



Technical Bulletin

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Hydrofluoric Acid

Supporting materials:

- Gradient Final Report (SAE CRP)
- Ineris Study – proprietary, but summarized in Gradient
- Hughes Associates – proprietary, but summarized in Gradient

Summary of concerns expressed in the media

Off and on highly critical articles on HFO-1234yf are published, particularly in German media. They claim that dangerous amounts of hydrofluoric acid (HF) can be formed in a car accident with a fire. Here are the facts about the conditions under which HF might be formed.

Conditions under which HF might be formed

HF can be formed when fluorocarbons are exposed to surfaces at very high temperatures (700°C) and when combusting or burning at even higher temperatures. This is true for all fluorocarbons, including R-134a and R-12, which have been used safely in mobile air conditioning (MAC) systems for more than 50 years.

If combusted completely, the theoretical HF yield of one kg of HFO-1234yf is 11 percent less than one kg of R-134a. HF formation has been tested in laboratory conditions by the French research institute Ineris and documented in the SAE CRP1234 (Society of Automotive Engineers, Cooperative Research Project) final report. SAE has decided to keep the Ineris attachments confidential. However, the conclusions of the investigations are part of the final report.

The formation of HF is strongly dependent on surface temperature, with temperatures below 550 °C producing negligible levels of HF (see page 66, SAE final report). The proportion of HF is dependent on the hot surface area size and temperature. Both R-134a and HFO-1234yf produce the same order of magnitude amount of HF under similar conditions (see page 57 and Table 3-4, page 69, SAE final report).

HF formation was also tested in under hood and interior vehicle tests by Hughes Associates and also documented in the SAE CRP1234 final report. Again, SAE has chosen to keep the Hughes attachments confidential. The conclusions of the investigation, however, are part of the final report.

When Hughes Associates assessed the situation in vehicle interiors they used butane lighters as ignition sources. The entire charge of refrigerant was then released into the passenger compartment. A flame was produced from a butane lighter at the driver face location. Under these conditions the HF concentration rose to a maximum of 35 ppm (parts per million), which is below the Acute Exposure Guideline level 2 (AEGl-2) of 95 parts per million (ppm) for ten minutes (see page 58, SAE final report).



For under hood testing, Hughes set up tests to generate HF on hot engine components and then aspirated the HF into the passenger compartment. Since HF levels were higher when the polyalkylene glycol (PAG) lubricant was present, Hughes applied a nominal oil circulation value of three percent when the oil and the refrigerant were directly sprayed onto the hot surfaces. The hot surface was a 36 cm long and 6 cm diameter steel cylinder. The test was conducted at temperatures of 450°C and 700°C. The mixture was directly applied to the hot surface from a distance of 5 cm to represent the worst possible case. In the worst case, the HF aspirated from the engine compartment into the passenger compartment measured 49.6 ppm. This is well below the AEGL 2 threshold of 95 ppm. In the engine compartment a level of 118.8 ppm of HF was reached (see page 60, SAE final report).

Amount of HF that can be formed theoretically from an average charge of HFO-1234yf

The theoretical maximum is of little relevance since the actual HF conversion is dependent on many other uncontrollable factors. It is generally acknowledged in the chemical processing industry that it is nearly impossible to achieve full conversion of a fluorocarbon to HF. HFO-1234yf is released as a gas that is free to flow around and out of the engine compartment. That's why the actual amounts of refrigerant that may pass in close enough proximity to hot surfaces to begin thermal decomposition into HF is very small.

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The risk of HF formation under real-life conditions

It is extremely difficult to measure concentrations under real-life conditions, because conditions vary according to a multitude of external factors, such as general weather conditions, wind, outside temperature, rain and others. In the context of the SAE Risk Assessment, HF concentrations have been measured using real car models. These measurements are part of the final report, and are summarized in the sections describing the experimental testing at Exponent (page 53, SAE final report) and Hughes Associates Inc. (pages 54, SAE final report).

HF in a car crash without fire

It is theoretically possible that HF is formed without a fire. In reality, the formation is dependent on so many circumstances that the likelihood is extremely low. The Fault Tree Analysis of the CRP looked at the following possibilities and evaluated them as extremely unlikely:

- thermal decomposition due to contact with exhaust manifolds and turbochargers in the engine
- fires emanating from sources other than the refrigerant
- fires potentially triggered by the refrigerant (see Section 4.5, page 70, SAE final report).





HF concentration in case of a car fire

The Gradient report (Table 2-5, page 40, SAE final report) explains that HF concentration is dependent on many mitigating variables such as wind, rain, charge size and the release point of the refrigerant. The expected concentrations are on the same order of magnitude as those currently produced by R-134a or historically by R-12; and, as far as we know, there are no records of HF concentrations in car accidents produced from either R-134a or R-12. HF is an irritant and easy to detect at levels of less than 5 ppm, far below the acute exposure limits.

There are thousands of poisonous substances in fires that occur in buildings, airplanes, cars, trains and outdoors. The most relevant ones are carbon monoxide, hydrocyanic acid and substances that irritate the lungs (see Daunderer, Klinische Toxikologie "Brandgase" 143. Erg. Lfg 02/00 p1). Materials such as wool and plastics that are often used in offices, factories, cars and airplanes can release both carbon monoxide and hydrocyanic acid. The theoretical impact of 600 grams of refrigerant in an auto air conditioning system under the hood pales in comparison to the many hundreds of kilograms of plastics, rubber, and foam used in the construction of a passenger vehicle.

Passenger trapped in a car compartment during a car fire

HF can only be formed when in contact with surfaces at very high temperatures or when combusting. Tests have shown that these circumstances do not occur in the passenger compartment, but could only possibly occur under the hood. The risk assessment shows that HF concentrations in the passenger compartment will remain below the AEGL-2 limit (exposure level that does not result in irreversible damage) and during worst case testing with direct aspiration into the passenger compartment, reached a value of 49.6 ppm (see page 60, SAE final report). Only in exceptional cases might this limit be exceeded; the expected likelihood, however, is a factor 10,000 times lower than that of one being in a plane accident. (Table 4-4, page 90, SAE final report).

In case of the refrigerant catching fire, HF will quickly dissolve in water and be washed out. In view of the large quantities of water used in extinguishing a car fire, the concentration levels will be insignificant. HF further reacts with minerals and the road surface to form naturally occurring salts.

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Tunnels and underground garages

Tunnels and Parking Garages are special structures that must meet stringent safety requirements. The ventilation system must be engineered and constructed to avoid the buildup of noxious carbon monoxide and other combustion products, as well as to handle eventualities such as car fires. The SAE risk assessment considered these structures and concluded that based on the mandatory safety precautions they do not warrant additional assessment.



Flammability

Supporting Materials:

- Gradient SAE Final
- Honeywell (Spatz & Minor – SAE 2009)
- Ineris Study – proprietary, but summarized in Gradient
- Hughes Associates – proprietary, but summarized in Gradient
- Chilworth Laboratories Ltd.
- EU CLP Reference tests
- Monforte and Caretto. Safety Issues in the Application of a Flammable Refrigerant Gas in MAC Systems: The OEM Perspective. SAE 2009

Flammability tests under real-life conditions

Under the EU CLP Regulation (Classification, Labelling and Packaging), a substance must be tested for flammability using a standard OECD (Organization for Economic Cooperation and Development) test. Based on the test results, the Lower and Upper Flammability Limits have been determined and HFO-1234yf is classified as Flammable Category 1. Moreover, extensive additional testing has been conducted by Chilworth Laboratories addressing several critical parameters such as minimum ignition energy, energy of combustion and flame propagation. Based on these parameters, HFO-1234yf has proven to be a very mildly flammable gas compared to propane or gasoline. Under the CRP computer modelling, laboratory testing and in-vehicle testing have been conducted. At least one automotive OEM has conducted a real crash test with no refrigerant ignition.

Ineris performed contract work to determine potential electrical ignition sources in the passenger compartment (Monforte and Caretto, 2009). Based on this work, the SAE CRP concluded the most credible ignition sources are high powered battery shorts (greater than 50 amps), matches, and fires started by other components in the vehicle that are unrelated to the refrigerant.

Ineris and Hughes Associates performed ignition testing on hot cylindrical bodies with flow and geometry variables found in the engine compartment. Ineris found that PAG lubricant itself could be ignited by the hot body at temperatures of 400 °C. Ignition testing with HFO-1234yf alone did not ignite until the hot body was raised above 1000 °C. Investigations with HFO-1234yf and PAG lubricant at concentrations from 1-7 mass percentage lubricant lowered the geometry dependent ignition temperature of HFO-1234yf to 750 ± 50 °C (see page 51, SAE final report). This temperature was confirmed by testing at Hughes Associates, who found a single ignition at 700°C during engine compartment testing.

According to our SDS, R-1234yf has an auto-ignition temperature of 405°C. The auto-ignition temperature is the lowest temperature at which a gas spontaneously ignites in a homogeneous mixture with air. The auto-ignition temperature is measured in a laboratory set-up, where the mixture is gradually heated up. Such laboratory conditions cannot be duplicated in real-life situations, and in fact they do not represent real-life situations.

Ineris confirmed the auto-ignition of pure HFO-1234yf in the laboratory at 405°C. Upon continued investigation, Ineris found out that the ignition temperature of

... HFO-1234yf has proven to be a very mildly flammable gas compared to propane or gasoline.



pure HFO-1234yf on a hot cylindrical body to be in the order of 1050°C due to flow and geometry variables (see page 26). Investigations with PAG lubricant at concentrations from 1-7 mass percent lowered the geometry dependent ignition temperature to 750 ± 50 °C. This temperature was confirmed by testing at Hughes Associates, who found a single ignition at 700°C during an engine compartment flammability test.

Risk to Passengers

Risks for car passengers in a car using an R-1234yf A/C system

We believe that the risks associated with the use of HFO-1234yf are the same as those currently undertaken by people in the normal use of their cars today. We have shown that HFO-1234yf is difficult to ignite, produces the same amounts of HF when consumed in a fire, and produces approximately the same amount of HF when exposed to hot surfaces. However, if the blower is still intact, turning it off will prevent combustion gases from entering the passenger space.

These risks have been addressed by the SAE CRP1234. The members of the CRP risk assessment were all major vehicle OEMs, refrigerant suppliers Honeywell and DuPont, and independent consultants and institutes.

Comparison of R-1234yf risks with risks of other fluids

The SAE CRP risk assessment has found that using HFO-1234yf does not pose any additional risks above and beyond those that car drivers experience and accept today. The industry has created standards to govern the safe use and construction of heating, ventilation and air conditioning (HVAC) components in the US (SAE J639) and in Europe (ISO 13043). This has been achieved by working with government agencies and approval authorities to ensure the vehicles of tomorrow are just as safe as, or safer than the vehicles of today.

Leak into the passenger compartment

In almost all conditions, nothing will happen if the refrigerant leaks into the passenger compartment. Corrosion leaks have been shown not to generate flammable concentrations. In addition, the presence of ignition sources that are large enough to provide sufficient energy to ignite the refrigerant are exceedingly rare and would have to occur at a specific time during a potential leak scenario.

Benefits of the Fault Tree analysis

Fault Tree analysis is used in many instances to determine which events may cause risk and which events will not. While most of us do this to some degree subconsciously in our everyday lives, a true Fault Tree Analysis relies on a structured set of tools. These tools allow users to perform a rationally structured analysis to identify predominate risk scenarios.

The SAE CRP risk assessment has found that using HFO-1234yf does not pose any additional risks above and beyond those that car drivers experience and accept today.



Risk to First Responders

Risks for well-intentioned bystanders who try to rescue passengers from a burning car

The amount of HF generated in a collision is not expected to be any worse than the other toxic gases produced by a burning car, such as carbon monoxide and cyanide gas. HF, by itself, is an extremely repulsive gas that a person cannot tolerate even in concentrations below the AEGL-2 level. This will drive well-intentioned bystanders, “Good Samaritans”, away from vehicles involved in a crash and fire. Since R-134a will produce the same irritant effect when exposed to a car fire, we expect the same behaviours and reactions as are found for bystanders today.

Difference between well-intended bystanders and professional rescue workers?

Professional rescue workers have undergone significant training to teach them how to approach many dangerous situations such as car accidents and car fires. They have been taught how to best protect themselves while working to most efficiently remove affected persons from the accident scene.

Protective equipment for emergency staff in case of a car fire

We recommend that emergency staff and professional rescue workers observe and practice their training while responding to car fires. We make information and services available to any professional organization that requests it. We will also provide additional information to ensure that professional staff has the training to

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safely respond to vehicle accidents involving HFO-1234yf. The refrigerant charge size in cars is typically less than 600 grams and it should be noted that the safety data sheet (SDS) for R-134a and in fact any other fluorocarbon contains exactly the same requirement for protective equipment.



Self-contained breathing apparatus and chemical protective suits

Our SDS prescribes breathing apparatus and chemical protective suits in case of storage fires. These could involve several tonnes of material which could be released and there is a serious risk to HF exposure at levels well above the AEGL-2 level (95 ppm). This situation is very unlikely to occur in case of a car fire and no change is indicated compared to the current situation with R-134a in the car A/C. The charge size in cars is typically less than 600 grams. It should be noted that the SDS for R-134a and in fact any other fluorocarbon contains exactly the same protective equipment requirement.

To our knowledge, no HF events have been recorded in the 50 years that fluorocarbons or chlorofluorocarbons have been used in car A/C systems.

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Risk mitigation measures to prevent HF formation

The industry has created standards to govern the safe use and construction of heating, ventilation and air conditioning (HVAC) components in the US (SAE J639) and in Europe (ISO 13043). This has been achieved by working with government agencies and approval authorities to ensure the vehicles of tomorrow are just as safe as, or safer than the vehicles of today.

The primary risk mitigation technique to protect the vehicle occupants against exposure to HF or any other gases from the engine compartment is turning off the HVAC blower in the event of an accident.

Trifluoroacetic Acid (TFA)

Supporting Resources:

- All TFA studies (EPA, Japan, US, Scientific literature)

Classification of TFA

The stable form of TFA in the environment is the trifluoroacetate ion (CF_3COO^-), which combines with counter-ions such as sodium, in seawater, or calcium or ammonium in land to form neutral salts. However, TFA is used in short for both the acid and its neutral salts.

In its 100 percent pure acid form, TFA, like most acids, is a corrosive material. In significant concentrations, not attainable through the decomposition of HFO-1234yf, it can inhibit growth of certain algae species very sensitive to TFA.

Every model of TFA rainout that we are aware of shows that even in vernal pools, there is a safety factor of at least one or more order of magnitude, even in the most liberal scenarios and assuming that all cars are equipped with HFO-1234yf.

Studies on accumulation in fresh water reserves used for drinking water

We are not aware of such specific studies. However the factor of safety noted above for vernal pools and the most sensitive algal species (not typically used for drinking water) would indicate to most people that the safety factor for drinking water is much higher.

The environmental fate of TFA

TFA appears to be resistant to biodegradation by the majority of natural or laboratory microbial systems that have been tested. However, laboratory study has shown that certain bacteria, under special conditions, can degrade TFA.

TFA and acidification

The processes of TFA transport or formation make a negligible contribution to acid rain. There is no significant addition to the acids or fluoride already present in the biosphere from natural sources. The pKa value of 100% pure TFA is 0.24, making it a much weaker acid than H₂SO₄ (pKa=-3.2).

Other uses of TFA

TFA has been used in the production of pharmaceutical and agricultural chemicals, as well as in many other specialized applications. It is used in peptide synthesis and as a solvent and catalyst in polymerization and condensation reactions, as well as in synthesis of ceramic superconductors.

Other sources of TFA

The very significant amount of natural TFA in ocean water (over 200 million tonnes, about 10,000 times more than possible from, say 20,000 tonnes of HFO- 1234yf) , has been attributed to venting from ocean floor fumaroles in scientific literature.



Naturals

Criteria for natural versus synthetic fluids

The term “natural” suggests that the fluid is the result of a natural process. In fact, so-called natural refrigerants are all produced on an industrial scale in chemical plants. Therefore the distinction is artificial and not really meaningful. It is mostly applied for marketing reasons. The term “natural” is also misleading to the extent that “natural” substances are supposed to be, or presumed to be safe. In fact most are classified as hazardous or toxic, including CO₂, hydrocarbons and ammonia.

Natural refrigerants under consideration for MAC

Both hydrocarbons and CO₂ (R-744), as well as R-152a have been considered as replacements for R-134a. All were rejected by the global auto industry for performance, cost-efficiency or safety considerations or a combination of these.

The term “natural” suggests that the fluid is the result of a natural process. In fact, so-called natural refrigerants are all produced on an industrial scale in chemical plants.

In contrast, HFO-1234yf has been thoroughly assessed by all major auto manufacturers and has been judged to be safe for use in this application.

Hydrocarbons used in Australia

Although there is some use of hydrocarbons in auto air conditioning systems in Australia, they are not used in new cars as they have not been judged safe to use in this application by any major vehicle manufacturer. In contrast, HFO-1234yf has been thoroughly assessed by all major auto manufacturers and has been judged to be safe for use in this application.

Natural fluids and SNAP approval

There are no natural fluids SNAP-approved for use in auto air conditioning. At one point in time, there was a proposed SNAP ruling on the use of CO₂ that contained conditions of use but no final rule was issued. It limited the maximum CO₂ levels that could result from a leak into the passenger cabin. Hydrocarbons blends have been specifically listed as unacceptable for use in auto air conditioning as their safety has not been adequately demonstrated.

Cost of natural fluids compared to synthetic fluids

When we discuss cost we need to look at the total cost of the system and not just the refrigerant cost. Although the cost of CO₂ is fairly low, there is a significant system cost increase for the use of CO₂ in auto air conditioning. There was one reported value by GM at an SAE meeting of \$350. Likewise, if highly flammable hydrocarbons were to be used, secondary loop systems would be required to keep this material out of the passenger compartment. This would also cause a significant increase in the cost of the system and make it less energy efficient.



Chemical industry and IP on naturals

We cannot speak for the entire chemical industry but we are not aware of any intellectual property (IP) owned by the chemical industry that has any significant impact on the use of natural refrigerants in this application.

Advantages and disadvantages of naturals

Honeywell acknowledges that under certain operating conditions and in certain applications so-called natural refrigerants can be cost-effective and efficient fluids. Several Honeywell businesses are involved in the design and maintenance of systems depending on these fluids. Honeywell is the largest supplier of air-based cooling systems in aerospace applications.

Blends that contain hydrocarbons

There are some HFC/hydrocarbon refrigerant blends that have a small percentage of hydrocarbons (<5%). They are used to replace either CFCs or HCFCs which are used with a mineral oil lubricant. Due to the small amount of hydrocarbons, these blends generally remain non-flammable even under worst case fractionation. The small amount of hydrocarbons improves the solubility of these refrigerants with the existing mineral oil lubricant so the oil in these systems does not require changing during the retrofit process.

Life Cycle Climate Performance (LCCP)

Supporting Resources:

- LCCP presentations, SAE website
- Atmospheric Lifetime CO₂
- Papasavva Study
- Green MAC website
- CO₂ production processes (LCA)

Better performance of R-1234yf compared to R-744

A number of studies have shown the superior LCCP performance of HFO-1234yf over R-744. One of these studies was published in a peer reviewed journal, "Environmental Progress and Sustainable Energy" in 2011 by Stella Papasavva and Stephen O. Anderson. This publication used the publicly available GREENMAC calculation tool. It showed a 7 percent improvement for HFO-1234yf in reduced CO₂ emissions over R-134a. In contrast to that, the CO₂ emissions were increased by 2 percent with R-744. In addition to this study, detailed presentations by the Japanese Automobile Manufacturers Association (JAMA) and Hyundai/Kia also showed significantly lower CO₂ emissions for HFO-1234yf versus R-744.

A number of studies have shown the superior LCCP performance of HFO-1234yf over R-744.

Assumptions for the LCCP study (driving cycle, CoP, Coefficient of Performance or efficiency, fuel consumption, climate conditions)

These studies have followed the Green-Mac-LCCP® model. It is a model that has been peer-reviewed and accepted as global standard by more than 50 experts represented by 25 companies and other organizations. All the assumptions were clearly defined in the analyses and identified in the publications and presentations:

<http://www.epa.gov/cpd/mac/compare.htm>

The model itself, as well as the publication noted above, have been peer-reviewed.

The analyses performed to date have centred on the car cooling application as this is the system used in almost all vehicles today. There are only a very small number of heat pumps today that provide heat as well as cooling. If these systems become more popular, the models would likely be modified to include heating as well as cooling.

Currently most LCCP calculations conducted have centred on the most popular vehicle types, gasoline or diesel-powered. If and when other vehicle types such as hybrids or electric vehicles become more popular, the calculation methods will probably be extended to these as well.



Intellectual Property (IP)

Honeywell's patents and jurisdictions

Honeywell has filed a large number of patents in all major regions of the world. These patents are related to both the process for making HFO-1234yf as well as the use of HFO-1234yf for mobile air conditioning (MAC) and other applications.

Honeywell has filed a large number of patents in all major regions of the world. These patents are related to both the process for making HFO-1234yf as well as the use of HFO-1234yf for mobile air conditioning (MAC) and other applications. Some of these patents have already been issued and others have been filed but have not yet been issued.

There have been multiple challenges from both competitors as well as auto OEM's. They have challenged these patents based on a number of different arguments.

Rejection of the EU Patent authority of one of Honeywell's patents

We have filed a number of patents in Europe and one was recently rejected based on a legal technicality. We have already appealed the decision and are confident that we will win the appeal.

Question of licensing to other producers

We have not ruled out the possibility of licensing some of our patents, but will only do so if the value we receive is appropriate. Innovation requires steady and significant financial investment to support the years of research and development that are required to bring successful new products to market. To reward and encourage innovation, intellectual property must be protected.

ACEA's view that Honeywell intentionally withheld its IP position on HFO-1234yf

We believe that this argument is baseless. We made it very clear on numerous occasions that Honeywell had applied for patents on this product. All of our patents and many of the applications can be easily found in public databases by anyone who searches this information. In addition we actually issued a press release before one of our European patents issued.



Supply Issue and status of plant in China

Which production facilities are currently available, who operates each of them, and what is the capacity of each?

We do not disclose the capacities of our production facilities and supply agreements. We are currently producing HFO-1234yf in Buffalo, New York and will be receiving material from a plant in China later this year.

Production capacity and shipments to date

We consider this information confidential.

Antitrust

Jurisdictions in which there are currently investigations on anti-trust grounds

There are antitrust inquiries in Europe, the United States and South Korea.

An allegation that Honeywell is abusing a dominant position to extract unreasonably high prices for HFO-1234yf

This is not an allegation currently under investigation. Honeywell and DuPont each spent tens of millions of dollars to develop and commercialize HFO-1234yf, an innovative and new product. As is common, Honeywell and DuPont have secured IP protection for the fruits of these investments. Further, no one has made HFO-1234yf on a large commercial scale yet and it is significantly more complex and expensive to manufacture than the existing product, R-134a. However, we do not disclose prices or production cost for HFO-1234yf as we consider this information sensitive and confidential.

Also, we do not share the view that HFO-1234yf is a de facto standard mandated under the EU law. There is no standard that requires the use of HFO-1234yf. The EU Directive, adopted in 2006, only requires a gradual phase-in of refrigerants for automotive air conditioning with a lower global warming potential (GWP) from 2011 to 2017. There are several competing alternatives that meet these requirements and our competitors continue to invest in alternative solutions. Many car manufacturers have selected HFO-1234yf because it offers what Honeywell believes to be the most cost-effective and efficient low GWP refrigerant for automotive air-conditioning.

In the United States, there is no mandate for the use of a low GWP refrigerant in cars. However, in 2010, the U.S. government announced rules requiring that auto manufacturers meet certain new emissions and greenhouse gas requirements with their fleets. One of the many ways they can earn credits to meet these requirements is through use of a low GWP refrigerant in their automobiles. Several auto manufacturers have indicated that they believe use of a low GWP refrigerant is among the most cost effective ways of meeting such U.S. emissions and greenhouse gas requirements.

There is no standard that requires the use of HFO-1234yf. The EU Directive, adopted in 2006, only requires a gradual phase-in of refrigerants for automotive air conditioning with a lower global warming potential (GWP) from 2011 to 2017.

Possible consequences if authorities take the view that Honeywell is violating antitrust rules

We strongly believe that Honeywell's highly innovative efforts to identify, develop, and commercialize HFO-1234yf are pro-competitive and will be found so by the investigating agencies. Honeywell has at all times been clear that HFO-1234yf is a proprietary product on which it holds valid IP. There is no basis for forced licensing or any other remedy. Honeywell believes that its actions are fully compliant with competition laws and sees no basis to do so.

Negotiations with OEMs

Honeywell always has been clear that HFO-1234yf is a proprietary, IP-protected product, and believes that auto manufacturers have selected HFO-1234yf because it is a cost-effective low GWP refrigerant. Honeywell is working closely with its very sophisticated OEM customers to meet their needs on a timely basis as the auto manufacturers adjust plans for new models and their use of HFO-1234yf. Our negotiations with customers have been straightforward and professional.



Honeywell has consistently communicated with auto manufacturers that it would need their commitments to buy HFO-1234yf at least two years before a commercial scale plant could be built in order to supply industry demand. GM was the first auto manufacturer to sign a contract for HFO-1234yf in July 2010; other auto manufacturers took much longer to determine if and at what volume they might use the product. Thus, a delay in the building of plants, given such uncertain demand, is understandable. As with any entirely new, never before commercially produced product, there also can be delays in manufacturing start-up. Moreover, regulatory approvals, in part because of competitors and other efforts initially to create some delay, also were pushed back in time.

These tests have followed internationally accepted OECD guidelines. Based on the results of these studies, HFO-1234yf is not toxic.

Toxicology – REACH- CoRAP

Introduction

Honeywell takes safety very seriously. During product development the company submits new substances to extensive testing to determine if and under what conditions a substance can be used safely. The goal of toxicity testing is to evaluate the potential hazards of a compound and determine the acceptable exposure levels which will have no lasting adverse or irreversible impact on humans and the environment. This often involves and sometimes requires animal testing. The general approach is to use exposure levels that are sufficiently high to detect any adverse effects. These levels provide guidance on acceptable exposure concentrations using generally accepted safety margins. So it is not surprising when not all test animals survive certain toxicity tests. A comparison with R-134a shows no substantial difference between the toxicity end-points for this product and R-1234yf. All regulatory authorities have accepted that. These tests have followed internationally accepted OECD guidelines. Based on the results of these studies, HFO-1234yf is not toxic.

Acute and Chronic Toxicity

It is important to make a distinction between acute and chronic (long-term) toxicity. Acute toxicity evaluates the hazard following a one-time exposure to high levels of a compound. It is relevant in cases of incidental or accidental exposure to a substance. This could involve people who have not been trained or are not expected to be exposed to the substance under normally foreseeable conditions of use. The most common reference value used under these instances is the Emergency Response Planning Guidelines (ERPG) which focuses on the acceptable levels that do not result in irreversible or lasting damage. The ERP is also used in Europe. The



ERPG-2 for HFO-1234yf is 24,000 parts per million (ppm) which equals 2.4 percent of the substance. There was no acute toxicity observed, even at concentrations as high as 40 percent.

Chronic toxicity focuses on evaluating the hazard of a compound following repeated exposure to it. These data are used to determine levels which would not result in irreversible or lasting injury to people who have been trained in handling the substance under foreseeable conditions of use. This is usually expressed as the 8-hour Time Weighted Average (TWA) concentration. The TWA for HFO-1234yf is currently set at 500 ppm, which is a factor 25 times above the generally observed maximum concentration in manufacturing plants, which has been measured at less than 20 ppm, and typically less than 1 ppm.

The testing of HFO-1234yf

Honeywell has contracted toxicology studies with leading institutes that follow Good Laboratory Practices (GLP). These institutes are based in the US, Europe, Japan and China and provide specific expertise and world class capabilities. All the contracted institutes have performed the requested tests under GLP and internationally recognized protocols, in particular the OECD guidelines. The test results have been submitted for review to the national competent authorities.

Legal Requirements

Most countries have adopted legislation that identifies and controls the hazards of the use of chemical substances. The European Union has the REACH regulation (Registration, Evaluation and Authorisation of Chemical Substances, EU Regulation 1907/2006) and the CLP Regulation (Classification, Labelling and Packaging of chemical substances, EU Regulation 1272/2008). The USA has its Toxic Substances Control Act (TSCA). These laws require producers and importers to prove if and under what circumstances chemical substances can be used safely. They also require them to provide adequate information to users to prevent unsafe use

conditions. Under these laws, companies must conduct tests to determine the potential hazards associated with the substances they produce and sell. Companies also need to assess the risks associated with the intended use of their products. They are also required to communicate the risks to the intended users, both via the product labels on the packaging and via so-called Material Safety Data Sheets (MSDSs). These MSDSs summarize the hazards and the risk control measures, especially for professional users and emergency responders such as fire-fighters, physicians and other rescue organizations. The MSDS can be compared to the package insert in any pharmaceutical product sold to consumers. It lists all possible risks and provides guidance to avoid complications or unwanted side effects.

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Interpreting Toxicity Test Results

The interpretation of toxicity test reports requires very specific expertise. Toxicologists undertake comprehensive university-level training, usually with advanced degrees, as well as on-going, on-the-job training that enables them to design and interpret the tests assessing the hazards associated with a specific substance. Usually the results of studies that have a significant relevance for society are published in peer-reviewed authoritative publications. One critical element in the assessment of results is the existence of generally accepted protocols and the availability of reliable reference data and results. Especially in the case of chronic, long-term exposure, it is often very difficult to attribute a certain observed effect to a particular substance. This is the reason why Honeywell appealed the decision of the European Chemicals Agency (EChA) requiring a 90-day test in rabbits, noting that the results of such a study, in the absence of a generally accepted protocol and the lack of a body of reference material, (such tests have not been conducted in 20 years) would be meaningless. This view is shared and supported by leading toxicologists. Since rabbits are extremely sensitive to stressful situations, especially to conditions encountered in a 90-day exposure test, any observed effect could be the result of many factors, including those unrelated to the exposure to a test substance. In this context, it must be noted that Honeywell did conduct a 90-day repeated inhalation study in rats, which are much more stress resistant, and for which generally accepted protocols and methodologies exist.

Access to Toxicology Data

The results of the toxicity testing are summarized in the MSDS. As noted above, making the body of test reports available to the general public would be an extraordinary step which would not necessarily lead to clarification for the consumer. It would be similar to an individual patient requesting a pharmaceutical company to disclose the full battery of pharmacological test reports for products offered for sale – a demand that is both uncommon and unnecessary. Today, in the vast majority of countries around the world, governments, through their regulatory agencies, assume the responsibility for permitting the sale of safe and effective products. To that end, Honeywell has submitted the full test reports and the expert assessment to the regulatory authorities, including EChA, Japan, Korea and the US EPA, as well as specialist third parties – SAE-CRP, ASHRAE and WEEL Committees, German MAK Committee, and others – and the automotive OEM community – members of ACEA, VDA, JAMA, etc. As noted above, there are regulatory requirements to summarize critical data points in a Chemical Material Safety Data Sheet.

Conducting toxicity tests with reputable external specialized laboratories constitutes a substantial investment and the resulting test reports are considered proprietary information. Existing legislation recognizes that such information represents a substantial value and should be protected to prevent free-riders from taking advantage of it for securing their own regulatory approvals. In general, summaries of the study results are available on the websites of the regulatory agencies.

Status of the 28-day test

The purpose of the 28-day test in rabbits was to evaluate the toxicity in rabbits following repeated exposure. This test was performed because in a limited toxicity study rabbits were more sensitive to HFO-1234yf than rats.

Analysis of tissue samples from the study subjects is still on-going. A final report is expected during the fourth quarter of 2012. Honeywell will continue to update regulators and customers as the information warrants. Once we have conclusive results, we will also communicate to the user communities affected – namely repair and service personnel, OEMs and supply chain – and update our REACH registration.

Fluid H

Fluid H was an early candidate molecule under study as a replacement for R-134a. It showed material compatibility issues with certain automotive components as well as stability issues. Consequently it was not considered a viable option as a replacement of R-134a.

China

The Chinese authorities have expressed an interest in performing certain toxicity tests on HFO-1234yf in China in local laboratories. DuPont is cooperating with the Chinese authorities and is having the requested studies performed.

HFO-1234yf versus natural refrigerants

Based on the existing body of evidence, HFO-1234yf is not classified for any type of toxicity. The automotive industry has carefully considered various options and concluded that R-1234yf is the best overall solution in terms of performance and safety. R-744 (CO₂) was part of the SAE CRP and was considered to carry greater safety risks. HFO-1234yf shows no acute effects at concentrations up to 12 percent. This level cannot be reached in the event of a car accident and therefore does not pose any real risk to vehicle occupants. CO₂, however, causes dizziness and loss of awareness at concentrations of 2 percent. At 10 percent it may cause loss of consciousness and may result in death.

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