Cleaning power that’s new as well as “green”

Cleaning clothes using liquefied gas and solid amides
Whenever you take your clothes to the dry-cleaners they usually come back as good as new, but always with that peculiar smell. Up to now the business of dry-cleaning has been associated with health hazards because of the potentially toxic and environmentally harmful solvents, the most commonly used one being perchloroethylene. Chemical engineer Maaike van Roosmalen has optimised a method for cleaning fabrics using liquid carbon dioxide. The process uses an amide derived from an amino acid to act as the cleansing agent. The results are already very close to those of conventional dry-cleaning methods, which may soon become obsolete, as the new system replaces the perchloroethylene with CO₂, thereby minimizing the impact on the environment.

The “dry” in “dry-cleaning” is there because the process does not involve water. Instead, various chemicals are used, most of them highly noxious. One of these solvents, perchloroethylene, when heated produces hydrochloric acid and phosgene (chlorocarbon oxide), a poison gas used by the German army during the First World War. The maximum acceptable concentration of airborne perchloroethylene is 35 ppm. Indications are that the material is carcinogenic and may induce genetic defects.

As in normal laundering, the conventional dry-cleaning process uses a drum containing the garments to be cleaned, to which the solvent is added at room temperature and atmospheric pressure. Although the actual cleaning only takes about ten minutes or so, removing the perchloroethylene from the clothing takes another hour. The fabric emerges from the machine dry and without creases, but does have a bit of a chemical smell to it. The dirt remains in the solvent, from which it is removed by means of distillation. Perchloroethylene is an excellent solvent, but it is a hazardous compound, as was demonstrated in an incident in July 2001 at the town of Papendrecht (20 km south-east from Rotterdam), when 80 litres of the chemical escaped from a washing machine in a dry-cleaner’s, probably as a result of a leaking viewing hole gasket. As the owner entered his establishment, he was overcome by the gas. In addition, the ceiling proved insufficiently gas tight, allowing the perchloroethylene to penetrate into the houses over the shop, causing fifteen people to be hospitalised with respiratory problems.

Immediately following the incident, the minister of public health ordered an investigation to see whether dry-cleaning establishments should be categorised as ‘hazardous industries in residential areas’. A large-scale survey revealed that more than sixty per cent of the dry-cleaning shops in residential areas failed to meet safety requirements. In many cases, excessively high levels of perchloroethylene were measured in dwellings over the establishment even without accidental leaks. All in all, a flat above a dry-cleaning shop is not the healthiest of...
places to live.

Hydrophobic
The time was ripe for an environmentally friendly alternative. The first prototypes of CO2 washing machines, by Swedish manufacturer Electrolux, are now being tested by Dutch dry-cleaning company, Krom Stomerijen, and its Danish counterpart, Kymi Rens. In the United States, the Hangers dry-cleaning chain are also experimenting with CO2 washing machines. At the Laboratory for Process Equipment, doctoral candidate Maaike van Roosmalen has been working on an improved method for cleaning fabrics using CO2 combined with detergents specifically developed for the purpose. So where did the idea come from to use carbon dioxide to do the laundry?

Maaike van Roosmalen explains: “The cleaning action of CO2 had been known for quite some time. It has a low viscosity and a high diffusion constant - ideal properties for moving freely through fabrics. Since the molecule’s structure makes it hydrophobic, i.e. water-repellent, it is good at dissolving oil and grease. To make it more hydrophilic so that it becomes better at dissolving other types of stains, a co-solvent is often added in the form of a low-molecular alcohol (e.g. isopropyl alcohol). Carbon dioxide can be considered a ‘green’ solvent with many advantages over perchloroethylene. It is available in large quantities, non-corrosive, non-toxic, and environmentally friendly. In low concentrations it is absolutely harmless to man and the environment alike.”

Maaike van Roosmalen who is working on her doctorate research under the supervision of Prof. Dr. Geert-Jan Witkamp and is being coached by Dr. Ir. Geert Woerlee, whose company, FeyeCon, has been developing industrial applications for CO2 now for a number of years. These include the extraction of active ingredients from medicinal plants, and the micronisation (reducing in size) of fats for food applications. Originally, the research was to focus on the design of a CO2 washing machine. After all, this is the Delft Laboratory for Process Equipment we’re talking about. However, it did not take long before Van Roosmalen found herself engrossed in the chemical and physical aspects of the cleaning process itself. Her desk is covered in stacks of books on surfactants (chemicals acting on boundary layers) and detergents.

Amide
Dry-cleaning is not the first application to use CO2 for cleaning purposes. The process industry already uses CO2 to replace noxious chemicals. Over a century ago, believing his father had died as the results of overindulging in coffee, the German chemist, Ludwig Roselius developed a method to extract caffeine from coffee beans, using methyl chloride. The remedy probably created more problems than it solved, considering the fact that in 1980 methyl chloride was added to the list of potentially carcinogenic chemicals. Since then, the industry has been using supercritical CO2, which is passed through soaked coffee beans at a temperature of 165 Celsius and a pressure of 250 bar.
At room temperature, CO₂ liquefies at a pressure of 57 bar. This may seem high, but compared with other gases, it is a rather modest figure. Nitrogen for instance will not liquefy at all at room temperature, but needs to be cooled to below its critical temperature of -147 Celsius. Nonetheless, it will be clear that technically speaking, a CO₂ washing machine is quite a different proposition from a run-of-the-mill household appliance.

In the laboratory, Van Roosmalen shows her high-pressure test washing machine, with a capacity of about 500 grammes of laundry. The machine, which has had to pass a test under the government's pressure equipment legislation, consists of a thick-walled tubular vessel with a viewing hole at each side. On the front, a heavy door, reminiscent of a strong room, provides access to the interior, which contains a stainless steel drum with baffles on the inside to lift the laundry. Just as in a normal washing machine, the drum rotates in both directions at a speed of about 75 revolutions per minute. Into the vessel go six kilos of liquid CO₂ - as much as you will find in a standard household fire extinguisher. To enhance the solvent properties of the CO₂, 25 grammes of water and 250 grammes of isopropyl alcohol are added, and of course the 'surfactant', in the form of 10 grammes of an amide derived from an amino acid, Amihope LL - the secret ingredient.

Van Roosmalen: “The washing cycle takes about thirty minutes, although most of the stains will have been removed after ten minutes. The washing cycle is followed by a rinse cycle that uses CO₂. There is no need to spin-dry the contents. The remaining CO₂ immediately evaporates, so the fabrics emerge from the machine perfectly dry.”

The original plan was to recycle the CO₂ after use by means of distillation. However, Van Roosmalen did not have time to look into that part, so now the ‘washing water’ simply disappears into thin air.

Guaranteed dirt
It would be a mistake to think that scientists bring in their own dirty laundry for the experiments. Instead, they have a specialist company, the Center for Test Materials, to produce dirty pieces of cloth for them. The company is located in Vlaardingen, along the canal that connects Rotterdam with the North Sea, close to the research centre of Unilever, the manufacturer of a large number of well-known household detergents. The pieces of cloth are made to precise specifications, so they all are exactly equally dirty. Each piece of cloth is covered in a homogeneous and highly concentrated layer of dirt.

Van Roosmalen: “We use small pieces of wool, polyester, cotton, and a polyester/cotton mix to test five types of stains that often occur on clothing. These are butterfat, egg yolk, vegetable oil coloured with chlorophyll, clay, and a ‘mixed’ stain of skin grease (sebum) and carbon black.”

The latter is the laboratory version of a dirty collar. The dirty pieces of cloth are sewn onto larger pieces of fabric - the ‘filler charge’ that ensures the machine is about half full - to simulate stained clothing.
cleaning results are assessed using a spectrophotometer to determine the colour of the cloths in ‘UV-less daylight’. A perfectly white cloth is equivalent to “completely clean”. The first experiments used only CO2 for the cleaning process, with no further additions. The results on the butyric acid were excellent. The egg yolk stains were removed reasonably well. However, the results with the other test cloths, and in particular the ones with the particle stains, were insufficient. Grease stains can be dissolved, but solid dirt has to be soaked off.

Washboard
Without the aid of surfactants, particle stains can only be removed by means of mechanical action, like the old washboard, or like hitting wet laundry against the rocks on a river shore like women in poor regions do.

Van Roosmalen: “I asked my students to test various different ways to increase the mechanical action, for instance by adding metal balls to the contents of the drum. We tested the effect on pieces of cloth we had dirtied with sand ourselves. This type of dirt consists of relatively large particles, enabling us to better observe the effect of the mechanical action. For small particles, however, the tests showed that increased mechanical action did not lead to better results. So we looked at surfactants to remove those.”

Even a normal washing machine cannot work using water and nothing else. You have to add a detergent. The same applies to washing with CO2. The carbon dioxide acts as the solvent and as the means of transporting the active ingredient (the surfactant). So the team had to start looking for a suitable surfactant to use in the CO2 washing machine.

Soap
So what is the secret underlying the cleaning action of soap? Maaike van Roosmalen closely studied the physical and chemical processes involved in cleaning. Do the active ingredients in the washing powder really lift the stains from the clothes the way some detergent commercials suggest? As it turns out, there is some truth in the concept. Detergents contain what are known as amphipolar compounds (surfactants), molecules with a hydrophilic head (which is attracted to water), and a hydrophobic as well as lipophilic tail (which repels water and attracts grease). During the cleaning process, the apolar tail attaches itself to the particles of dirt, which are then pulled into the surrounding water by the polar head. The cleaning properties of a detergent are based on the action of these surfactants, which impart a negative charge to the dirt particles. The particles repel each other as a result, keeping the dirt suspended in the dirty washing water.

Combination
This is how soap in water works. So how do you find the right detergent to use in CO2?

Van Roosmalen: “We tried practically everything, starting with surfactants we thought might work in CO2. When this proved not to be the case, we tried surfactants that are used in water. These do not dissolve in CO2,
but to our amazement they improved matters. So then we tried various compounds with different groups of hydrophilic heads. That is how we ended up with amines, which proved to be just the ticket.”

Amines are organic nitrous compounds, in this case long molecules containing an NH2 group. Amines are neutral, but in a reaction with CO2 they probably form so-called zwitterions. These dipole ions carry both a positive and a negative charge (NH2+ and COO-). A zwitterion is also referred to as an internal salt, a molecule containing both an acid and a base group.

Van Roosmalen: “We do not know yet exactly which of the two charges results in the cleansing action. It is the last piece of the puzzle which I intend to solve for my doctorate.

Van Roosmalen gets the CO2 for the washing process from a high-pressure vessel adjacent to her test set-up, but outside the building.

Irritation
A disadvantage of amines is that they cause irritation of the skin, as Maaike herself discovered. “I once touched the rim of a jar from which I was scooping some amine, and it immediately caused a burning sensation. So we had to find something else, since traces of the amine were bound to remain behind in clothing after dry-cleaning. In June of last year I was at a conference in Barcelona, where someone gave a talk that put me on the track of a Japanese company that manufactures surfactants based on amino acids. Their range of products contained exactly what we were looking for, a compound derived from an amino acid (l-lysine) and an acid (lauric acid, also known as dodecanoic acid). This is an amide with the same group as our zwitterion. The chemical name is N-lauroyl-L-lysine, and it is marketed under the name Amihope LL. Amihope LL is produced from materials that occur naturally. It is used in cosmetics, so it does not harm the skin. In addition it is fully biologically degradable.”

Again, surprisingly, the surfactant does not dissolve in CO2 at all.

Van Roosmalen: “Everyone had always assumed that solubility was a prerequisite, the way a detergent dissolves in water, but in our CO2 washing machine you can see the particles float around in the drum, and that was something we did not expect to see at all.”

As it is, the process does not work with most of the liquid surfactants that were tested. Again they do not dissolve in the CO2, but they do have a great affinity for the fabric, which after washing comes out covered with stains caused by the surfactants. The test cloths came out dirtier than they were when they went into the machine.

Sponsor tie
The results of CO2 washing with added Amihope LL are comparable to those of dry-cleaning using perchloroethylene.

Van Roosmalen: “The CO2 results are better where the butterfat and egg yolk stains are concerned. For particle stains we have not quite reached the same level yet. Perchloroethylene is still better at removing those, but we are getting close.”

The Delft research fails to provide unequivocal answers to some questions, such as do fabrics exist that can be...
cleaned using CO2, but which cannot be cleaned using perchloroethylene or vice versa, or are there materials that will not survive a CO2 bath whereas they can be a dry-cleaned without a problem.

Van Roosmalen: “Questions of this nature are not within the scope of my research, but in all our experiments with various types of fabric we never observed anything unusual. I have had quite some positive comments from other people experimenting with CO2 cleaning, but never anything negative.”

Real clothing is something Maaike van Roosmalen has not yet washed in her CO2 washing machine. “I have had many offers from people who kept promising to bring me their dirty laundry, but they never kept their promise. We did once, as a practical joke, wash the tie of a sponsor who came to see a demonstration. It went without a hitch, but then the tie was not dirty, we just wanted to see how it would come out of the washing process.”

The only dirty clothes in sight are the laboratory coats hanging from their pegs, which is odd in a laboratory where a revolutionary washing method is being developed.

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A selection of test cloths. The three piles represent different types of stain on different fabrics. Top left shows butterfat on cotton, top right shows butterfat on polyester/cotton, and bottom centre shows chlorophyll-coloured olive oil. The cloths marked 512 (at the bottom of each pile) are guaranteed dirty cloths, the ones marked 173 have been cleaned using CO2, and the topmost cloths, marked 37, have been cleaned using perchloroethylene. The conclusion is that for these types of stains, CO2 gives better cleaning results than perchloroethylene.

The operating pressure in Van Roosmalen’s system is approximately 50 bar. The pressure vessel of her CO2 washing machine consists of a stainless steel cylinder with an internal diameter of 250 mm and a wall thickness of 15 mm. The same material has been used for the flange that receives the patented 97 mm thick Quick Closure door, manufactured by the British company of T.D. Williamson from Swindon. The door is a bit oversized for the pressures involved since it was selected primarily for its ability to provide rapid access to the pressure vessel.

Just like any household washing machine, the Delft CO2 machine features a stainless steel drum to hold the laundry, with a capacity of 500 grammes. Nonetheless, this machine does have a unique feature, since the drum shaft, which is driven by an external electric motor, has been fitted with a mechanical seal that will withstand operating pressures of up to 150 bar. The seal was developed by Saint Gobain from Kontich in Belgium.
A look inside the CO2 washing machine during the cleaning process, clearly showing the liquid CO2.

In addition to the normal visual evaluation, a spectrophotometer is used to accurately measure the results of the CO2 cleaning process.

A spectrophotometer reading. The x axis plots the wavelength, the y axis plots the reflection value.
Cleaning results of a number of different methods.

After a long search for the ideal surfactant, Maaike van Roosmalen decided on N-lauroyl-L-lysine, an amide that is biodegradable. It is also used in cosmetics, so the people operating the system need not worry about skin problems.

After doing the laundry, the dirty water is normally discarded. In the test set-up, the same goes for the CO2. The impact on the environment is minimal, as the CO2 used for the process is a waste product of another industrial process.