

Cryogenic Recovery of HCFCs and VOCs from refrigerators

The use of Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) has been restricted since 1995 but they have still not disappeared from our normal day-to-day life. Experts estimate that in EU countries alone around 230 million old refrigerators and freezers are still in use – and 95 percent of them are still filled with HCFCs. Within the polyurethane foam insulation between the outer and inner layers sits the chlorofluorocarbon R11. This material was formerly used as a propellant/blowing agent for the manufacturing process of the foam insulation. When old refrigerator and freezer equipment is shredded, the CFCs or HCFCs are released and contaminate the air extracted from the recycling system.

Old and young: a dangerous mixture

Since the maximum emission level for CFC/HCFC was reduced in 2002 to below 20 mg/m³, recycling refrigerators has become a demanding task. In addition to strict emission regulations, the challenges are intensified by the fact that modern refrigerators have to be disposed of alongside the old refrigerators containing CFC/HCFC. The newer models contain the propellant cyclopentane as a substitute for the banned R11. Unlike the less reactive, non-flammable and non-explosive CFC/HCFC, this propellant is flammable which presents the recycling company with new difficulties: with R11 the shredding procedure can be carried out in the normal atmosphere, which was subsequently cleaned. Now a highly explosive mixture of oxygen and the volatile cyclopentane forms inside the recycling plant. As sparks can be generated during shredding there is an acute danger of explosion. In addition there are also limits on the emission of cyclopentane; 58mg/m³ may not be excluded. Depending on grinding technology we can have additional dust explosion danger with all kinds of fridges.

Base technology with cryogenic nitrogen

The specialists at Air Products have taken up the double challenge – the danger of explosion and problematic emissions. Air Products, the globally active company, is one of the leading providers of industrial, process and specialty



gases as well as chemical substances and intermediary products. It benefits from many years of experience in nitrogen-based freezing technology, low temperature condensation and inert gas technologies. This competence has fed the development of a new recycling system for all refrigerators. Air Products CRYO-CONDAP® process, a method for cleaning exhaust air and recovering volatile organic materials (VOC), served as the basis. In the CRYO-CONDAP® method, exhaust air containing VOCs is cleaned with the aid of cryogenic nitrogen. The VOCs are condensed in the extracted air flow and can be easily separated in fluid form.

In traditional refrigerator recycling an active carbon adsorption is normally used to treat the CFC/HCFC from the extracted air but tightening environmental regulations have made this method increasingly difficult. The recycling of old VOC refrigerators and freezers requires the recycling system to have a LEL (lower explosion limit) in the exhaust of <25 % and therefore a ten-fold exhaust volume relative to inert systems. This means that in order to adhere to this limit, the exhaust flow needs to be “diluted” with many times more air. This has a tremendous effect on the processing and running costs for such a system.



Air Products and Chemicals Inc. has developed a way to recycle refrigerators with various PU foam agents in one single plant – without risk of explosion and with excellent emission values.

Hans Erler (Business Development CRYO-CONDAP® systems)



A further challenge for recycling companies with active carbon systems is that 5-12% R12 is mixed in with R11 in the production of a refrigerator in order to improve the foam formation. Although the R12 is thoroughly absorbed by activated carbon it is subsequently lost again during the regeneration step if the desorption gas is not then subjected to low temperature condensation.

Dual nitrogen usage

Both problems can be solved by deploying nitrogen:

- with gaseous nitrogen the danger of explosion in the interior of the system can be avoided
- with liquid nitrogen harmful substances in the exhaust can be condensed and separated.

Air Products makes use of this parallelism and deploys liquid nitrogen initially as a refrigerant for cryogenic condensation. The vaporised “disposal product” – clean gaseous nitrogen – is subsequently fed into the shredding chamber where it ensures the necessary protection from explosion. This results in a closed circulation of gases.

Initially, conventional mechanical refrigeration technology, combined with water adsorption on molecular sieves, releases the contaminated exhaust flow from its water parts, so that no water ice can subsequently form. In a second step it is brought to cryogenic temperatures with liquid nitrogen – which condenses VOCs. In order that the process is not obstructed by propellant ice formation, the condensation takes place under pressure and with an intermediary refrigerating agent, cooled by liquid nitrogen. With this method there are no thawing processes necessary, which would increase running costs. Because of tightening legislation the process is then followed by pressure swing adsorption using molecular sieves.

Recovery for new base chemicals

The emission values for the CRYO-CONDAP® process are below 5 mg/m³ for R11 and for R12 (ozone depleting) which means confirmed compliance with environmental regulations. The regained hydrochlorofluorocarbons are

distributed to companies in the chemical industry and split into hydrochloric acid and hydrofluoric acid, which can then be used as base chemicals for chemical processes.

Nitrogen therefore fulfils a dual function – as refrigerant for the CRYO-CONDAP® condensation method and as inert gas for a safe inert process without danger of explosion. The use of nitrogen for two processes results in relatively low operating costs and high safety levels. With more than 100 systems installed and operating worldwide, the method has already stood the test of time. As experience has grown our latest CRYO-CONDAP® method for PU foam recycling is already being used at 22 locations around the world.

“Chlorofluorocarbons make a significant contribution to intensifying the greenhouse effect. Even though the progressive phase-out of CFC production has been agreed, the CFCs that have been produced to date still retain their full capacity to cause environmental damage. Every gram that is allowed to escape into the atmosphere will attack the ozone layer. In Germany alone, there are an estimated 47 million refrigerators containing around 23.5 billion grams of fully halogenated CFCs.”

– RAL Quality Assurance Association for the Demanufacture of Refrigeration Equipment Containing CFCs

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