more layers of surfactant may be adsorbed by physical adsorption. On polyester, two or more layers may be adsorbed by physical adsorption.

Adsorption of surfactants does not lead to charge increase of the fibres and the particulate soils; it probably decreases or does not influence the charge of the substrates. Furthermore, the charge that is still present after sorption of the surfactant is concentrated at the surface of the fibre (or adhered soil particle) and will therefore not be ”felt” by the adhered soil particle (or fibre). Therefore, we can conclude that mutual repulsion of the soil and the textile by charge increase is probably not the mechanism that governs soil removal using the surfactant Amihope LL.

In the model of Timmerman, a bilayer of surfactants is adsorbed by the textile surface. Using Amihope LL, such a bilayer is probably not adsorbed on wool. The layer that is adsorbed on wool is bound by chemisorption and, therefore, probably not able to move. Therefore, it is unlikely that the cleaning of wool using Amihope LL follows the model of Timmerman.

Although adsorption does not play a role in particulate soil removal by repulsion through charge increase, adsorption of surfactants can still play a role in particulate soil removal in CO_2. By adsorption of a layer of surfactants, a wedge is formed between the fibre and the particle [1], which may cause the release of the particle from the fibre with the aid of hydrodynamic forces. Furthermore, adsorption of surfactants may reduce the Van der Waals attraction between the fibre and the soil.

This hypothesis is confirmed in experiments using a soluble liquid nonionic surfactant in CO_2 (adsorbed via physical adsorption) [22]. These experiments showed an increase in cleaning performance for small particulate soils compared to when no surfactant was used.

7.3 Mechanical effects

After discussing adsorption, the possible mechanical effects in cleaning with Amihope LL are now considered. In the model of Batra et al. the surface roughness of the fibre is taken into account by the presence of hemispherical asperities. The asperity height (height varied between 0 and 0.4 nm) is a parameter that strongly influences the critical hydrodynamic force. According to Batra et al., when the asperity height becomes comparable to that of the equilibrium distance between the fibre and soil, the distance of separation between the fibre and particulate soil becomes extremely low and the interactions very strong, and, therefore, the force required to dislodge the particle is very high. Therefore, a higher surface roughness leads to a larger critical hydrodynamic force. Fibres with a higher surface roughness will thus give lower cleaning-results. Polyester fibres are smooth, wool is covered with scales; therefore, according to the model of Batra et al., polyester should give better cleaning-results than wool. Our cleaning-results, however, show higher results for wool. This may be caused by the higher flexibility of the wool, which makes it easier to bend. This deformation can cause local changes in pore velocity and loosening of particles captured in or between the yarns [23], which may result in higher cleaning-results. Furthermore, polyester can become charged with static electricity, helping to attract dirt particles [24]. Surfactant adsorption on polyester may also be less favourable than adsorption on wool, which may also explain the lower cleaning-results for polyester.

From the above and the discussion about adsorption (showing that charge increase is probably not the mechanism that governs soil removal using the surfactant Amihope LL), we conclude that particle removal with Amihope LL does probably not occur according to the model of Batra et al.

Certain aspects of the model of Timmerman, like plug flow of solution along the fibre surface, may play a role in cleaning with Amihope LL. Adsorption of surfactant on the surfaces of the particle and fibre may be enhanced by small movements of the particle caused by the flow along the surface.

The surfactant particles present during all experiments with Amihope LL may also be responsible for the cleaning action; they may cause more mechanical action and/or an abrasive effect. According to Jackson and Carver [25], particles can remove adhered soil particles by transfer of momentum by impact. The impulse from the impacting particles dislodges the adhered soil particles from the surface. The influence of the presence of particles on the removal of soil particles was investigated by tests using wheat flour and sand. The experiments were performed at 5.7 MPa and 293 K. 6 kg CO_2, 25 g water, 250 g IPA and 10 g wheat flour or sand were used. Amihope LL consists of small particles with a diameter between 5 and 35 μm (see Figure 13, this picture was taken of Amihope LL directly from the jar). Wheat flour has particles with a diameter between 5 and 250 μm (see Figure 14). The used sand particles have an average diameter of 200 μm. From Figure 15, we conclude that the addition of particles can increase the cleaning-results. Clay on wool shows the largest increase in particulate soil removal by the addition of particles. This confirms that the removal of clay from wool is sensitive to the amount of mechanical action, which we already found in [7]. This might be because clay particles tend to agglomerate and collect in cracks and holes [7], instead of carbon black particles, which are deposited at the fibre surface.

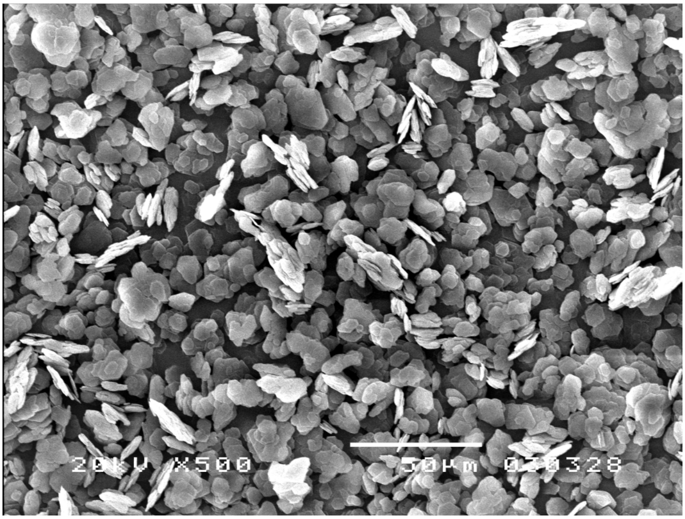


Figure 13: Amihope LL

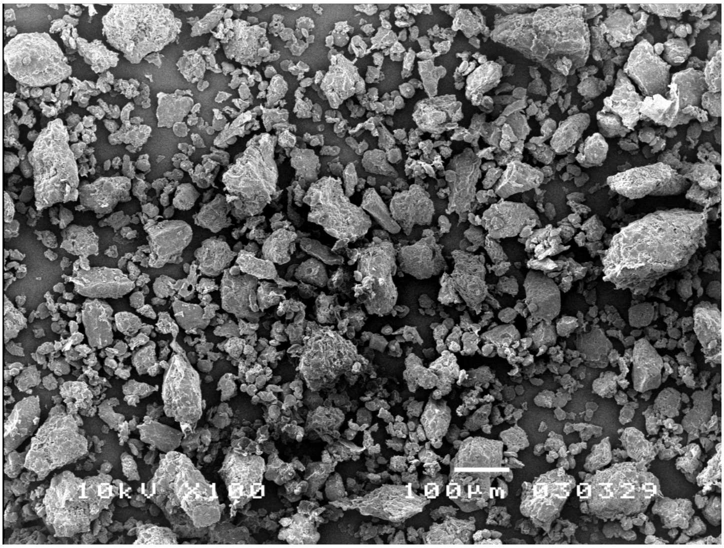


Figure 14: Wheat flour

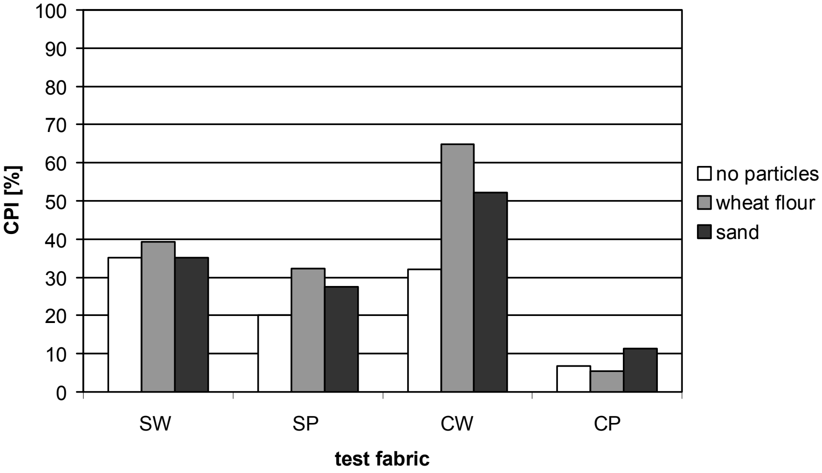


Figure 15: Influence of addition of particles on removal of soil particles

7.4 Combination of adsorption and mechanical effects

From the discussions about adsorption and mechanical action, we conclude that the cleaning action of Amihope LL may be a combination of adsorption and mechanical effects. Adsorption of the surfactants may cause a wedge between the fibre and the particles. Furthermore, adsorption of surfactants may reduce the Van der Waals attraction between the fibre and the soil. Adsorption of surfactant on the surfaces of the particle and fibre may be enhanced by small movements of the particle caused by the flow along the surface. The presence of surfactant particles may create more mechanical action and may cause an abrasive effect by impact of the surfactant particles with the soil particles.

To investigate this hypothesis, we consider the results for the use of amines as surfactants [8]. The results with amines show that the use of more amine and therefore the presence of more particles increased the cleaning-results. This would suggest that the surfactant particles are responsible for a part of the cleaning action. However, the results with the surfactant TBA (tribenzylamine) show that the presence of surfactant particles is not enough. TBA is a solid surfactant and surfactant particles are visible during the cleaning process with this surfactant. The cleaning-results using this surfactant are, however, low. This is probably caused by the fact that TBA is not able to adsorb at the surface of the fibre and the soil particle, because of steric hindrance. This would confirm our hypothesis that the removal of particulate soil by surfactants that form solid particles in CO_2 is a combination of adsorption and mechanical action.

This hypothesis was also investigated by performing experiments. The experiments were performed at 5.7 MPa and 293 K. 6 kg CO_2 and 250 g IPA were used. In the experiments, 25 g water, 25 g water and 10 g wheat flour, 0.2 g Amihope LL, 0.2 g Amihope LL and 0.8 g wheat flour, or 1 g Amihope LL were used. The results of these experiments are shown in Figure 16.

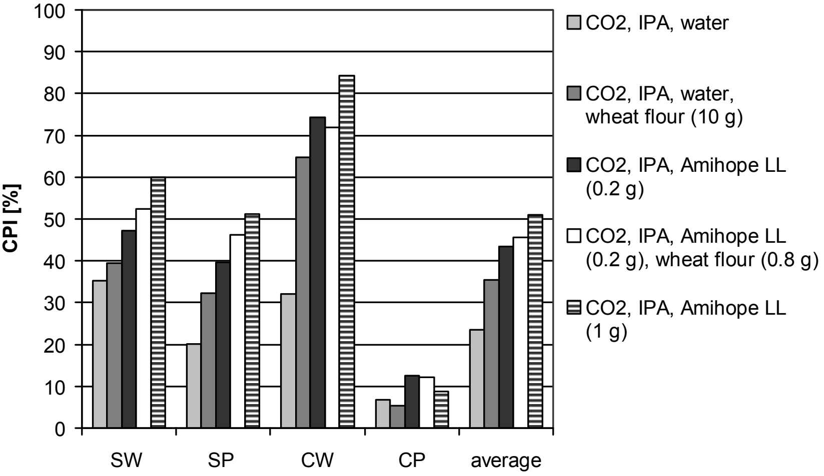


Figure 16: Results of experiments using surfactant and wheat flour

When we compare the results without the presence of particles and with the presence of particles, we see that addition of only particles (10 g wheat flour) gives an increase in cleaning-results. This confirms our hypothesis that the cleaning-action of Amihope LL may be based on the presence of surfactant particles. When we, however, compare the results using 0.2 g Amihope LL, 0.2 g Amihope LL and 0.8 g wheat flour, and using 1.0 g

Amihope LL, we can conclude that the cleaning-action of the surfactant is not only based on the presence of particles, but also on the presence of surfactants. This confirms our hypothesis that the cleaning-action of our surfactants is based on adsorption of the surfactants as well as mechanical action caused by the presence of surfactants particles.

7.5 The influence of water

The most pronounced effect on the cleaning-results had the addition of free (tap) water [9]. This might be because the addition of tap water means the addition of extra ions. These ions can compete with the surfactant in adsorption. The concentration of ions in tap water (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}) is approximately 3 mmol/l [26]. When 50 ml tap water is added (0.15 mmol ions) and 10 g Amihope LL (30 mmol Amihope LL), there are approximately 200 times more Amihope LL molecules present than ions from the tap water (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}). Therefore, it unlikely that the addition of such a small quantity of ions has such a huge effect on the cleaning-results. To investigate the influence of the presence of salt on the cleaning-results, four experiments were carried out. In the first experiment, no water was used, in the second experiment UP water was used, in the third experiment tap water was used and in the fourth experiment a saturated NaCl solution was used. In the experiments, 6 kg CO_2, 250 g IPA (2-propanol), no water or 25 g (UP, tap or salt) water, and 10 g Amihope LL was used. The pressure was 5.7 MPa, the temperature 293 K. The results are shown in Figure 17.

From this Figure, we can conclude that the presence of ions in the tap water is not the reason why the addition of water has a pronounced negative influence on the cleaning-results. Moreover, the addition of salt seems to have a positive influence on the results. As soon as the saturated NaCl solution was mixed with IPA, there was a precipitation of salt. The precipitated salt is completely insoluble in CO_2 and will therefore be present as particles. The addition of salt particles may cause an increase in the cleaning-results, just as the wheat flour particles do. Furthermore, the salt ions can behave as second surface active component [27]. The adsorbed salt may reduce the electrostatic repulsion within the

adsorbed layer and may therefore lead to an increase in the surface density of the adsorbed surfactant. The addition of a salt can also result in conformational changes in the surfactant tail, which may give rise to a greater packing density at the surface [28].
The addition of water might have a negative effect because the water is adsorbed by the textile (and the soil) and makes the textile (and the soil) inaccessible for the surfactants, but also for the CO_2. This would also explain why the results adding 50 g of water during an experiment using surfactant are lower than the results using pure CO_2 [9]. For this explanation to be true, the water should also have some affinity for polyester, at least more affinity for polyester than CO_2.

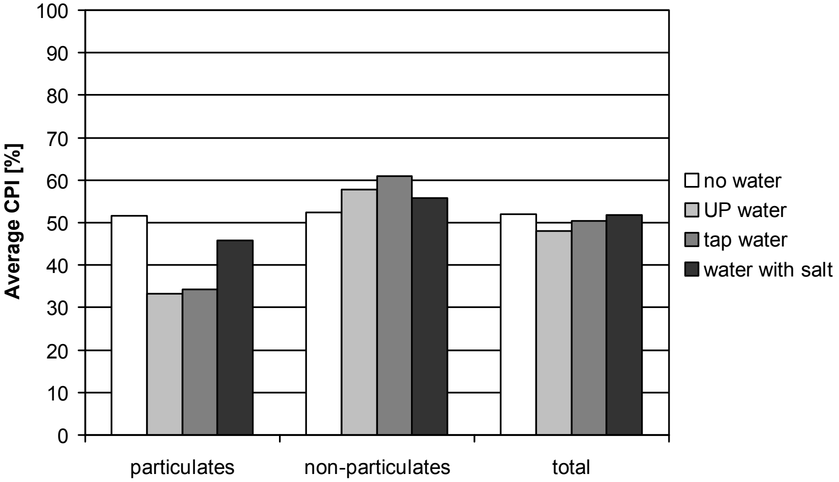


Figure 17: The influence of salt addition on cleaning-results

7.6 Recommendations for further research

To study adsorption of surfactants on substrates, the zeta-potential is often measured before and after adsorption [e.g. 13, 21, 29-31]. The zeta-potential is used as a measure of surface charge, because surface potentials cannot be measured directly. Measuring the zeta-potential does not only give information about the adsorption of the surfactant but may also show what mechanism plays a role in particle removal; if the zeta-potential of the fibre and/or the particulate soil is decreased after adsorption, charge increase and, hence, mutual repulsion of the particulate soil and the textile is not the mechanism that governs soil removal.

The zeta-potential can be measured by using the streaming potential method [e.g. 13] or using electrophoresis [e.g. 29-31].

Measuring the adsorption density together with the zeta-potential would be a very good way to study the mechanisms of adsorption.

Furthermore, the solubility of the surfactant should be measured.

The mechanical effects of the surfactant particles may also be studied in more detail. Modelling of the different forces may show if particulate soil removal by collision with surfactant particles is possible. Furthermore, the influence of the size and shape of the formed surfactant particles may be studied.

7.7 Conclusion

The cleaning action of the used surfactants is probably a combination of adsorption and mechanical action. Adsorption of the surfactants may cause a wedge between the fibre and the particles. Furthermore, adsorption of surfactants may reduce the Van der Waals attraction between the fibre and the soil. The presence of surfactant particles creates more mechanical action and may cause an abrasive effect by impact of the surfactant particles with the soil particles.

Appendix

Zeta-potential

The zeta-potential is the potential between the charged surface and the solution at the surface of shear (see Figure 18). Rarely the zeta-potential is identical to the surface potential; mostly it is lower, if not much lower. When superequivalent counterion adsorption occurs even the signs of the zeta-potential and the surface potential differ [11].

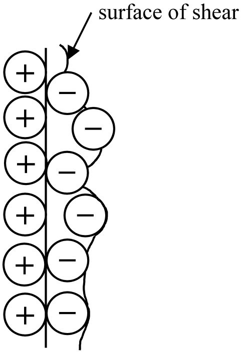


Figure 18: Schematic representation of the structure of the electric double layer (redrawn from [32])

References

[1] W.G. Cutler, R.C. Davis, Detergency; theory and test methods Part I, Dekker, New York 1972.

[2] A. Batra, S. Paria, C. Manohar, K.C. Khilar, Removal of surface adhered particles by surfactants and fluid motions, AIChE J., 47 (2001) 2557.

[3] G. Jakobi, A. Löhr, M.J. Schwuger, D. Jung, W.K. Fischer, P. Gerike, K. Künstler, Detergents - Theory of washing process, in: Ullmann's Encyclopedia

of Industrial Chemistry, Sixth Edition, 2000 Electronic release, Wiley-VCH Verlag GmbH, Weinheim 2000.

[4] A.M.D.E. Timmerman, Understanding detergency; The role of surfactant dynamics in efficient textile cleaning, Dissertation, Delft University of Technology, Delft 2002.

[5] J.C.J. van der Donck, A. So, G. Frens, The influence of stretching on salt release from porous yarns, Tenside Surf. Det., 35 (1998) 119.

[6] S. Asada, Ajinomoto Europe Sales GmbH, personal communication.

[7] Chapter 3 of this thesis; M.J.E. van Roosmalen, M. van Diggelen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide; The influence of mechanical action on washing-results, J. Supercrit. Fluids, 27 (2003) 97.

[8] Chapter 5 of this thesis; M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Surfactants for particulate soil removal in dry-cleaning with high-pressure carbon dioxide, The Journal of Supercritical Fluids, in press.

[9] Chapter 6 of this thesis; M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Amino acid based surfactants for dry-cleaning with high-pressure carbon dioxide, submitted to The Journal of Supercritical Fluids.

[10] SciFinder Scholar, American Chemical Society.

[11] J. Lyklema, Fundamentals of interface and colloid science; Volume II Solid-liquid interfaces, Academic Press, London 1995.

[12] T.J. Edwards, G. Maurer, J. Newman, J.M. Prausnitz, Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes, AIChE J., 24 (1978) 966.

[13] A. Petterson, J.B. Rosenholm, Streaming potential studies on the adsorption of amphoteric alkyldimethylamine and alkyldimethylphosphine oxides on mesoporous silica from aqueous solution, Langmuir, 18 (2002) 8447.

[14] P. Chavez, W. Ducker, J. Isrealachvili, K. Maxwell, Adsorption of dipolar (zwitterionic) surfactants to dipolar surfaces, Langmuir, 12 (1996) 4111.

[15] www.basf.de/basf/img/produkte/farbmittel/leder/pdf/pb/raw_skin23_3_2001.pdf

[16] E. Özarslan, A. Tolunay, Ç. Öztugran, The processes in furriery manufacturing, www.chem.boun.edu.tr/FacultyStaff/TerezaVarnali/TVFolder/Deri/projeler/furriery.html

[17] K.H. Toews, R.M. Shroll, C.M. Wai, pH-defining equilibrium between water and supercritical CO_2. Influence on SFE of organics and metal chelates, Anal. Chem., 67 (1995) 4040.

[18] O. Vohler, F. von Sturm, E. Wege, H. von Kienle, M. Voll, P. Kleinschmit, O. Vostrowsky, A. Hirsch, Carbon - carbon black, in: Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 2000 Electronic release, Wiley-VCH Verlag GmbH, Weinheim 2000.

[19] J.R. Lu, T.J. Siu, B.J. Howlin, R.K. Thomas, Z.F. Cui, J. Penfold, J.R.P. Webster, Protein adsorption at interfaces, www.isis.rl.ac.uk/isis98/feat988.pdf.

[20] M. Cox, J.R. Rus-Romero, T.S. Sheriff, The application of montmorillonite clays impregnated with organic extractants for the removal of metals from aqueous solution Part I. The preparation of clays impregnated with di-(2-ethylhexyl)phosphoric acid and their use for the removal of copper (II), Chem. Eng. J. , 84 (2001) 107.

[21] P. Somasundaran, S. Krishnakumar, Adsorption of surfactants and polymers at the solid-liquid interface, Colloids Surf. A, 123-124 (1997) 491.

[22] M.P. Garate, G. Frens, Detergent performance in dry-cleaning with liquid CO_2, in: A. Bertucco (Ed.), Chemical Engineering Transactions, Volume 2, 2002. Proceedings of 4th International Symposium on High Pressure Process Technology and Chemical Engineering, High Pressure in Venice, September 22-25, 2002, Venice, Italy, 2002, p.873.

[23] L.D.M. van den Brekel, Hydrodynamics and Mass Transfer in Domestic Drum-Type Fabric Washing Machines, Dissertation, Delft University of Technology, Delft 1987.

[24] P. Carty, Fibre properties, Formword Ltd, Newcastle 1992.

[25] D. Jackson, B. Carver, Today's forecast: it looks like snow, Precision Cleaning, 8 (1999) 17.

[26] www.lenntech.com/samenstelling.htm

[27] V.L. Kolev, K.D. Danov, P.A. Kralchevsky, G. Broze, A. Mehreteab, Comparison of the van der Waals and Frumkin adsorption isotherms for sodium dodecyl sulphate at various salt concentrations, Langmuir, 18 (2002) 9106.

[28] J. Penfold, E. Staples, I. Tucker, L. Thomson, R.K. Thomas, Adsorption of non-ionic mixtures at the air-water interface: effects of temperature and electrolyte, J. Colloid Interface Sci., 247 (2002) 404.

[29] D.N. Rubingh, T. Jones, Mechanism of detergency in systems containing cationic and non-ionic surfactants, Ind. Eng. Chem. Prod. Res. Dev., 21 (1982) 176.

[30] Y. Yoneyama, K. Ogino, The behaviour of carbon black in a detergent solution, Bull. Chem. Soc. Jpn., 55(1082) 3079.

[31] R.G. Alargova, I.Y. Vakarelsky, V.N. Paunov, S.D. Stoyanov, P.A. Kralchevsky, A. Mehreteab, G. Broze, Properties of amphoteric surfactants studied by ζ-potential measurements with latex paticles, Langmuir, 14 (1998) 1996.

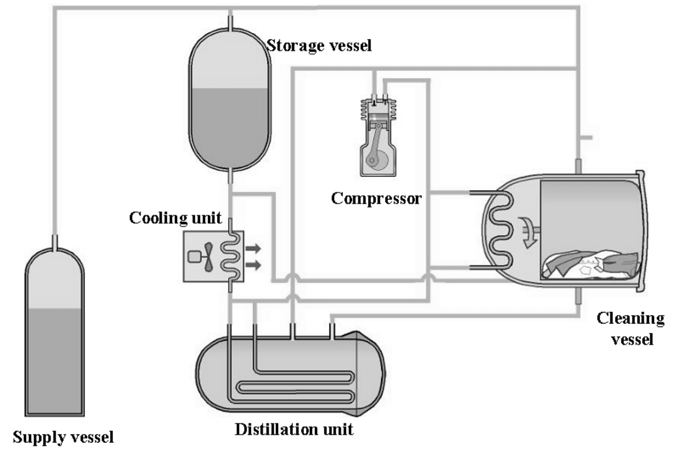
[32] D.J. Shawn, Introduction to colloid and surface chemistry, Butterworth Heinemann, Oxford 1992.

Chapter 8

Economic evaluation of dry-cleaning with carbon dioxide

In this chapter, the costs of the process of dry-cleaning with carbon dioxide are compared with the costs of the conventional process of dry-cleaning with perchloroethylene (PER). The evaluation is based on the method used by Van der Donck and Verbeek [1]. In this report, the costs are calculated per kg of cleaned fabric. Some fixed costs, like general facilities, are not considered, because these are equal for both processes. The cost evaluation of the process using PER is based on a 30 kg machine. For this machine, the time per cycle is approximately 1 hour. The amount of cycles per day per machine is 6. The price of a PER-machine is based on literature data [1,2], the costs for a ventilation chimney and cooling unit are added to these costs giving a total prize of € 75 500.

The cost evaluation of dry-cleaning using CO_2 is based on the costs of the dry-cleaning machine of Electrolux Wascator. The flow sheet of this machine is shown in Figure 1.



Flowsheet: Electrolux Professional B.V.

Figure 1: Flowsheet of Electrolux Wascator CO_2 dry-cleaning machine

Other machines can be used, for these machines, however, the investment costs, energy consumption (for e.g. compression of the CO_2) and CO_2 consumption will be comparable to the Electrolux Wascator machine. The Electrolux machine has a capacity of 15 kg clothing per cleaning cycle. The cost evaluation is based on the use of a 2-bath process. The cycle time for this machine (using a 2-bath process) is 29 minutes [3]. The amount of cycles per day is estimated to be 12. The CO_2 machine costs € 88 000 [3]. The amounts of chemicals used in this evaluation, are based on the amounts that were applied in experiments with a full-scale CO_2-machine. The data used for both processes are summarized in Table 1.

Table 1: Data for PER and CO_2 machines

	PER	CO_2
Capacity	30 kg	15 kg
Cycle time	~ 1 hr	29 min
Cycles per day	6	12
Costs	€ 75 500	€ 88 000

The amount of working days per year is assumed to be 250.

The costs are divided into two categories: costs for cleaning and drying, and costs for spotting and finishing.

Finishing and sorting of the fabrics takes less time using CO_2 than using PER. Finishing is easier in CO_2 (e.g. less wrinkles) and, therefore, cheaper. For the PER-process the fabrics need to be sorted according to colour and weight. Weight is important because of the drying step in the PER-process (too long drying times for delicate clothes should be avoided). In CO_2, less sorting is required, because colours bleed less and no sorting according to weight is needed. Therefore, we estimated that 20 % more kg clothing per hour could be sorted using the CO_2 process.

The estimated price for the surfactant Amihope LL is based on the prices of the raw materials (lauric acid: 1 €/kg [4] and L-lysine 2.40 €/kg [5]) multiplied by a factor of 2 for production costs.

The results of the evaluation are shown in Table 2.

Table 2: Economic evaluation of the PER- and the CO_2-process

	PER		**Costs [€/kg]**	**CO_2**		**Costs [€/kg]**
Cleaning and drying						
Labour costs	25 €/hr	5 min/cycle [1]	0.07	25 €/hr	5 min/cycle	0.14
Depreciation	Time: 10 yr Interest rate: 5 %	Investment € 75500	0.22	Time: 10 yr Interest rate: 5 %	Investment € 88000	0.25
Electricity	0.11 €/kWh	13 kWh/cycle	0.05	0.11 €/kWh	4 kWh/cycle	0.03
Steam	0.05 €/kg	15 kg/cycle [1,3]	0.03	-	-	-
Chemicals	Detergent	5.5 €/kg [1] 200 g/cycle	0.04	Co-solvent: 2-propanol	0.90 €/kg [6] 3 kg/cycle	0.18
	Solvent	0.6 €/kg 0.6 kg loss/cycle	0.01	Water	1.20 €/l 940 ml/cycle	0.00
	Purge	0.6 kg/cycle 0.7 €/kg [1]	0.01	Surfactant (Amihope LL)	3.20 €/kg 100 g/cycle	0.02

	PER		**Costs [€/kg]**	**CO_2**		**Costs [€/kg]**
				Solvent	0.95 €/kg (food grade [7]) 1.2 kg loss/cycle [3]	0.08
				CO_2 tank rental	2340 €/yr [7]	0.05
Maintenance	2 % of investment	Investment € 75500	0.03	2 % of investment	Investment € 88000	0.04
Total Cleaning and drying			**0.46**			**0.80**

Spotting and finishing						
Labour costs finishing	25 €/hr	29.2 kg finishing/hr [1]	0.86	25 €/hr	39 kg finishing/hr [1]	0.64
Labour costs spotting	25 €/hr	1 hr/day [1]	0.14	25 €/hr	1 hr/day [1]	0.14
Labour costs sorting	25 €/hr	28.6 kg sorting/hr [1]	0.87	25 €/hr	35 kg sorting /hr	0.71
Depreciation	Time: 10 yr Interest rate: 5 %	Investment € 18000 [1]	0.05	Time: 10 yr Interest rate: 5 %	Investment € 18000 [1]	0.05
Electricity	0.11 €/kWh	9 kW/hr [2]	0.03	0.11 €/kWh	12 kW/hr [2]	0.03

	PER		**Costs [€/kg]**	**CO_2**		**Costs [€/kg]**
Steam	0.05 €/kg	60 kg/hr [1]	0.10	0.05 €/kg	80 kg/hr [1, 2]	0.10
Maintenance	2 % of investment	Investment € 18000	0.01	2 % of investment	Investment € 18000 [1]	0.01
Total Spotting and finishing			**2.06**			**1.69**
Total			***2.52***			***2.49***

From Table 2, we can conclude that the costs for dry-cleaning using CO_2 are equal to the costs using PER. The cost determining parameters are the investment costs of the machines (in both processes), costs of the chemicals (in the CO_2-process), and the labour costs of finishing and sorting of the fabrics (in both processes).

The CO_2-process could become cheaper by recycling of the co-solvent 2-propanol (IPA) and the surfactant Amihope LL. If we assume that 90 % of the IPA can be recycled and 90 % of the surfactant, and if we assume extra investment costs for recycling of € 20 000 then the total cleaning costs for CO_2-cleaning become 2.39 €/kg.

In the CO_2-process, the loading of the machine will be 100 % because almost all garments can be mixed. In the PER-machine, however, in 10-30 % of the cases the dry-cleaner does not run a full load due to be able to meet delivery times [8]. If we assume an average loading of 90 % for PER, the total cleaning costs for PER become 2.59 €/kg instead of 2.52 €/kg.

Conclusions

The costs for dry-cleaning using CO_2 are equal to the costs using PER. Recycling of the surfactant and the co-solvent can lower the costs of the CO_2-process.

References

[1] J.C.J. van der Donck, M.A. Verbeek, Inzetbaarheid van alternatieve reinigingsmethoden, TNO Rapport 007.60067/60068, TNO RTT, Delft 2001.

[2] H. Heerings, Kostprijsvergelijking tussen verschillende reinigingssystemen in de stomerijbranche, CONTRAST Advies – Milieu, Amersfoort 1998.

[3] Electrolux Professional B.V.

[4] www.tradeintelligence.com/sitetour/apr1chemical.doc

[5] www.asasea.com/technical/an18-1998.html

[6] Chemproha Chemiepartner Dordrecht

[7] Linde AG

[8] P. Stoffels, Textile cleaning in liquid carbon dioxide-from idea to reality, in: Proceedings of the 41st wfk International Detergency Conference, Düsseldorf, Germany, 2003, p.270.

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Publications

M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide, experimental set-up and washing-results, in: G. Brunner (Ed.), Proceedings 2nd International Meeting on High Pressure Chemical Engineering, Hamburg, Germany, 2001.

M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, The influence of mechanical action and commercially available surfactants on particle removal in dry-cleaning with high-pressure carbon dioxide, in: A. Bertucco (Ed.), Chemical Engineering Transactions, Volume 2, 2002. Proceedings of 4th International Symposium on High Pressure Process Technology and Chemical Engineering, High Pressure in Venice, September 22-25, 2002, Venice, Italy, 2002, p.885.

M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Surfactants for particle removal in dry-cleaning with high-pressure carbon dioxide, in Proceedings of the 6th International Symposium on Supercritical Fluids, Versailles, France, 2003, p. 2107.

M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide, in: Proceedings of the 41st wfk International Detergency Conference, Düsseldorf, Germany, 2003, p. 236.

M.J.E. van Roosmalen, M. van Diggelen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide; The influence of mechanical action on washing-results, J. Supercrit. Fluids, 27 (2003) 97.

M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Dry-cleaning with high-pressure carbon dioxide- the influence of process conditions and various co-solvents (alcohols) on washing-results, J. Supercrit. Fluids, 27 (2003) 337.

M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Surfactants for particulate soil removal in dry-cleaning with high-pressure carbon dioxide, J. Supercrit. Fluids, in press.

M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Amino acid based surfactants for dry-cleaning with high-pressure carbon dioxide, submitted to The Journal of Supercritical Fluids.

C. Kersch, M.J.E. van Roosmalen, G.F. Woerlee, G.J. Witkamp, Extraction of heavy metals from fly ash and sand with ligands and supercritical carbon dioxide, Ind. Eng. Chem. Res., 39 (2000) 4670.

Patent

G.F. Woerlee, M. van Roosmalen, A. Breijer, J.W. van Ganswijk, M. Wichhart, A method of dry cleaning articles using densified carbon dioxide, WO 03/062520 (2003).

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