HFC-152a:
A Valuable Propellant for the Reduction of Volatile Organic Compounds

Lynn E. Applegate, Ph.D.
E.I. du Pont de Nemours and Company

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Introduction

The propellant 1,1-Difluoroethane (HFC-152a) is extremely valuable for the aerosol industry. It is not a volatile organic compound (VOC), has an intermediate vapor pressure, is compatible with common ingredients in aerosol formulations as well as packaging components and many of its properties are similar to hydrocarbons. Although used as a propellant for many years, the use of HFC-152a in aerosol formulations has significantly increased to meet the VOC regulations in California and other states.

HFC-152a is also used as a blowing agent, refrigerant blend component and as an intermediate for the manufacture of fluoropolymers. DuPont is presently the sole manufacturer of HFC-152a and, as a propellant, HFC-152a is sold as Dymel® 152a.

To keep pace with increasing demand, DuPont has doubled its manufacturing capacity since 1992 and has sufficient capacity to meet expected supply requirements for the aerosol industry. DuPont is also reviewing plans to build a second manufacturing plant for HFC-152a, which could be on stream the second half of 1996.

Physical and Chemical Properties of HFC-152a

Physical properties of HFC-152a are given in Table 1. HFC-152a has a vapor pressure in the intermediate range and it is miscible with DME, 1,1,1,2-tetrafluoroethane (HFC-134a) and hydrocarbons, e.g., propane, isobutane and n-butane. HFC-152a is also miscible with a variety of common aerosol solvents, including alcohols. Higher or lower vapor pressures can be obtained, if required, when blended with hydrocarbon propellants or low-boiling solvents.

Based on a Kauri-Butanol value of 11 (Table 1), HFC-152a is not an outstanding solvent and is similar to hydrocarbons. Thus, aerosol systems which now use hydrocarbons can typically use HFC-152a as well. Because HFC-152a is soluble in DME, hydrocarbon propellants and a wide variety of common aerosol solvents and products, HFC-152a can be blended to provide effective delivery of water-based or solvent-based products.

HFC-152a is a very good propellant for emulsion systems/foam products, such as hair mousses or skin creams. DME yields quick breaking foams and hydrocarbons often produce brittle foams that are very slow to break. By comparison, HFC-152a yields foams creamier than those made with straight hydrocarbons and the most aesthetically pleasing foams are propelled with HFC-152a/hydrocarbon blends. Since HFC-152a is not an aggressive solvent, it is usually compatible with materials commonly used in valve gaskets, such as Neoprene, butyl rubber and Buna N. HFC-152a requires no special materials of construction for storage and filling facilities.

Table 1 shows that the lower explosive limit (LEL) for HFC-152a is 3.9 volume percent, which is about twice as high as the LEL for hydrocarbons. In the flame projection test using a standard valve, HFC-152a does not give a flame extension as compared to isobutane, which has a flame extension greater than 22 inches. The chemical heat of combustion, as given by the National Fire Protection Association (NFPA) for HFC-152a, is only 6.3 kilojoules/gram (kJ/g). Hydrocarbon propellants (propane, isobutane and n-butane) have chemical heats of combustions in the 42-44 kJ/g range. This is important with respect to warehouse storage requirements. With respect to risk hazard, the summation of the chemical heat of combustions of the various components in the aerosol formulation is used to define level classification.

The highest flammability risk (Level 3) is defined as having a total chemical heat of combustion of greater than 30.0 kJ/g. Level 2 is greater than 20 but equal to or less than 30.0 while Level 1 is less than or equal to 20 kJ/g. If HFC-152a is substituted for a hydrocarbon propellant, the level classification for some formulations can be decreased. This depends, of course, on the amount of propellant used and the chemical heats of combustion of the other components in the formulation and every formulation must be evaluated on a case-by-case basis.

Flammability of HFC-152a can be nullified by mixing with HFC-134a, a nonflammable propellant. The flammability envelope for mixtures of HFC-134a with HFC-152a is given in Figure 1. The maximum concentration of HFC-152a in HFC-134a which yields a nonflammable binary blend is 12.0 wt. percent. Since the flammability of the blend may not reflect the flammability of the total formulation of which they are a part, tests are needed on final formulations to determine the flammability hazard. In case of a spill or leak, nonflammable blends may fractionate, i.e., the components may separate, producing compositions that are flammable. Thus, in filling operations, this nonflammable blend should be handled as if it were a flammable propellant.

One unique feature of HFCs is the tendency to form azeotropes with other propellants. HFC-152a is not different in this respect. The following azeotropes at 25°C are known:

- HFC-152a/Propane (45.9/54.1 wt.%)
- HFC-152a/Isobutane (75.5/25.5 wt.%)
- HFC-152a/n-Butane (85.0/15.O wt.%)
- HFC-152a/DME (53.6/46.4 wt.%)

Table 1
HFC-152a PHYSICAL PROPERTIES

Formula	CH_3CHF_2
Molecular Weight	66.1
Boiling Point (°F)	-13
Vapor Pressure (psi-g)	
70°F	63
130°F	177
Solubility in water 70°F—Autogenous pressure (wt.%)	1.7
Density (g/cc), 70°F	0.91
Kauri-Butanol value	11
Flammability limits in air (vol.%)	3.9-16.9
Flash point (°F)	<-58

Azeotropes can be important for aerosol packages which use vapor tap valves or for applications where the gas phase is used (dusters and air horns, for example), since the composition of an azeotrope does not change during evaporation. For all of the azeotropes above, the vapor pressure is higher than the vapor pressure of either component, except for the HFC-152a/DME azeotrope which has a slightly lower vapor pressure than the vapor pressure of either component.

HFC-152a is both thermally and hydrolytically stable and it does not react with conventional solvents used in aerosol system.

Safety (Toxicity)

HFC-152a has a low order of toxicity on both an acute and chronic basis. DuPont has established an allowable exposure limit (AEL) for HFC-152a of 1,000 ppm [v/v; 8-hour time weighted average (TWA)]. The AEL is the atmospheric concentration of any airborne chemical to which nearly all workers may be exposed repeatedly, day after day, during an 8-hour day, or 40-hour week without adverse effect.

An AEL of 1,000 ppm is the highest value that can be given for an organic compound. The main physiological action of HFC-152a is that of a weak anesthesia at high inhaled levels. Its 4-hour approximate lethal concentration in rats is 383,000 ppm. Like other halocarbons and hydrocarbons, HFC-152a is capable of sensitizing the heart to the body's own adrenaline if misused or abused. However, in experimental screening studies using dogs and simulating stress with a large intravenous dose of adrenaline, cardiac sensitization was not observed at exposure levels below 150,000 ppm.[1]

In a subchronic inhalation study[2], rats were exposed to HFC-152a at 100,000 ppm for 16 hours daily for two months with no adverse effects except for microscopic evidence of slight respiratory irritation. In another study, when rats were exposed at 100,000 ppm for six hours/day, five days/week for two weeks, there were no significant effects relative to clinical, hematological, blood chemistry, urine analytical, or histopathological indices.

A lifetime inhalation toxicity study using rats showed HFC-152a was not carcinogenic and produced no life shortening toxic effects in rats exposed by inhalation for 24 months at concentrations less than or equal to 25,000 ppm (v/v).

In a study designed to determine reproductive toxicity potential, groups of pregnant rats were exposed by inhalation to 5,000 or 20,000 ppm HFC-152a for six hours/day on days 6-15 of gestation. There was no evidence of maternal toxicity, embryotoxicity or teratogenicity under these experimental conditions. An Ames Test designed to screen for mutagenic potential showed HFC-152a was not mutagenic in *Salmonella typhimurium* bacteria, with or without metabolic activation.[3]

Based on acute and chronic animal toxicity studies and many years of human experience, HFC-152a at or below an occupational limit (8-hr TWA) of 1,000 ppm should pose no hazard relative to general toxicity, carcinogenicity, mutagenicity or teratogenicity.

Table 2
ENVIRONMENTAL PROPERTIES OF DME, HFC-152a AND HFC-134a

	DME	HFC-152a	HFC-134a
Ozone depletion potential (ODP)	0	0	0
Volatile Organic Compound (VOC)	Yes	No	No
Atmospheric Lifetime (years)	<0.1	1.5	14
Global Warming Potential (100 yr. Integrated Time Horizon)	Negligible	140	1300

Environmental properties

Environmental properties of HFC-152a are given in Table 2 along with those of DME and HFC-134a. All three propellants have zero ozone depletion potential. Thus, there are no current restrictions on the use of these three propellants as chlorofluorocarbon (CFC) or hydrochlorofluorocarbon (HCFC) replacements under the U.S. EPA Significant New Alternative Program (SNAP).

HFC-152a and HFC-134a are not classified as VOCs while DME is a VOC. Since DME has a very high (35%) solubility in water, reduced VOC formulations have been developed by substituting water for VOC solvents, e.g., alcohols. Since neither HFC-152a nor HFC-134a are VOCs, replacing VOC propellants all or in part with these propellants reduces VOC on a weight-for-weight basis. The total nonflammability of HFC-134a under normal aerosol conditions would be considered a very desirable property. However, the significantly lower atmospheric lifetime and global warming potential of HFC-152a make it the propellant of choice in most applications. HFC-134a should be used where total nonflammability is a critical factor.

Since the cost of HFC-152a is significantly higher than hydrocarbon propellants, most formulators use only sufficient HFC-152a to meet VOC requirements, then fulfill any additional propellant requirements with hydrocarbons. Although HFC-152a has a higher vapor pressure than n-butane and isobutane, it is typically miscible with any concentrates normally propelled with hydrocarbons and vapor pressure depression usually results. This is helpful in reformulation to very low VOC levels to maintain pressure within D.O.T. requirements. Nonetheless, it is important to recognize that any reformulation can affect product efficacy. Tables 3 through 6 illustrate VOC reduction for several prototype aerosol formulations. Unless stated otherwise, VOC limits given in these tables represent present VOC requirements of California's Clean Air Act. All prototype formulations shown are experimental aerosols given to illustrate VOC reduction. Efficacy of these aerosol formulations has not been evaluated in detail.

The prototype shave foam[4] given in Table 3 uses a combination of HFC-152a and n-butane to easily meet the VOC limit of 5%. This foam has good stability and density, along with a creamy texture and noticeable post expansion. As typical for most shaving creams, this formulation has a low alcohol content and a low amount of propellant. **Continued on next page**

Table 3
PROTOTYPE SHAVE FOAM

Ingredient	Wt.%
Stearic Acid	6.0
Myristic Acid	1.5
Cetyl Alcohol	0.5
Mineral Oil	0.5
Acetylated Lanolin	1.0
Propylene Glycol	1.0
Triethanolamine	5.0
Water	78.5
HFC-152a	2.4
n-Butane	3.6
VOC Limit	5.0
Actual VOC	3.6
Vapor Pressure at 70°F psig	50.0

Propellant 152a
continued from preceding page

Table 4 gives two prototype formulations for a hair mousse[4], both of which easily meet the 16% VOC limit for this product. As with the shave foam, both the alcohol content and propellant contents are low. Formula A only uses HFC-152a as the propellant while Formula B employs a blend of HFC-152a and n-butane. By adjusting the ratio of HFC-152a to n-butane, either a creamier or a more brittle foam can be obtained.

In contrast to the foam products discussed above, aerosol hairsprays typically have high alcohol and low water content. Table V gives two prototype formulations for 55% VOC hairspray[4] .This California VOC limit is scheduled to become effective in 1998. Formula A uses only HFC-152a as the propellant and a low water content while Formula B employs a combination of HFC-152a and DME with a much higher water level. These prototype formulations show promise based on cloud point as well as curl retention tests.

A prototype formulation for furniture polish is given in Table 6 using HFC-152a as the propellant. Since the actual VOC is 18.5% compared to the 25% VOC limit, blends of HFC-152a/hydrocarbons or HFC-152a/DME could be used, if needed, to optimize efficacy and/or to reduce cost.

Table 4
PROTOTYPE HAIR MOUSSE

Ingredient	Wt.% A	Wt.% B
Sodium Polystyrene Sulfonate	7.0	7.0
Steareth-21	2.0	2.0
Lauryl Alcohol	4.0	4.0
Fragrance	0.1	0.1
Water	79.4	78.9
Butane	—	4.0
HFC-152a	7.5	4.0
VOC Limit	16.0	16.0
Actual VOC	0	4
Vapor Pressure at 70°F, psig	72.0	60.0

Table 5
PROTOTYPE 55% VOC HAIRSPRAY

Ingredient	Wt.% A	Wt.% B
Resin	5.0	6.0
AMP[1]	1.0	0.4
Dimethicone Silylate	0.5	—
Water	3.5	29.0
Ethanol	55.0	34.6
DME	—	20.4
HFC-152a	35.0	9.6
Vapor Pressure at 70°F, psig	47.0	40.0

1) AMP=2-amino-2-methyl-1- propanol

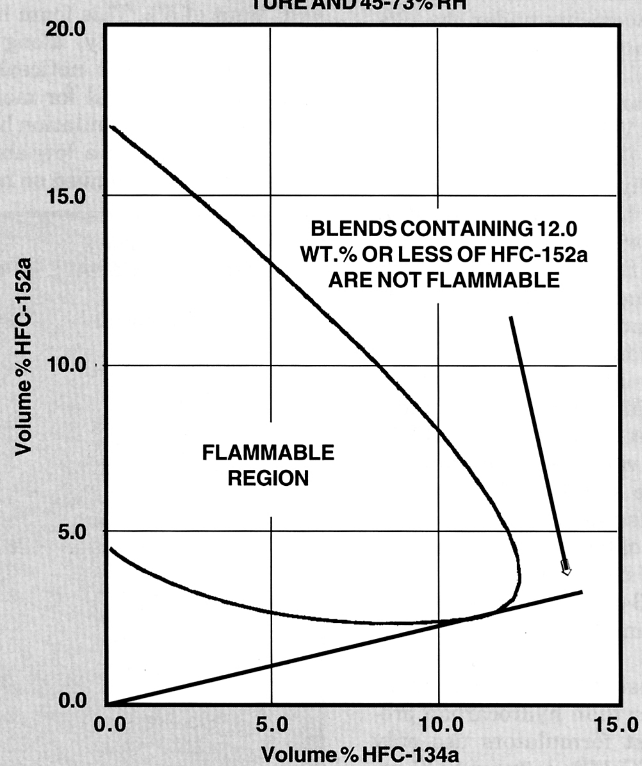
Table 6
PROTOTYPE FURNITURE POLISH

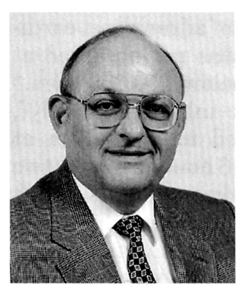
Ingredient	Wt.%
Paste Wax	1.0
Surfactant	0.5
Kerosene	18.5
Water	70.0
HFC-152a	10.0
VOC Limit	25.0
Actual VOC	18.5
Vapor Pressure at 70°F, psig	54

Conclusions

HFC-152a offers the aerosol industry versatility, safety and value. This high quality, easy-to-use propellant can play a significant role as conversion in low-VOC aerosol formulations accelerates. HFC-152a can be used in hairsprays, antiperspirants, paints, air fresheners and a variety of other aerosol products. Improved availability should allow formulators to specify HFC-152a with confidence. ❑

FIGURE 1
FLAMMABILITY ENVELOPE OF HFC-152a/HFC-134a BLENDS AT ROOM TEMPERATURE AND 45-73% RH





Dr. Applegate, who has been with DuPont for 27 years, joined DuPont's Dymel® Aerosol Group, part of the company's Fluoroproducts business, in March, 1994. As a Senior Technical Service Consultant , he has global responsibility for technical service and development activities for DuPont Dymel® aerosol propellants.

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