

# HFC-containing Propellants in Canned PU Foam (OCF)

Estimation of the reduction potential of emissions from  
OCF with regard to a clarification of the provisions given  
in §9(1) of Regulation (EC) 842/2006

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842/2006**

by

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## Summary

The propellant gases of OCF – first CFCs, then HCFCs, finally HFCs – have been subject to environmental legislation. In 1998, the application of OCF still constituted the major source of HFC emissions at that time by causing global warming emissions of 1.5 million t CO<sub>2</sub> equivalents in Germany.

The study shows that a lot of time was required before the European manufacturers were able to produce canned PU foam without HFC containing propellants but within the German fire protection standards for buildings. All of the eight manufacturers featuring the market in Germany can offer HFC-free OCF of commercially available type classified into Building Material Class B2. In Germany, no legal regulations require the use of materials classified less flammable than Building Material Class B2 which would apply to materials classified into Building Material Class B1 only.

As examined within this study, this is not required by any technical standards either including the following sectors:

- Road construction,
- Tunneling,
- Ship building,
- Lines for supply and discharge of water, gas and power supply lines,
- District heating pipelines,
- Automotive industry (refrigerated trucks).

While fire protection standards apply to cured foam, explosion protection requires measures against flammable gases which are released from the can during the application process. The German labour protection laws set regulations for the handling of explosible hazardous substances but do not ban them. These laws are considered to set adequate safety standards for the use of OCF containing flammable hydrocarbon gases.

The underground coal mining sector is the only exemption. Due to the high explosion risk in this sector, the use of substances featuring a flashpoint < 55°C (flammable) is interdicted by law. The authorised OCF contain exclusively incombustible propellant gas, i.e. pure HFC-134a. The number of cans used in coal mining amounts to approximately 10,000 per year.

The ban of flammable gases in the coal mining industry is the only "national safety standard" which requires the use of OCF containing propellant gases which show a GWP >150 according to annex II of the EU F-Gas Regulation.

From mid-2009, the sale of normal OCF will no longer be allowed in self-service stores because of its content of free isocyanates (MDI). MDI-free OCF is already available Europe, but only its B3 quality is produced without HFCs. HFC-free OCF of B2 standard, as required for the German market, cannot be produced without HFC-134a, so far. The manufacturers are developing isocyanate-free and HFC-free products (GWP < 150) and might be able to place them on the market in the near future.

In an additional chapter (annex), a new approach to estimate HFC emissions will be presented. Estimations for HFC emissions are given for the years 2006 to 2008 as well as emission prognoses for the years 2010 and 2020.

In Germany, climate-relevant emissions resulting from the application of OCF were cut from 1.5 million to 20,000 t CO<sub>2</sub> equivalents in the period from 1998 to 2008. They are expected to decrease to 2,000 t by 2020.

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## Scope of the Study

Regulation (EC) No 842/2006 on certain fluorinated greenhouse gases (F-Gas Regulation) [1] interdicts in countries of the European Unions from 4<sup>th</sup> July 2008 onwards to place one component foams on the market if the total global warming potential of the propellant gas mixture exceeds 150. Exceptions are possible if the use of these foams is required to meet national safety standards. The German Chemicals Climate Protection Ordinance [2] does not give any further regulations.

The regulations do not treat some open questions important for both Germany and the EU as a review of the EU F-Gas Regulation will take place (Art 10).

1. Which safety standards require the use of OCF (1K, 2K) containing propellant gas mixtures of GWP > 150 (i.e. the non-flammable HFC-134a)? This question has first to be answered for the case of Germany.
2. Which high-risk applications do exist in Germany? What HFC emissions are caused by the application of OCF in these sectors in 2008-2010?
3. Which potential for emission reductions results for the period from 2010 to 2020 from a possible extension of the ban of OCF containing propellant gas mixtures of GWP < 150 from 2010 onwards?

As a basis for the discussion of these issues, the German Federal Environmental Agency asked for an overview of manufacturers in the EU and an estimation of the current production and market situation of both OCF containing HFC and HFC-free OCF in the EU and in Germany.

Based on these data, reliable statements whether or not the exception clause of the EU F-Gas Regulation is relevant for Germany have to be made.

The compilation of data is expected to serve as an appropriate basis for decisions concerning an amendment of the F-Gas Regulation by the EU Commission.

In order to meet the international reporting commitments of the UNFCCC, the study presents data on emissions of fluorinated greenhouse gases from the production and application of OCF in Germany to the German Federal Environmental Agency.

The study follows the subsequent structure:

1. Application and specifications of canned polyurethane OCF.
  2. Overview of manufacturers and market in the EU and in Germany.
  3. Importance of the propellant for canned OCF.
  4. Change of Propellant Gas in EU and in Germany since 1990
  5. Fire safety requirements for hardened foam.
  6. Explosion protection requirements, high risk provisions and applications in Germany.
  7. Recommendation for a special regulation for the mining industry
  8. Special case: Isocyanate-free foam with HFC-134a.
- Annex: Emission estimations 2007 and projections for 2010 and 2020.



## 1. Application and types of Canned Polyurethane OCF

Preliminary remark: In this study, the term OCF (one component foam) is generally used for canned PU caulking foam although there is also two-component foam (market share: ca. 5%). The technical quality of the foam is not discussed as the study focusses on propellants contained in foam products.

Polyurethane foam (PU foam) applied from aerosol cans (compressed gas containers) was introduced to the market in the 1970s (1974). The new packaging allowed the non-industrial use of PU foam by craftsmen and do-it-yourselfers.

The main fields of application of canned PU foam are interior works on buildings (new constructions, old buildings and renovations). Today, it is used only to a small part for mounting in the literal sense of the word (e.g. for fixing of door frames). It is mainly used for caulking and sealing of joints and gaps between door and window frames, for filling of different types of cavities, for sealing of ducts in wall penetrations and bushings, etc. The prevalence of OCF is facilitated by their easy applicability, the pressure stability of the hardened foam, their insulation effect, and their adhesion to most surface materials. The technical advantages of OCF, the climate relevance of the propellant gases contained in OCF, and technical alternatives are discussed in a report by the Federal Environmental Agency (2004) [3].

In chemical-technical terms, OCF is a synthetic which is generated by polymerisation of the two components isocyanates and polyols.

For some foam specifications, the two reacting agents are stored in separate containers at normal pressure and are only mixed when used. During this reaction, the components form a chemical compound and release carbon dioxide which bloats the foam. This type of foam is called "two component foam" (2K). No physical propellant is necessary for using it but the handling is rather difficult so that it is almost exclusively used by professionals.

Foam from one container only is a lot easier to handle and is stored in an aerosol can.

The two components already form a prepolymer inside the can which continues its reaction when exposed to the humidity of the ambient air and hardens quickly. This type of foam is called "one component foam" (1K). A physical propellant is needed to release the polymer from the can and to start the bloating of the foam.

Finally, two component foam is also available in one aerosol can. Similarly to one component foam, the can already contains a prepolymer generated by the two reacting agents and released by means of a physical propellant. Yet, the prepolymer does not depend on humidity but reacts with polyols. They are stored in a separate compartment of the can (most often at the bottom of the can) which has to be opened before use in order to trigger the reaction. This 2K foam contains a physical propellant just like 1K foam.

1K foam accounts for about 95% of the market of foams with propellants, 2K foam with propellants plays a minor role (5%). The market share of propellant-free 2K foam (in two containers) is rather small as its market share compared to the foam types with propellants (1K and 2K) amounts to only 5%.

This study focusses on foam in aerosol cans because only this type of foam contains propellants. 1K foam and 2K foam comprise propellant-containing products in general,

The propellant gases – first CFCs, then HCFCs, finally HFCs – have repeatedly been subject to environmental legislation. In 1998, the application of OCF was the major source of emissions of HFCs in Germany at that time by causing climate-relevant emissions of 1.5 million t CO<sub>2</sub> equivalent [4]. Since then the manufacturers have undertaken considerable effort to use environmentally friendly propellants and were, thus, therefore prepared for the ban of HFCs in OCF production by the EU F-Gas Regulation (see chapter 4).

## 2. Market and Manufacturers in the EU and in Germany

During the past ten to fifteen year, production and market of canned OCF have increased significantly. In the early 1990s, the use was virtually limited to Central Europe and Scandinavia. Almost half of the production of some 60 million cans (standardised volume 750 ml) was sold in Germany [5].

### 2.1 Growth in sales and new foam specifications

For 2008, the manufacturers interviewed within this study [6] estimated the production in the EU and in Switzerland to range around 230 million cans and the European market around 190 million units. The market in the EU-27 comprises about 150 million units (750 ml average volume per can).

Despite the foundation of new companies in Eastern Europe in the early 1990s (TKK 1992, Selena 1993, Kim Jarolim 1993, Krimelte 1998), the number of European manufacturers has not increased. This is due to the fact that mergers were formed in the past few years by incorporating several independent producers into major manufacturing groups (Hago, BÜKA, Makroflex) and that some manufacturers gave up their filling plants (e.g. Baxenden – UK and Denmark, Ara-Werk - Germany, Czewo - Germany, Ramsauer and Hanno - Austria).

Out of the total of approximately 230 million cans filled in the EU-27 and in Switzerland, 90 million units are sold in Western Europe (EU-15) and about 100 million units in Eastern Europe (new EU Member States and Russia, Belarus, Ukraine). Around 30 million cans are sold in Russia which also produces about 10 million cans on its own. Further customers of the European production are Turkey (8 million cans and own production), Kazakhstan (6 million cans), Africa (6 million cans), Israel and rest of the world (20 million cans).

From 2000 onwards, the diversity of products containing propellant gas has increased considerably. In former times only one- or two-component general-purpose foams were offered in two dispensing forms such as gun and adapter (straw), each in the Building Material Classes B2 and B3. Nowadays, additional specifications are available such as winter foam (for low processing temperatures), mega foam (higher yield than usually), fountain foam (sealing of manholes) – each of them in B2 and B3 – and also fire protection foam (Building Material Class B1). See table 1.

| Components     | One component   |    |          |    |      |    |        |    |                    | Two-component   |    |   |
|----------------|-----------------|----|----------|----|------|----|--------|----|--------------------|-----------------|----|---|
|                | General purpose |    | Fountain |    | Mega |    | Winter |    | Fire Protect. (B1) | General purpose |    |   |
| Material class | B3              | B2 | B3       | B2 | B3   | B2 | B3     | B2 | B1                 | B3              | B2 |   |
| Application    | A               | G  | A        | G  | A    | G  | A      | G  | A                  | G               | A  | G |

Explanations: Building Material Classes B1-B3 acc. to DIN 4102. A: Adapter (straw); G: Gun.  
Source: Manufacturers' survey 2008 [6].

The OCF market can be split into two submarkets of different size: First, craftsmen (professional market), and second, do-it-yourself sector (do-it-yourself-stores). The professional market covers approximately three quarters of the production. The

market shares vary between the manufacturers. It is a characteristic of the branch that the vast majority of the products are not sold as the manufacturer's brand, but as an external brand on behalf of companies that supply building materials to craftsmen.

## 2.2 Leading Manufacturers in EU and Switzerland in 2008

Table 2 shows the nine leading manufacturing groups and their head quarters. Six of them are located in Western Europe (incl. Switzerland) and three are situated in the new EU member countries in Eastern Europe. Five of the nine groups use more than one production site. The number of filled cans (standardised 750 ml) amounts to about 230 million units.

| <b>Manuf. Group</b>     | <b>Headquarter</b> | <b>Site</b>              | <b>Million cans</b> |
|-------------------------|--------------------|--------------------------|---------------------|
| <b>Soudal</b>           | Belgium            | Belgium                  | >40                 |
| <b>Rathor-Polypag</b>   | Switzerland        | Switzerland (2), Germany | >40                 |
| <b>Henkel-Makroflex</b> | Germany            | Finland, Estonia         | >40                 |
| <b>Den Braven</b>       | Netherlands        | Germany (2), Romania     | 30                  |
| <b>Selena</b>           | Poland             | Poland(2)                | 30                  |
| <b>Krimelte</b>         | Estonia            | Estonia                  | 20                  |
| <b>Tremco-Ilbruck</b>   | Netherlands        | Netherlands              | 12                  |
| <b>TKK</b>              | Slovenia           | Slovenia                 | 9                   |
| <b>Kim Jarolim</b>      | Germany            | Czechia, Slovenia        | 7                   |
| <b>Other</b>            |                    |                          | < 5                 |
| <b>Total</b>            |                    |                          | <b>230</b>          |

Source: Manufacturers' survey 2008 [6].

The three leading manufacturing groups Soudal, Rathor-Polypag and Henkel are of the same size, each of them producing 40 million cans per year.

- Soudal in Belgium produces only at one site. They mainly feature foreign trademarks of the do-it-yourself market (hardware stores) but also have their own brand "Soudal".
- In contrast, the Swiss Rathor group, which runs the German company HAGO in addition to its two Swiss plants, manufactures OCF almost exclusively by order of traders of construction materials under their band name.
- Henkel ceased the production in Germany and took over the Finnish company Makroflex with sites in Finland and Estonia in 2003. Henkel is strongly represented in Eastern Europe. Their most important own brand is Sista.
- The Den Braven group recently extended their production in Germany by taking over the manufacturer BÜKA and consolidating it with their company Autra. The primary markets are Central and Western Europe. Eastern Europe is supplied from a new plant in Romania.
- Selena (since 1993 production in Poland), Krimelte (since 1998 production in Estonia) and Kim Jarolim (since 1993 production in Czechia and Slovenia)

mainly supply the East-European and Russian market. Selena markets OCF its own brand "Tytan".

- Central and Western Europe are also supplied by Tremco-Ilbruck, a company in the Netherlands (formerly Cocon) and by the Slovenian manufacturer TKK (filling since 1992).

### 2.3 Suppliers of 1K- and 2K-Foam in Germany

The number of OCF cans (containing HFCs and HFC-free) annually sold in Germany amounts to about 18 to 24 million units (standardised 750 ml cans) depending on the activity of the building sector. The foam products are classified in different Building Material Classes according to their flammability (see chapter 5). The use of highly flammable foam (B3) is not authorized for buildings in Germany so that almost no foam of the Building Material Class B3 is sold. While the market focusses on products of Building Material Class B2 (normally flammable), foam of Building Material Class B1, which shows low flammability and, thus, is often called "fire protection foam", plays a minor role (~ 3%). The latter is not required neither by law nor technical norms, but some house builders and architects put emphasis on low flammability.

Today there are eight relevant European manufacturing groups (own brands and external brands) featuring the German market. The ninth European manufacturer of considerable size, AS Krimelte from Estonia, does not sell to Germany.

Table 3 shows the supplying manufacturing groups by estimated market shares.

| Supplier  | Market Share |
|---|--------------|
| Soudal (Belgium)                                    | 30%          |
| Rathor/Hago (Switzerland/Germany)                   | 30%          |
| Tremco Ilbruck (formerly. Cocon) (Netherlands)      | 15%          |
| Den Braven/Debratec [BÜKA] (Germany, Romania)       | 15%          |
| Henkel (Germany, Production in Finland and Estonia) | 5%           |
| Selena-Orion (Poland)                               | < 3%         |
| TKK (Slovenia)                                      | < 3%         |
| Kim Jarolim (Production in Czechia and Slovenia)    | ~ 1%         |

Source: Manufacturers' survey 2008 [6].

The two manufacturers Soudal and Rathor (incl. Hago) serve almost two thirds of the German market.

Medium-sized suppliers in Germany are Ilbruck, Den Braven and Henkel.

The market shares of the three Eastern European manufacturers Selena, TKK and Kimtec are very small.

## 2.4 The OCF Specifications on the German Market

The structure of the German OCF market by important specifications is shown below (overall market 20 million cans).

| Specification                | Market Share (%) |
|------------------------------|------------------|
| 1K General purpose foam      | 73               |
| 1K Mega foam                 | 18               |
| 1K Fountain foam             | 1                |
| 1K Winter foam               | 1                |
| 1K Fire protection foam (B1) | 3                |
| 2K General purpose foam      | 4                |

Source: Manufacturers' survey 2008 [6].

- One component foam for general purpose is by far the most important product with a share of three quarters of the domestic market.
- The market share of high-yield (Mega or Maxi) foam amounts to about 18 percent.
- The market share of fire protection foam of the Building Material Class B1 is estimated to range around 3 percent.
- While winter foam accounts for up to a quarter of the market in Northern Europe, the share is rather small in Germany. The same is true for fountain foam, which rather is a waterproof version of general purpose foam.
- Two component OCF for the professional market accounts for a share of less than five percent in total.

## 2.5 The manufacturers of OCF in Germany

In Germany only three filling plants for OCF are run by two groups of companies.

| Manufacturer  | Annual Output (mn units/y) |
|---|----------------------------|
| 1. Hago (Rathor-Group) in Landsberg am Lech (Bavaria)         | 10                         |
| 2. Den Braven Aerosols in Reichenberg-Albertshausen (Bavaria) | 20                         |
| 3. Debrattec (Büka) Den Braven in Schwepnitz (Saxonia)        | 5                          |

Source: Information from the three plants in the frame of the manufacturers' survey 2008 [6].

While Hago produces B2 and B3 foam, Den Braven Aerosols produces only B3 foam. B2 and B1 foam is produced by Debrattec. In total about 35 million cans are produced per year.

Almost two thirds of the OCF units filled in Germany meet only the Building Material Class B3 (easily inflammable) and are exported.

### 3. The Importance of the Propellant for canned OCF

In chemical terms, polyurethane foam is a plastic resulting from the polymerisation reaction of isocyanates with polyols. An oligomeric intermediate (prepolymer) originates in the aerosol container (can) from the two components (and its additives). After being released from the can, it polymerises to form a macromolecular compound. The can contains pressurised gas which propels the prepolymer mixture and acts as initial blowing agent of the foam formation immediately after releasing. Outside of the can, the free isocyanates of the prepolymer react with ambient water (humidity) and separate carbon dioxide. This chemical blowing agent continues and completes the foam formation.

The combustibility of PU foam requires flame-retarding equipment. Consequently, in standard formulations flame retardants are the third major component in the prepolymer mixture - after isocyanates and polyols [7]. Most of them are additives but some are reactive components of (halogenated) polyols. Their amount and type depend on the fire safety requirements of the cured foam. Further additives are used such as cell-stabilizers, agents for the control of viscosity, plasticizers, catalysts, etc. The fourth main component of the formulation is the propellant gas.

#### 3.1 The three main functions of the propellant gas

The propellant (pure gas or gas mixture) has to meet three key requirements.

- Firstly, in liquefied state it acts in the can as a solvent of the viscous prepolymer mixture including all the additives.
- Secondly, in gaseous state it generates pressure in the can to release the prepolymer mixture through the spray tube.
- Thirdly, it causes the expansion of the prepolymer immediately after the output and supports the inflation of the foam by carbon dioxide.

Besides, it serves as a cooling agent for the short-term stabilisation of the foam before the start of the hardening reaction [8].

The propellant highly contributes to the formation of the fine structure of the foam cells. However, it does not remain inside the pores of the cured foam for long enough to enhance the insulation effect. Unlike blowing agents in PU insulation boards with cover layers, the propellant degasses quite fast – as a function of its molecular size. In the case of HFC-152a (as well as propane and butane) instant and complete degassing is presumed, in the case of HFC-134a about five percent of the propellant gas is assumed to remain in the foam for one year. Then at the latest, an insulation effect of HFCs does not exist any longer so that the insulation quality of the propellant gas does not play a significant role in practice.

The three functions of the propellant as solvent, as agent of release and as agent of the first expansion had been fulfilled best by CFCs (-11 and -12) and HCFCs (-22) up to the nineties. This was still the case when limited quantities of hydrocarbons (propane and butane) were added. HFC-134a, which replaced the ozone-depleting substances, also features most of the properties of the previous propellants. Hence,

the manufacturers could easily supply foam of the same quality and adapt their formulations to the new propellant gas (with and without doses of hydrocarbons).

Likewise, the application of the foam remained unchanged. In the same way as CFCs and HCFCs, HFC-134a was incombustible and did not require special measures to prevent explosions.

Both, the requirements to undertake effort to adapt the formulations and the need to undertake safety precautions increased as the share of HFC-134a in the propellant gas mixture was reduced or even abandoned.

### **3.2 HFC-134a is not a flame-retarding agent**

At this point it is necessary to underline that the inflammability of the propellant does only affect the safety of application but not the reaction to fire of the cured foam.

As mentioned earlier, the propellant gas only remains in the foam cells in small amounts and for a short time. Therefore, it does not act as flame-retardant on the hardened foam. The incombustible HFC-134a cannot reduce the combustibility of the foam for a long time, on the other hand propane/butane or HFC-152a do not increase its fire load<sup>1</sup>.

It is true that it was not easy for the manufacturers (see chapter 4) to achieve "normal" flammability (the German Building Material Class B2) without HFC-134a and to further guarantee at the same quality of the foam. However, this was primarily related to the fact that the given prepolymer with its specific fire-retardant characteristics was completely adapted to the physicochemical properties of HFC-134a. The use of HFC-152a and pure hydrocarbons required the reformulation of the prepolymer including fire-proofing and other additives like stabilisers, cell openers, plasticizers, etc. This was due to the new propellant gas which is characterized by different pressure, solubility, and expansion behaviour; but not to its flammability .

The conversion of the propellant was a long and costly process which was, however, successful in the end – as shown in the next chapter.

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<sup>1</sup> The wording "not for a long time" in the case of HFC-134a means that a minimal and short-term reduction in combustibility cannot be excluded. Possibly, on the fire test on Building Material Class B2, which is carried out with fourteen-days-old foam, a minimal fire suppressing effect can be found. In this case the adequacy of this test must be questioned because the product shall show a lifetime of up to 50 years.



## 4. Change of Propellant Gas in EU and in Germany since 1990

At begin of the 1990s HFC-134a became commercially available in large amounts so that ozone-depleting propellant gases in PU foam cans were replaced gradually: At first in Scandinavia, then in Germany and finally in the rest of Europe. The European manufacturers abandoned the use of CFC-11 and -12 from 1.1.1992 as well as the use of of HCFC-22 from 1.1.1996.

### 4.1 Early to mid-1990s: CFC phase-out and the 50 g-rule

In Germany, the CFC-Halon-Ordinance prohibited the production (but not the use) of OCF with HCFC-22 (and with CFCs) from 1.1.1993 [9]. In the late 1980s, HCFC-22 had become a general OCF propellant gas all over Europe. In the five years before 1992, its quantity per can significantly decreased, from 40% to 15-20% [8]. At the same time more and more flammable hydrocarbons were added to the non-flammable gas as they were a lot cheaper.

At the beginning of the 1990s, even before the conversion from HCFC-22 to HFC-134a, the leading European manufacturers discussed in their organisation AKPU the maximum content of flammable gases in the propellant gas mixture [9]. They wanted to prevent explosions in confined spaces seeing that the customers were not used to handle flammable propellant gases. The manufacturers in the AKPU voluntarily agreed on the so-called 50 g rule. This rule implied that a standardised 750 ml can should not contain more than 50 grams of hydrocarbons and ether. The concentration of hydrocarbons must remain below the minimum threshold for explosions (propane: 31 g/m<sup>3</sup>, butane: 33 g/m<sup>3</sup>) when emptying a can in one go in a space of 1.56 m<sup>3</sup> [10].

Although this rule was applied to propane and n-butane only, it also implied that the quantity of gases with higher thresholds for explosion could exceed 50 grams per 750 ml can. Hence, the "50 g rule" allowed 80 g of dimethyl ether per can and even 158 g of HFC-152a. This interpretation of the rule made it even possible for manufacturers to use pure HFC-152a as propellant gas, without HFC-134a. However, HFC-152a was not available on the market in sufficiently large quantities before 1996 [11].

### 4.2 Three ways of HFC use in the EU before 2000

Concerning the propellant gases, the development throughout Europe was not uniform in the 1990s. There were three different ways of dealing with these issues.

In Scandinavia, the 50 g rule has never applied. In the early 1990s, OCF cans with higher quantities of hydrocarbons had already been in use for a long time and without any accidents. Therefore the European manufacturers decided to not set a limit for the content of hydrocarbons.

In the other European countries, except for Germany, the HCFC-22 phaseout was decided relatively late (1995) and the 50 g rule was not followed for a long time. As early as 1995/1996, the manufacturers started using more hydrocarbons than HFCs

with reference to the good experiences in safety in Scandinavia. By 2000, only 20% of the cans sold still contained HFC-134a [5].

In Germany, the regulations for explosion protection in OCF applications did not differ from those in the rest of Europe. However, cans without HFCs were not sold until 2000 [12]. This was due to specific fire protection requirements for hardened foam. It is not allowed to use "easily flammable" materials (Building Material Class B3) in buildings, but they have to be at least "normally flammable" (Building Material Class B2).

For many years, this requirement could not be met without HFCs. The reason for that was not that incombustible or hardly flammable propellants would make hardened foam more fire-resistant but HFCs, especially HFC-134a, were most suitable to solve, to release and to expand the more fire-resistant prepolymer (which contained more and other flame retardants) without changing its stability, volume, and, above all, the cell structure of the cured foam.

There were two different groups amongst the OCF manufacturers.

One was the Swiss Rathor group who had used almost exclusively HFC-152a for B2 foam already from 1995/1996 onwards. As mentioned above, due to its relatively high threshold for explosions, this HFC made it possible to stick to the 50 g rule [13].

The other manufacturers continued using HFC-134a to meet the Building Material Class B2 specifications.

Thus, for a long time the propellant gases for the German market kept on containing HFCs, primarily HFC-134a [14]. It should be noted that the 50 g rule and the use of high shares of non-flammable HFC-134a were not maintained because of the safety regulations but as the technical properties of B2 foam were not yet achieved without HFC-134a by some manufacturers.

### **4.3 Reduction in HFC share also in Germany by 2002/2003**

Between 1995 and 2002, HFCs were not completely replaced by flammable gases in products for the German market, but the quantity of HFCs per 750 ml can was steadily reduced in favour of flammable gases [12].

This was partly due to economic factors as the costs of propane/butane were ten times lower than the costs of HFCs.

Furthermore, some progress in formulation made it possible to realize the production of Building Material Class B2 with relatively high shares of hydrocarbons in the gas mixture. In 1995 the HFC quantity per 750 ml can amounted to 100 g on average, in 2000 only 65 g were used, and in 2002 only 40 g [15]. The 50 g rule was no longer of importance in production.

In 2002, the manufacturer organisation AKPU took this trend into account as they replaced the 50 g rule by a 100 g rule. In a gas mixture of 150 g (per 750 ml can) at least 50 g of HFC-134a should be contained. This rule, however, was not followed for

a long time. Nowadays, this measure is seen as attempt to stop the substitution of HFC. The safety concerns which the 50 g rule was based on were no longer of importance.

#### **4.4 New foam specifications from 2002 not without HFC-134a**

Afterwards, the HFC substitution died down for some time. This was not so much a consequence of the recently introduced 100-g-rule but rather related to new specifications for foams such as fire protection foam, winter foam, and foam of higher yield (Mega or Maxi foam). Unlike the common all-purpose foam, the new specifications required HFC-134a as propellant gas. At the first pure HFC-134a was used as expanding agent, afterwards it was added in combination with hydrocarbons.

- Fire protection foam is consistent with Building Material Class B1 specifications when hardened. The high content of flame retardants poses specific requirements to the propellant gas.

- High-yield foam (Mega or Maxi foam) provides much higher quantities of foam (60 litres of high-yield foam and more compared to 45 liters of normal foam) while the size of the can remains the same, and the same quantity of foam can be taken from a smaller can respectively. The customer uses a smaller number of cans and can access narrow spaces more easily.

- Winter foam is no longer limited to the previously known minimum temperatures for storage and processing of about +5°C, but can be applied at -5 to -10°C. Thus, the use of OCF is also possible in colder areas such as Northern and North-Eastern Europe. In Central Europe winter foam comes in handy when the cans are stored outside etc. HFCs are particularly useful to create high pressure in the can at low temperatures.

These three special types of foams account for up to twenty percent of the output of some manufacturers depending on the climate in their main sales areas.

#### **4.5 EU-Regulation on fluorinated gases and HFC phase-out from 2002**

From 2002/ 2003 onwards the trends in production were characterised in anticipation of the EU F-Gas Regulation. All suppliers of the German market reduced the HFC contents per can [15]. In 2002 the first all-purpose foams (B2) without HFC propellants were sold in Germany. Within several years all producers for the German market were able of to supply this type of general-purpose OCF. The substitution of HFC in winter foam, mega foam (B2) and fire protection foam (B1) took some more time.

Only today (end of 2008) we can say that all the canned PU foam offered in Germany does meet the defined requirements of the F-gas Regulation. The regulation does not require that all foam products have to be free of HFCs but specifies in Art 2(5) only that "the total global warming potential of the preparation is less than 150" [1]. Consequently, the propellant may consist of pure HFC-152a (GWP 140). Furthermore, a propellant gas mixture ("preparation") may even contain up to 11.5

mass percent of HFC-134a (GWP 1,300), provided that the other gases do not show a considerable greenhouse gas potential.

Given that the propellant gases account for 18 mass percent on average in a 750 ml can (propellant gas mixture 150 g), a HFC-content of up to 17 g of HFC-134a is legally still allowed<sup>2</sup> and can be found in some products.

#### 4.6 State 2008: No more propellant mixtures with GWP over 150

Table 6 shows the situation of the German market at the end of 2008. Products with propellant gas mixtures of GWP < 150 are available in all OCF specifications of at least Building Material Class B2 both in adapter dispensers (A) and spray guns (G).

**Table 6: OCF Specifications of Building Material Classes B2/B1 with Propellant Gas GWP < 150, on the German Market, End of 2008**

| Manufacturer | 1K All purpose |   | 1K Mega |    | 1K Winter |    | 2K All purpose |   | 1K Fire Protection (B1) |   |
|--------------|----------------|---|---------|----|-----------|----|----------------|---|-------------------------|---|
|              | A              | G | A       | G  | A         | G  | A              | G | A                       | G |
| Den Braven   | A              | G |         | G  |           | G  | A              |   | A                       | G |
| Soudal       | A              | G | A       | G  |           | G  | A              |   | A                       | G |
| Rathor       | A              | G | A       | G  | A         | G  | A              | G | A                       | G |
| Henkel       | A              | G | A       | G  |           | G  | A              |   |                         | G |
| Illbruck     | A              | G |         | G  |           | G  | A              |   |                         | G |
| Selena       | A              | G |         | G  |           |    |                |   |                         |   |
| TKK          | A              | G | A       | G  | A         |    | A              |   | A                       | G |
| KimTec       | A              | G |         | G* |           | G* | A              |   |                         | G |

\* KimTec does not offer one type of winter foam and one type of mega foam but supplies a combined winter-mega-foam.

In general, all-purpose foams are completely free of HFC-134a and HFC-152a (1K and 2K) and are offered by all of the eight manufacturers.

Five of the seven suppliers of mega foam and fire protection foam in Germany do not use any HFCs in their products according to their own statement. One manufacturer meets the F-Gas Regulation using HFC-152a in a small number of his products, and another manufacturer adds HFC-134a in authorized quantities. The eighth manufacturer (Selena) does not sell these special types of foam in Germany. Krimelte, an Estonian producer, uses HFC-152a in all his products, but does not supply the German market.

<sup>2</sup> The possibility to continue using HFC-134a in small amounts forms the legal basis for manufacturers to fill OCF cans with propellant gas which is recovered by the PDR from used cans.

## 5. Safety Aspect I: Fire Safety after Hardening

The critical factor for the safety of hardened OCF is its fire reaction. The safety regulations for the use of foam inside buildings differ from those related to the use outdoors.

### 5.1 The Material Classes B1 and B2 for Buildings

According to the German Standard DIN 4102 [16], OCF can be classified into three different Building Material Classes: B3 (easily flammable), B2 (normally flammable) and B1 (hardly flammable). In general, OCF do not achieve Class A (not flammable), due to their polyurethane basis. The classification into Class B1 or B2 is based on a fire reaction test carried out by a material testing institute [17]. B3 foam is not tested at all. It is hardly sold in Germany as easily inflammable construction materials are not allowed to be used in buildings.

OCF are mostly used in buildings. Construction materials for long-term use in buildings have to be "normally inflammable". This is a minimum requirement of the Building Code (Musterbauordnung) [18] and the State Building Regulations (Landesbauordnungen) which explicitly prohibit the use of easily inflammable construction materials. Therefore, OCF of Class B3 is must not be used for the construction of buildings but materials of Class B1 and B2 are allowed.

#### **Building Material Classes B3, B2, B1 and test on fire safety**

In buildings, caulking foam has to meet the requirements of Building Material Class B2 as defined in the German Standard DIN 4102-1.

To determine whether or not a material meets the requirements of Building Material Class B2, the samples are stored for at least two weeks under normal climatic conditions before their fire performance is tested. The material has successfully passed the test, when in none of five samples the flame reaches within 20 s the 150-mm mark (flame exposure time: 15 seconds).

The test on Building Material Class B1 ("materials that are difficult to ignite") includes a simulated fire on an object inside a room. This category requires low flame spread and limited heat release. In practice, the testing institutes attach definite conditions to the B1 certificate, saying *mutatis mutandis*: The building component meets B1 only on conditions that the foam is applied between solid mineral materials (e.g. concrete).

Flammable building materials that do not meet the requirements of Class B1 or B2 automatically fall into Class B3.

In Germany, there is no law that prescribes Class B1 for building materials. The suppliers of B1 OCF justify the production with the fact that some builders and architects demand fire safety standards higher than necessary. A legal basis for B1 foam does not exist [17]. Even technical norms stipulating increased fire resistance could not be identified in the course of this study.

The question is whether or not in Germany for fire safety reasons the exception clause of Annex II F-Gas Regulation must be maintained, which requires the admission of propellants with GWP >150 if national safety standards cannot be met otherwise.

The exception clause would make sense for the application inside buildings if the manufacturers were not able to formulate the diverse specifications of their B2 products without considerable doses of HFC-134a (> 11.5% of the gas mixture).

As shown in the preceding chapter (Table 6), since the end of 2008 a sufficient quantity of PU-OCF of Building Material Class B2 and even B1 is commercially available with propellant gases of GWP below 150 in all relevant specifications.

**Conclusion:** As a sufficient amount of HFC-free OCF of Building Material Class B2 is available, it is no longer necessary to maintain the exception clause of the F-Gas Regulation for fire protection inside buildings.

## 5.2 Fire safety restrictions outside of buildings

The Building Regulations and their fire protection requirements for construction materials apply to buildings only. According to § 1 (2) Building Code, the following constructions are explicitly excluded:

1. Installations of public transport including equipment and ancillary facilities except buildings.
2. Installations under the control of the mining authorities, except buildings.
3. Lines for public supply of water, gas, electricity, heat, sewage discharge or telecommunication,
4. Long-distance pipes for the transport of substances.

Except for the mining sector, all fields of civil engineering are concerned. Although the Building Regulations do not apply, it is not evident that B2 products may be used as construction materials. It rather means that the classification of building materials into B3, B2, and B1 (in accordance with DIN 4102) is not applicable [19].

The search for relevant fire protection regulations for OCF as a building material resulted in the finding that no concerns towards the use of flammable foam (easily, normally, hardly flammable) are expressed at all

- Roadworks: Safety regulations for flammable building materials do not exist at all, not even in tunnel construction [20].
- No regulations restrict the use of synthetic materials (plastics) for supply and discharge lines for drinking water, waste water, gas and electricity. However, OCF is not used in these areas of work [21].
- Even for long-distance heat pipes which are insulated by synthetic materials (inside PU, outside PE), no fire protection regulations restrict the use of

plastics [22]. Just inside buildings (e. g. in lift shafts) the flammable plastic insulation is usually removed as required by the Building Code.

*Different fire protection regulations rule the use of identical applications inside and outside of buildings e.g. the use of water-resistant OCF (fountain foam) for the construction of sewage ducts and wells. According to the Building Regulations, only OCF of Building Material Class B2 may be used for sealing rings or shafts in the basement or in other areas of a building. Outside of buildings, any OCF can be used for the same purposes, including OCF of Material Class B3.*<sup>3</sup>

- No requirements concerning the flammability of plastics exist in the automotive industry, which uses OCF to seal insulating superstructures (cargo holds) of refrigerated vehicles (jointing of thermal bridges) [23].

Only in underground mining substances are generally prohibited, which are "combustible and pass on automatically a fire"<sup>4</sup> and substantially increase the fire hazard. As a consequence, "solid plastics" including hardened OCF are not admitted in mining. However, in the non-coal-mining industry (salt, ore, stones, and earths) the use of limited amounts of "solid plastics" is allowed under specific circumstances. Special fire protection requirements apply to the coal mining industry and are not explained in this study. When used under ground, explosions during the application procedure of OCF pose a significantly higher risk than the flammability of hardened foam. For details see the following chapter.

**Conclusion:** The use of hardened polyurethane foam outside of buildings is not restricted by any fire protection regulations. This statement is qualified by underground mining peculiarities; the next chapter goes into details of mining.

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<sup>3</sup> In Germany there is no general ban on OCF of Material Building Class B3. However, it must not be used inside buildings – neither by craftsmen nor by do-it-yourselfers. Only very small amounts of this type of foam are applied outside of buildings.

<sup>4</sup> The fire performance of solid plastics for underground use is tested referring to DIN 22100, 1-7 [24].

## 6. Safety Aspect II: Explosion Protection on Application

Today, the demand for national safety standards for OCF is no longer relevant in Germany as far as the fire performance of hardened foam is concerned. However, the demand still exists in case of direct applications of OCF when extremely flammable gases<sup>5</sup> are released, which are considered hazardous substances<sup>6</sup>. This problem has to be taken into account by occupational safety and health regulations.

### 6.1 General rules for handling of dangerous substances

In Germany, the handling of hazardous substances is regulated by the Labour Protection Act (Arbeitsschutzgesetz, ArbSchG) [25] which also includes the handling of flammable substances.

The Labour Protection Act constitutes the legal basis for the Ordinance on Industrial Safety and Health (Betriebssicherheitsverordnung, BetrSichV) [26] which contains a comprehensive set of rules for the assessment of hazards and suitable measures according to the state of the art (technical rules for industrial safety - TRBS).

The Labour Protection Act (and the Chemicals Act) also serves as the legal basis for the Ordinance on Hazardous Substances (Gefahrstoffverordnung; GefStoffV) which aims to increase health and safety in the workplace [27]. It specifies the establishment of technical rules for the handling of hazardous substances (TRGS). A key regulation concerns the information on dangerous substances by material safety data sheets (MSDS).

In fact, the MSDS play an important role since the employer or his occupational safety officer is obliged to carry out a risk assessment related to the handling of hazardous substances. The MSDS summarize the most important information such as potential hazards, first-aid measures, measures for fire protection, measures when accidentally released, data on handling and storage, information on exposure limits, safety equipment, toxicological information, etc.

In Germany it is generally considered appropriate to observe the above mentioned regulations for handling of OCF containing extremely flammable propellant gases. The labour protection law does not prohibit the handling of hazardous substances but regulates their safe handling.

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<sup>5</sup> Directive 67/548/EEC classifies the following substances as extremely flammable (symbol F+, risk phrase R12):

- Liquids featuring a flash point below 0°C and a boiling point below 35°C.

- Gases which are flammable when exposed to air at room temperature and at normal pressure.

<sup>6</sup> In this study dangerous substances other than propellants used for foam production are not considered (e.g. isocyanates).



## 6.2 Particularities of tunnelling industry and ship-building industry

In the following, we look at sectors where the basic labour protection regulations are not considered appropriate so that national safety norms are amended (“national safety standards” in the legal sense of annex II F-Gas Regulation).

At the beginning of this study, several specialists of the sector supposed three sectors to be crucial for the application of flammable propellant gases. The work accomplished in these sectors is characterised by narrow spaces and poor ventilation so that it might be possible to reach the threshold for explosions when emptying a can without interruption: tunnelling, ship-building and mining.

### 6.2.1 Tunnelling

In tunnelling OCF is used occasionally to grout fissures in concrete and to seal cavities behind concrete. So far, no accidents caused by the application of extremely flammable gases of OCF cans have been reported.

The Employer’s Liability Insurance Association of the German building industry in Stuttgart [20] undertakes risk assessments for tunnelling and highlights specific working conditions inside tunnels such as compressed air. Both tunnelling machines and conventional tunneling methods increase the ambient pressure to more than 3 bars which also influences the partial pressure of flammable gases. Thus, the thresholds for explosions of OCF differ from those known for normal conditions.

These particularities must be taken into account in risk assessments. However, no other specific safety and health regulations for the use of flammable substances apply in tunneling than the industrial safety regulations (BetrSichV) and the Ordinance on hazardous substances (GefStoffV). The use of flammable substances is not illegal but the warning notices and safety tips in the material safety data sheet must be observed closely, in particular those on fire and explosion protection in the chapter "handling and storage".

### 6.2.2 Ship building

An expert from a leading company for the filling of OCF cans remembered that a big passenger shipyard had launched an enquiry for canned PU foam containing non-flammable propellant gases several years ago. They were planning to seal the fire walls of the hull no longer with rubber but with PU foam.

The occupational health and safety officer of the shipyard [28] explained that the yard was not using any particular OCF but the normally available type. Regulations on dangerous substances beyond the regulations of the industrial safety regulations (BetrSichV) and the Ordinance on hazardous substances (GefStoffV) do apply neither in this shipyard nor in the German ship building industry in general as these two laws are considered sufficient to provide an appropriate framework.

### 6.3 Special explosion protection in mining

In underground mining, the conditions for the application of flammable substances are difficult. Spaces are narrow and fresh air as well as short escape routes are not available. Especially in coal mining, an extremely high risk for explosions exists as mine gases contain methane. Hence, the use of flammable working materials is considered very dangerous.

Canned OCF is used in coal mining, in particular in boreholes. As a protection from rockfalls and the influx of potentially explosive colliery gases, holes are bored into the coal and the adjacent host rock for exploration, for aimed sucking of colliery gas or for relaxation of the rock. OCF is used in order to seal the annular spaces of drill pipes<sup>7</sup> and abandoned boreholes which would otherwise trigger the influx of colliery gas into the airflow [29].

#### 6.3.1 Registration requirements according to the Health Protection Regulations in Mining (GesBergV)

The Industrial Safety Regulations (BetrSichV) and the Ordinance on hazardous substances (GefStoffV) are not considered sufficient to guarantee occupational health and safety in mining. The Health Protection Regulations in Mining (Gesundheitsschutz-Bergverordnung, GesBergV) give additional regulations for the handling of hazardous substances in the mining industry [30]. According to these regulations, a special registration approval of hazardous substances has to be undertaken before using them in mines.

§ 4 of the Health Protection Regulations in Mining says that workers must not handle "substances that substantially increase the risk for explosions or fire" if these have not been tested, approved and registered by the competent authority.

The competent authority for the registration of dangerous substances in the German mining is the regional government of Arnsberg in North Rhine-Westphalia (Bezirksregierung Arnsberg, NRW). They commission survey reports, decide on the registration of substances and publish the "list of approved products" [31], which gives registered products by manufacturer, brand name, size, etc. Only products of this publicly available list may be used in mining [32].

As outlined in the Health Protection Regulations in Mining (GesBergV), hazardous substances requiring official registration comprise "liquid synthetics" and therefore include OCF. At the request of the manufacturer, the regional government charges the "Hygiene-Institut des Ruhrgebiets", based in Gelsenkirchen, with a standardized test [33]. Approved products get registered and published on "list of approved products".

As registration fees have to be paid by the manufacturer, the registration of a product is not profitable unless high quantities of the product will be sold. Therefore, a special regulation applies to products in little demand since 2004 [34]. Within "basic approvals", so called "small trading units" do not require registration if less than 250

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<sup>7</sup> Annulus is the space between the drill pipe and the internal wall of the borehole.

units are used per mine and per year. This means that on average one container of the approved product may be used per workday (250 days per year). The list of products covered by the "basic approval" is published on the internet as well as the "list of approved products" [35].

### 6.3.2 Approved OCF products in German mining

OCF products are included in both lists of products by the regional government of Arnsberg. They are indicated on the "list of approved products" (no. 151 to 165) and on the list of products suggested for basic approval (no. 17 to 21 of "Substance Group 5: Sealing of Joints").

#### - OCF products requiring basic approval only\*

| No. | Name of the product                 | Manufacturer                               | Size of Container | File Hygieneinstitut |
|-----|-------------------------------------|--|-------------------|----------------------|
| 17  | Rapidschaum 750/1000 (B2)           | Hanno-Werk, Himberg b. Wien, Austria       | 0.75              | A-106770-03-To       |
| 18  | PU Schaum                           | Heidelberger Baustofftechnik, Traunreuth   | 0.75              | A-106770-03-To       |
| 19  | Polyurethan-Montageschaum           | Heidelberger Baustofftechnik, Traunreuth   | 0.5               | A-106770-03-To       |
| 20  | Pistolenschaum NBS                  | Paso Chemisch-Technische Produkte, Münster | 0.7               | A-106770-03-To       |
| 21  | Montageschaum BÜKA 2-K-PU Alpha Duo | BÜKA-Chemie, Erdmannshausen                | 0.6               | A-106770-03-To       |

\* Regional government Arnsberg: list of dangerous substances in small containers [35]

#### Results of a survey of the manufacturers on these products:

No. 17: Hanno-Werk mentions on 14.10.2008 that the listed 2K-Rapidschaum (approved on 14.01.2004) is no longer on sale but has been replaced by 2K Tempo which does not contain HFCs. This is due to the fact that filling and sale of HFC-containing OCF have been interdicted by national law in Austria since 2006. In 2004, the Rapidschaum had contained a small amount of HFC-134a as an admixture to propane/butane/DME.

No. 18 and 19 (no difference other than the size of the container): In 2004, the Heidelberger Baustofftechnik has been called Compact Technology GmbH, but is still based in Traunreuth. While the brand has been renamed Kompakta, the formulation of the foam has not changed since 2004 [36]. According to the sales department, this product is used in salt mining by the company Kali+Salz; its filling is carried out by Illbruck in the Netherlands. Already in 2004, the propellant gas did not contain any HFCs but propane, butane, DME (2.5-10% each).

No. 20: Since 2006, Paso is part of the Bostik GmbH and the headquarter has been relocated from Münster to Borgholzhausen. The laboratory director explained that at that time HFC-134a was used as an admixture to the extremely flammable mixture propane/butane/DME as recommended in the MSDS from 2003 [37]. Both, the former HFC-containing Pistolenschaum NBS and the new HFC-free version of this product, were filled by Rathor in Switzerland.

No. 21: Since 2008, BÜKA is called DEBRATEC and produces in Schwepnitz (Saxony). The laboratory director said that in 2005 HFC-134a was still added to the extremely flammable propellant gas mixture [38]. The mixture was composed of the following gases: < 15% tetrafluoroethane (HFC-

134a), < 10% isobutane, < 3% dimethyl ether, < 6% ethanediol. The gas mixture of the upgrade product 2-K Alpha Duo features a GWP < 150.

The update of the list of products in small-containers mentions four OCF products registered at 14.01.2004. Three of these four products are no longer available. However, their registration the official authorisation continues to be valid until the next update of the list. At approval, none of the products contained pure HFC-134a as a propellant gas and, thus, were non-combustible. Yet, all of them all of them contained extremely flammable gases. Only one of the products is still available today (Kompakta, respectively Heidelberger Baustofftechnik), but the foam has been HFC-free in 2004 already.

The safety standards of the mining industry do not require that propellant gases contained in products in small trading units have to be incombustible. This does not apply to products of the "list of approved products".

#### - OCF products on the "list of approved products"\*

| <b>Table 8: Extract from the "list of approved products", sheet 7-20, 7-26, 7-27, as at 05.08.2008</b> |  |  |                   |   |
|--|--|--|-------------------|---|
| No   | Name of the product                                      | Manufacturer                                     | Approval          | Container   |
| 162  | PU 1-K-Polyurethanschaum Geofix, Geofix Gold             | Schaum-Chemie Wilhelm Bauer GmbH & Co. KG, Essen | 06.03.2006        | Pressurised cans made of tinplate up to 0,75 l volume |
| 165  | 1-K-Polyurethan-Kunstharzschäume CARBOFIX, CARBOFIX DKD  | Minova Carbo Tech GmbH, Essen                    | 27.04.2006        | Pressurised cans made of tinplate up to 1 l volume    |
| 151  | <i>1-K-Polyurethanschaum. Volumax hardly inflammable</i> | <i>Zeißig GmbH &amp; Co. KG, Mülheim (Ruhr)</i>  | <i>21.10.2005</i> | <i>Plastics of 1 l volume</i>                         |

\* Regional government (Bezirksregierung) Arnsberg: List of approved products [35].

#### Results of the survey of the manufacturers on these products:

No. 162: According to Schaum-Chemie [39] and the information given in the MSDS, the propellant gas of this OCF is pure HFC-134a without any admixtures of flammable gases. The formulation has not been changed since the first approval. The product GEOFIX had been authorised many years ago, but had to be updated as the dispenser and the product name changed in 2006. It is now called GEOFIX Gold. The product is packaged by Hago in Landsberg, Rathor group.

No. 165: According to Minova [40], CARBOFIX contains pure HFC-134a propellant gas as safe application is required by the customer. The formulation has not been changed since the first approval, but the official authorisation was renewed in 2006 for CARBOFIX DKD. The product is the same as no. 162 and also gets filled by Hago. The mining company DSK buys both products. DSK is the owner of all coal mining companies which are still active in Germany.

The suppliers estimate that a quantity of total 10,000 aerosol cans is sold per year.

No. 151: According to Zeißig [41], the product is not canned OCF with propellant gases but a propellant-free 1K-product in a plastic container. The foam is said to be bloated by CO<sub>2</sub>, which is released when water is added. The company underlines that the product Volumax has been used in coal mining before canned OCF was introduced. Volumax is still used in higher quantities than OCF for the sealing of boreholes and of pipes diverting colliery gas. According to Zeißig, Volumax could basically replace canned OCF.

The listed "liquid synthetics" approved for underground mining comprise two identical OCF products which contain pure non-flammable HFC-134a as propellant gas. In a separate paragraph, the list limits their purpose to sealing of annuluses and cavities covering less than 400 cm<sup>2</sup>. In coal mining, a quantity of about 10,000 aerosol cans is estimated to be used per year.

### 6.3.3 Prohibition of flammable propellant gases in coal mining

The competent authority, the regional government Arnsberg (Bezirksregierung Arnsberg), division for mining and energy in North Rhine-Westphalia, explains the difference between products in small trading units and in the products mentioned on the "list of approved products" as follows [42].

- Products without individual approval (small trading units)

The potential hazard from small trading units of less than 250 cans per year is low so that the indications of the MSDS are considered sufficient for authorisation within a basic approval without an additional test report from the Hygiene-Institute. However, in an extra clause of the basic approval, the use for these products in coal mining is excluded. The listed OCF products are used in salt mining as the risk for explosions is significantly lower than in coal mining. Listed OCF products additionally labelled F+ may be used in mining (salt, earths, mineral ores, etc) but not in the coal mining industry.

The official statement continues as follows (wording in italics):

*Due to the regulations of the basic approvals as well as to the classification of these OCF into Tab. 7, Substance Class 5.1, the following limitations apply for the mentioned OCFs:*

- 1. These products must not be used in coal mining as the flashpoint of the propellant gas is reached at  $\leq 55$  °C<sup>8</sup>.*
- 2. As a basic principle, the content of one container must not exceed 5 kg (aerosol cans are always smaller).*
- 3. The total quantity used per mine and year must not exceed 250 trading units (a company who runs 10 mines is allowed to consume 2,500 containers per year at maximum. Given 0.75 kg content per container, the quantity amounts to 1.875 t / yr).*

*The total demand for products listed in Table 7 of this study, which has been reported by the mining companies to the regional government in Arnsberg, amounts to about 1.3 t / yr throughout Germany.*

- Products requiring individual approval

*Only the products listed in Table 8 of this study are suitable for the coal mining industry. The products no. 162 and 165 contain the non-combustible propellant gas*

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<sup>8</sup> Acc to Directive 67/548/EEC, substances and preparations are classified as flammable (risk phrase R10 Flammable) if their flash point is between 21 °C and 55 °C.

*HFC-134a. The manufacturers estimate that the maximum demand for these pressurised cans will not exceed 10,000 units in Germany.*

*In the mining regulations of the federal states, the use of flammable fluids with flashpoint  $\leq 55$  °C is interdicted (see also regulations of the specifications for the testing of for substances in accordance with § 4 GesBergV [43]):*

*1. According to § 13 (2) of the mining regulations for hardcoal-mining in Northrhine-Westfalia (BVOSt), the use of these products is interdicted without any exception. In Saarland, the only other federal country in Germany where hardcoal-mining is carried out, similar restrictions are given by comparable mining regulations.*

*2. Despite, according to the mining regulations for the ore-, salt-mines and rock pit and quarry-mines of Northrhine-Westfalia (BVOESSE), an exception includes use of OCF.*

The statement concludes with the following remarks.

*The application of OCF's in hardcoal-mines serves for aims of safety in mines concerning fire- and explosion-protection: The efficiency of aimed sucking of mine-gas via drilling-holes is supported by annulus space sealing. On one hand, the influx of mine-gas into the airflow of mine-ventilation out of abandoned drilling-holes by damming of these bore-holes is prevented. On the other hand, leakages for influx of air into the coal-seam via drilling-holes are closed, so the risk of self-ignition of the coal is reduced by that.*

*Caused by that, the dispense of an exception for further application of OCF's including non-combustionable propellant gas HFC-134a in hardcoal-mines ist still necessary without any alternative.*

### **6.3.4 Summary on mining**

In accordance with the Health Protection Regulations in Mining (GesBergV), canned OCF products need to be officially approved for use in German mining.

The use of canned OCF with flammable propellant gases is not generally prohibited in mining, but is strictly interdicted in hard coal mining. The use of substances with flashpoint  $< 55$ °C (flammable) is prohibited by law because of the high explosion risk in coal mines.

In German coal mining up to 10,000 cans of one-component PU foam are used annually. The propellant gas is non-flammable pure HFC-134a.

The used quantity of HFC-134a amounts to a maximum of 1.5 metric tons. The global warming potential (GWP) accounts for up to 1,950 t CO<sub>2</sub> equivalent<sup>9</sup>.

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<sup>9</sup> For comparison: In 1998, the global warming emissions of HFC propellant gases from canned OCF were 1.5 million t CO<sub>2</sub> equivalents in total.

#### **6.4 The only national safety standard of relevance**

The study shows that the European manufacturers needed a lot of time to develop canned PU foam without HFC containing propellants, which fulfilled the German fire protection standards for buildings. Today, all of the eight manufacturing groups represented on the German market can supply HFC-free OCF of any specification for the Building Material Class B2. Consequently, fire protection standards do no longer require the use of HFC-134a in OCF – neither inside nor outside of buildings.

While fire protection standards relate to cured foam, measures to prevent explosions are taken against flammable (extremely flammable) gases that are released from the can when used. The German legislation on health and safety at the workplace regulates the handling of explosible hazardous substances but does not prohibit using them. This legislation is considered an adequate standard for the safe use of OCF with extremely flammable hydrocarbon gases.

The hard coal mining industry under ground constitutes the only exemption as the use of substances with flashpoint  $< 55^{\circ}\text{C}$  (flammable) is interdicted by law in this sector. Officially approved OCF products contain incombustible propellant gas only, i.e. pure HFC-134a. The number of cans used in coal mines amounts to approx. 10,000 per year. The propellants cause climate-damaging emissions of up to 2,000 t  $\text{CO}_2$  equivalent.

The prohibition of flammable gases in coal mining is the only "national safety standard" in the meaning of annex II to EU F-Gas Regulation, which permits the use of OCF with propellant gases  $> \text{GWP } 150$  as an exception.

## 7. Special Case: Isocyanate-free OCF with HFC-134a

The 30<sup>th</sup> Adaptation of the EU-Directive 67/548/EED on classification, packaging and labelling of dangerous substances to technological progress (ATP) in the member states [46] has already been published on 15<sup>th</sup> September 2008. According to Annex 1, Methylene Diphenyl Diisocyanate (MDI) is classified in category 3 of carcinogenic substances (Carc. Cat 3). The package must be labelled R40 "Suspected of causing cancer" if the concentration of MDI is higher than 1%.

However, with coming into effect of the EC-GHS regulation (No. 1272/2008) the Annex I of the EC directive 67/548/ECC was reversed to 20<sup>th</sup> January 2009. This is why the legal position of the 30<sup>th</sup> ATP seems not clear. The former legal classifications has been taken as table 3.2 to Annex VI of the EC-GHS regulation but the changes of the 30<sup>th</sup> ATP have not been considered. The European Commission has informed that they will include the contents of the 30<sup>th</sup> and 31<sup>st</sup> ATP in the first half year 2009 in line with a first adaptation regulation to Annex VI of the EC-GHS regulation. Thus, the new classification of MDI will be legal mandatory after admission to Annex VI of the EC-GHS regulation.

Source: Announcement of the BMAS, 6<sup>th</sup> February 2009 – IIIb3 -35122 -

### 7.1 Self-service ban on isocyanate containing foam Admission of the 30<sup>th</sup> ATP to Annex VI of the GHS regulation

When applying commercially available OCF, the reactive isocyanates do not completely polymerize so that the concentration of 1% MDI (free isocyanates) is always exceeded. Thus, all OCF cans have to carry the label R40.

In Germany, the Chemical Restriction Regulation (§ 3 and § 4) states that preparations carrying the label R 40 must not be sold in retail by self-service<sup>10</sup> [47] in order to protect the amateur customer from health hazards. This means that a self-service ban for commercially available OCF will come into effect. Therefore, the sale of these products in hardware stores (do-it-yourself-stores) according to the common practice will not be possible any more. The manufacturers expect their products to be presented in show cases and are worried about a loss in revenue due to that regulation. Possible losses will affect in particular the manufacturers selling most of their products in hardware stores.

Several years ago, some big European manufacturers developed canned OCF with less than 1% fugitive isocyanates on application ("isocyanate-free") in order to satisfy the demand from Swedish construction firms who were trying to avoid regular health checks of their employees, which were required in case the employees are exposed to isocyanates. [48] Rathor generated foam whose prepolymer contains relatively low amounts of monomer isocyanates so that more than 99% of the isocyanates are no longer reactive and thus no longer toxic after release from the can. However, these OCF products were hardly sold in Germany as their price was four times higher than the regular price.

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<sup>10</sup> Basically the ban on self-service already applies to preparations with the label F+ (extremely flammable). According to prevailing interpretation of the exemptions in § 3 (4) OCF with F+ is excluded from the self-service ban. We thank Dr Peter Geboes from Soudal and Dr Wolfram Schindler from Wacker Chemie for the clarification of these facts.



Another way of manufacturing isocyanate-free foam was first found by Soudal. By now, Rathor and other manufacturers also follow this method which is called "silane based" as it is based on a new type of prepolymer linking to silane. The prepolymer (basically polyurethane) does no longer contain reactive groups of isocyanate but contains silane end groups<sup>11</sup>. When exposed to humid air and suitable catalysts, the silane-terminated prepolymers cross-link after release from the can and start the foam reaction. [50] The polymerisation does not release CO<sub>2</sub> so that the can must contain more propellant gas than before.

## 7.2 Isocyanate-free OCF is only available with HFC-134a

The first and to date unique silane based OCF has been available on the European market since the end of 2004 and is called Soudafoam SMX by the Belgian manufacturer Soudal. However, only the isocyanate-free foam of Building Material Class B3 contains a propellant gas mixture of GWP < 150 whereas the isocyanate-free product of Building Material Class B2 required in Germany still uses a propellant with HFC-134a (GWP > 150). [51]

Provided that until the self-service ban on isocyanate containing OCF no isocyanate-free foam without HFC-134a will be launched to the market, the following situation exists in German self-service stores:

- The current B2 foams contain propellants without HFC-134a but contain also isocyanates and, thus, need to be labelled R 40. The sale of these products can continue, but these products are no longer allowed to be sold openly in hardware stores.
- The new silane based B2 foam is isocyanate-free and does not need an R 40 label, but its propellant gas mixture contains HFC-134a. According to F-gas Regulation it must not be sold at all, not even outside of hardware stores<sup>12</sup>.

This conflict is not wanted for safety and occupational health concerns. It should be solved soon by manufacturers who place isocyanate-free OCF (B2) with propellants of GWP < 150 on the German market. This process is reported to go on with good prospects.

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<sup>11</sup> For this purpose, chemical industry has developed new silanes ( $\alpha$ -silanes). [49]

<sup>12</sup> Regarding this conflict situation starting in June 2009, the manufacturer Soudal refers to the exemption clause in Annex II to F-gas Regulation which tolerates the use of HFC-134a if national safety standards cannot be met otherwise. Acc to Soudal, the basic national fire protection standard (Building Material Class B2) cannot be met by isocyanate-free OCF without the use of HFC-134a. As the law requires the use of isocyanate-free foam for health reasons, propellant gases containing HFC-134a (GWP > 150) should be legalized for this purpose by exception [51].

## Annex Emissions Estimation for the Federal Environmental Agency

### 1. The HFC emissions resulting from the application of foams

So far, the emission data for the Federal Environmental Agency (UBA) are obtained by interviewing selected experts. They estimate both the number of cans annually sold in Germany and the average HFC contents per can (134a und 152a). The multiplication of the number of cans with their HFC content results in the total quantity of sold HFC. As only a short period of time passes between sale and application and the fact that HFC-134a is almost completely released within the same year, the sales quantity of HFCs and the HFC emissions are equated for the specific year [52].

The estimation by one or two experts became more difficult the quicker (1) the share of HFCs compared to other gases in the can decreased, (2) the wider that share varies from one manufacturer to the other, (3) the more cans without HFCs were placed on the market, and (4) the more frequently the relation 134a to 152a changed.

From 2007/2008 onwards, the estimation of annual HFC emissions has become even more difficult. The quantities per can are small, particularly in case of HFC-134a, and vary between manufacturers and foam types. An overview of the details of the market therefore is rather uncertain.

#### 1.1 A new approach based on of PDR data

By using the PDR, we developed a suitable method to estimate the emissions more precisely and more certain than existing systems, especially for future years. In addition, the new system can be used for monitoring the compliance with the F-Gas Regulation.

The PDR<sup>13</sup> Recycling GmbH + Co KG recycles used OCF cans on behalf of the shareholders that is to say the OCF manufacturers featuring the German market. The manufacturers fund the system by labels which they buy from the PDR to attach them to their cans. The PDR gains the remaining propellant gas from the returned cans and processes it for re-utilization by the manufacturers (trade mark TRIGAS). The composition of the gas extracted from used cans is regularly analysed (ca 100 samples per year). Thus, important data for the estimation of emissions are available at PDR.

1. The number of OCF cans sold in Germany per calendar year. This number is known from the number of tokens<sup>14</sup> sold. The PDR specifies the average volume of a can at 600 ml.

2. The average quantity of gas mixture per can amounts to 100 grams.

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<sup>13</sup> PDR originally was an abbreviation for "Polyurethan-Dosen-Recycling". The company was established 1993 in North Bavaria (Thurnau) by the leading OCF manufacturers of the German market in order to optimise their waste management.

<sup>14</sup> A small part of the cans on the German market does not originate from PDR share holders and, consequently, is not labelled. The subsequently used annual numbers of units communicated by the PDF include the non-labelled cans – based on own estimation by PDR.

3. The time period between sale and return of the can: Based on the number of tokens sold, they found that on the average a period of nine months (normal distribution) passes by between the delivery of the tokens and the return of used cans.

4. The return quota (returned vs. sold tokens): It is both sufficiently high and sufficiently representative to allow extrapolation of the composition of the gas from returned cans to the composition of gases of the cans sold in total nine months before. Accepting some uncertainty, the gas mixture measured in year n can be considered equal to the the gas mixture of the cans sold in the previous year n-1.

5. HFC-split: The shares of HFC-134a, HFC-152a and hydrocarbons in the recycled gas mixture are determined within regular measurements and refer to the gas mixtures used in specific years.

The PDR communicated the following shares of HFCs (average) in the gas mixture in mass percent (remain: hydrocarbon gas) [53]:

Measurements 2003 (year of sale 2002): HFC-134a: 26.7 %/HFC-152a: 6.8 %.

Measurements 2007 (year of sale 2006): HFC-134a: 12.6 %/HFC-152a: 1.9 %.

Measurements 2008 (year of sale 2007): HFC-134a: 17.9 %/HFC-152a: 0.9 %.

*The mass percentages of the two HFC types in the gas mixture decreased between 2002 and 2006 from 33.5% to 14.5%. Surprisingly, the share of HFC-134a in the gas mixture increased once more in the measuring year 2008 compared to 2007. The PDR considers this trend as temporary increase due to clearing of the stock and final sale of cans containing HFC-134a prior to the ban of these products in mid- 2008 [54]. In addition to that, an increase of the market share of Mega foam was observed as well which had been produced with HFC-134a for a very long time.*

## 1.2 Emissions from applications in 2002-2007

Domestic HFC application emissions in the three mentioned years of sale (for simplicity the 2003-2005 period is excluded) result from multiplication of three factors such as (1) the total number of cans sold, (2) the propellant gas mixtures per can in grams, and (3) the mass percentage of HFC-134a or HFC-152a. The calculation and the results are shown in Table 9.

| Year        | Cans in total (600 ml*) | Propellant mixture per Can | Propellant Quantity | Mass-% 134a | Mass-% 152a | Emission 134a | Emission 152a |
|-------------|-------------------------|----------------------------|---------------------|-------------|-------------|---------------|---------------|
| <b>2002</b> | 22.1 mn.                | 100 g                      | 2,210 t             | 26.7        | 6,8         | 590 t         | 151 t         |
| <b>2006</b> | 24.6 mn.                | 100 g                      | 2,460 t             | 12.6        | 1,9         | 309 t         | 47 t          |
| <b>2007</b> | 25.2 mn.                | 100 g                      | 2,520 t             | 17.9        | 0,9         | 451 t         | 23 t          |

\* PDR does not use the standard volume of 750 ml, but their own volume of 600 ml on average.

It is shown that the emissions of HFC-134a decreased less than those of HFC-152a in the time period from 2002 to 2006. This is in accordance with reports from manufacturers saying that HFC-134a is the better propellant which cannot be replaced as easily as HFC-152a [6].

*We compare the mass percentages of the first half year in 2008 with those measured the second half year 2008 in order to point out the recent trend:*

*1. half year: 18.9% HFC-134a and 1.0% HFC-152a.*

*2. half year (July- November): 16.2% HFC-134a and 0.8% HFC-152a.*

*The second half year shows a decrease of HFC-134a by 2.7% compared to the first half year. This means that within the year 2007 the emissions of HFC-134a decreased slowly.*

### **1.3 Forecast of application emissions 2010 and 2020**

Although the emissions from the application of HFC decreased in the second half year 2007, the level required by the F-Gas Regulation had not been reached yet by mid 2008. The reformulation for the production of some special foams was difficult so that only at the end of 2008 (cf. Table 6), the GWP of all propellant gas mixtures in cans sold in Germany was below 150.

Currently, two types of foams are offered by some manufacturers which contain shares of HFC-134a or HFC-152a (both in mixtures < 150 GWP): Mega foam and fire protection foam. Based on the market shares of these specific types (Table 5) and the market shares of their manufacturers (Table 3), it can be estimated that approx. 0.5 mn cans of Mega foam containing 152a and 0.2 mn cans containing 134a are sold per year. Assuming that about 15 g of HFC-134a and 60 g of HFC-152a are contained in one 750 ml can, the overall emissions from their application amount to 30 t of HFC-152a and 10.5 t of HFC-134a. In addition, emissions from foams used in the mining industry amount to ca 1.5 t HFC-134a. These quantities cannot be verified by comparing them to the PDR data before September 2009.

The present amount of emissions from application which amount to 30 t of HFC-152a and 12 t of HFC-134a can be considered to be a result of the F-Gas Regulation. Until 2010, no major changes are expected and will then constitute the annual quantity of emissions.

We assume that all manufacturers featuring the German market will be able to produce their foams without using any HFC by 2020. OCF used in the mining industry will continue to cause emissions which currently amount to 1.5 t of HFC-134a. The demand for OCF in mining, however, is expected to rather decrease in Germany, so that this amount of emissions will be the maximum.

To check on these data, s. Table 11 at the end of this annex which gives an overview.

## 2. HFC emissions on filling

Emissions from filling result from the production of OCF in three German filling plants. The way to estimate these emissions differs from the way of estimating the emissions from application. At first, the loss of gas during the filling process has to be assessed.

### 2.1 Emission factor (EF) of filling

The EF of filling depends on the way of filling the gas into the OCF cans.

*As soon as the non-fugitive components have been filled into the open can, the valve-cap is put on. The different liquid propellant gases are consecutively filled through the valve into the cans. After each filling, some liquid gas is left in the valve tube which shows a volume of approx. 0.4 ml. This quantum of gas is released into the air. In this way, approx. 0.5 g of HFC-134a (density 1.2) are set free at each filling, no matter if a small or high dose of gas is filled, HFC-152a has not more been filled any more in Germany for several years.*

The emission factor of filling amounts to 0.5 g of HFC-134a per can.

### 2.2 Filling emissions in Germany 2006-2008

The quantity of filling emissions of HFC-134a can be calculated by multiplying the total number of filled cans and the emission factor.

The number of filled cans containing HFC-134a was given by the three manufacturers in Germany. Additionally, they were asked about the annual use of HFC-134a, as these data are also subject to international reporting regulations.

The number of cans containing gas mixtures with HFC-134a amounted to 12% of the total number of domestically filled cans in 2006 (4.2 mn) on average of the three German manufacturers. This quantity has only slightly decreased to 11% in 2008 because of the high export ration of the German manufacturers. Cans for the domestic market contain only some 15 g of HFC-134a, in order to remain below the maximum GWP of 150. However, in cans for sale outside of the EU, the amount of HFC-134a is higher. Consequently, the average HFC per can amounts to some 40 g in 2008 (45 g in 2006 and 2007).

Given the emission factor (0.5 g/can), the HFC filling emissions do not depend on the HFC content of the cans but only on the number of filled cans.

| Year        | Cans in total | Share of 134a cans | 134a per can | Cans with 134a | Consumption | EF filling | Filling emissions |
|-------------|---------------|--------------------|--------------|----------------|-------------|------------|-------------------|
| <b>2006</b> | 35 mn         | 12%                | 45 g         | 4.2 mn         | 189 t       | 0.5 g      | 2.1 t             |
| <b>2007</b> | 35 mn         | <12%               | 45 g         | 4.0 mn         | 170 t       | 0.5 g      | 2.0t              |
| <b>2008</b> | 35 mn         | 11%                | 40 g         | 3.85 mn        | 154 t       | 0.5 g      | 1.92 t            |

The calculated filling emissions in the period from 2006 to 2008 result from multiplication of the number of units and the emission factor of filling (0.5 g) in Table 10 (last column) as well as the calculated quantity of HFC (see section 2.3).

### 2.3 Annual Consumption of HFC for Filling

In the 2006-2008 period, not only the number of cans with HFCs but also the average charge of HFC in these cans has decreased from 45 g (2006) to 40 g (2008) [6].

The annual consumption of HFCs for filling during the three mentioned years can be calculated by multiplication of (1) the number of all HFC containing cans and (2) the specific mean charge of HFC-134a in these cans. These figures are shown in Table 10 as well as the filling emissions.

The consumption of HFCs has decreased between 2006 and 2008 from 189 t to 154 t. The calculated value for 2006 (189 t) and 2007 (170 t) are largely conform to the quantity given to the Federal Board of Statistics by the manufacturers (191 t and 168 t). The results of the official survey for 2008 are not available before the end of 2009, so that they cannot be used to check on the estimated values<sup>15</sup>.

### 2.4 Projection of the filling emissions in 2010 and 2020

At latest from the end of 2008 onwards, filling of HFC-134a in OCF cans in Germany will meet the F-Gas Regulation. Until 2010, we do not anticipate substantial changes in the quantity used of HFC-134a and in the number of HFC-134a containing cans. However, the shares of HFC-134a contained in the cans for sale outside of the EU might be brought in line with the HFC charges of the cans sold in the EU. Therefore, the use of HFC might continue to decrease. However, this will not apply to the filling emissions because the number of units remains the same.

We assume that the German manufacturers will be able to formulate all of their products without using HFCs by 2020. Only products for use in the national and international mining industry will continue to contain HFCs as high shares of HFC-134a are required (at least 100 grams per 600 ml can). We estimate that maximum number of 50,000 units will be filled per year for use in the mining industry so that the filling emissions by 2020 might amount to about 25 kg and the annual losses of HFC-134a might be in the range of 5 tonnes.

## 3. Overview: Emissions Forecast for 2010 and 2020

Table 11 summarises all of the emissions mentioned in the study. Metric quantities are also shown as quantities of CO<sub>2</sub> equivalents.

|             | Application emissions |                        |          |                        | Filling emissions |                        | Total                  |
|-------------|-----------------------|------------------------|----------|------------------------|-------------------|------------------------|------------------------|
|             | HFC-152a              |                        | HFC-134a |                        | HFC-134a*         |                        | HFCs                   |
| Year        | Tonnes                | t CO <sub>2</sub> equ. | Tonnes   | t CO <sub>2</sub> equ. | Tonnes            | t CO <sub>2</sub> equ. | t CO <sub>2</sub> equ. |
| <b>2010</b> | 30                    | 4,200                  | 12       | 15,600                 | 1.0 t             | 1.300                  | 21,100                 |
| <b>2020</b> | -                     |                        | 1.5      | 1,950                  | 0.025 t           | 32.5                   | 1,980                  |

\* HFC-152a has not been used in Germany for several years.

<sup>15</sup> In the future, the use of HFC could be established completely by means of the annual survey of the Federal Board of Statistics acc. to the Law on Environmental Statistics (UStatG), taking into account that they are published too late for the for the national F-gas inventory, which will be closed in August. The number of HFC filled units, which determines the filling emissions, is not surveyed officially. Cooperation of the German manufacturers and the Federal Environmental Agency is vital.

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