3M™ Novec™ 612 Magnesium Protection Fluid

Introduction

3M™ Novec™ 612 Magnesium Protection Fluid is part of the family of 3M™ Novec™ fluids, designed as replacements for ozone depleting substances (ODSs) and materials with high global warming potentials (GWPs). Novec 612 fluid is an ideal replacement for sulfur hexafluoride (SF_6), widely used as a "cover gas" to prevent molten magnesium from burning during casting processes. With a global warming potential 22,800 times that of carbon dioxide (CO_2), SF_6 is the most potent greenhouse gas known. It has been targeted for significant emission reduction under the Kyoto Protocol and by European regulations. The U.S. Environmental Protection Agency (EPA) has set a goal of eliminating its use in magnesium casting by the end of 2010.

Novec 612 fluid strikes a balance of properties not offered by other potential replacement technologies. Hydrofluorocarbons (HFCs) such as HFC-134a can be used as cover gas agents, but these materials are also considered greenhouse gases, and are targeted for reduction under the Kyoto Protocol. HFCs, including HFC-134a, are now the subject of negotiations for a global production phase-down under the Montreal Protocol. Although sulfur dioxide (SO_2) was widely replaced by SF_6 in magnesium casting processes because of its toxicity and corrosive properties, it is still used in some regions.

Novec 612 fluid is a safe, sustainable cover gas for magnesium casting operations. It has been demonstrated to provide excellent protection for molten magnesium at operating costs comparable to SF_6, while enabling greater than 99% reduction in greenhouse gas emissions.

Material Description

Novec 612 fluid, dodecafluoro-2-methyl-3-pentanone or $(CF_3CF_2C(O)CF(CF_3)_2$, is a clear, colorless, and low odor fluid. Its properties, environmental profile, and margin of safety make it a sustainable material for protecting molten reactive metals such as magnesium and its alloys.

Novec 612 fluid has the advantage of being a liquid at room temperature. This makes it easy to transport in conventional liquid containers of all sizes. Because of its low viscosity, Novec 612 fluid also is easy to transfer by pumping. Yet it quickly and easily evaporates into a gas stream for use as a cover gas because of its high vapor pressure and low heat of vaporization.

Physical Properties

Data compiled from published information.

Not for specification purposes. All values at 25°C unless otherwise specified.

Typical Physical Properties	3M™ Novec™ 612 Magnesium Protection Fluid
Chemical Formula	$CF_3CF_2C(O)CF(CF_3)_2$
Molecular Weight	316.04
Boiling Point @ 1 atm	49.2°C (120.6°F)
Freezing Point	-108.0°C (-162.4°F)
Critical Temperature	168.7°C (335.6°F)
Critical Pressure	18.65 bar (270.44 psi)
Critical Volume	494.5 cc/mole (0.0251 ft^3/lbm)
Critical Density	639.1 kg/m^3 (39.91 lbm/ft^3)
Density, Sat. Liquid	1.60 g/ml (99.9 lbm/ft^3)
Density, Gas @ 1 atm	0.0136 g/ml (0.851 lbm/ft^3)
Specific Volume, Gas @ 1 atm	0.0733 m^3/kg (1.175 ft^3/lb)
Specific Heat, Liquid	1.103 kJ/kg°C (0.2634 BTU/lb°F)
Specific Heat, Vapor @1 atm	0.891 kJ/kg°C (0.2127 BTU/lb°F)
Heat of Vaporization @ boiling point	88.0 kJ/kg (37.9 BTU/lb)
Liquid Viscosity @ 25°C	0.39 centistokes
Solubility of Water in Novec 612 Fluid	<0.001% by wt.
Vapor Pressure	0.404 bar (5.85 psia)
Relative Dielectric Strength, 1 atm (N_2=1.0)	2.3

Note: 3M recommends that Novec 612 fluid not be used with fluoroelastomer o-rings, gaskets or seals.

3M™ Novec™ 612 Magnesium Protection Fluid has been shown to be compatible with typical materials of construction of furnaces and die casting equipment, including carbon steel and stainless steel. Materials used in gas mixing and cover gas transport equipment (carbon and stainless steel, aluminum, brass, and copper) also are unchanged by Novec 612 fluid. Polymeric seals and gaskets in valves and gas mixing meters have shown excellent compatibility.

Environmental, Health, and Safety

The environmental properties of Novec 612 fluid differentiate it from other fluorinated cover gas agents. Its short atmospheric lifetime of 5 days results in a GWP of 1, which is equivalent to CO_2.[1, 2, 3] When used to replace SF_6 in casting applications, greenhouse gas emissions can be reduced by more than 99% and by more than 68% when used to replace HFC-134a.[4]

The safety of Novec 612 fluid has been determined by both 3M and independent laboratories. Studies have revealed very low toxicity in both acute and repeated dose testing. The No Observed Adverse Effect Level (NOAEL) for all endpoints of acute toxicity is 10% (100,000 ppmV) based on a cardiac sensitization study and a four hour acute inhalation study.

The 8-hour time weighted average (TWA) exposure guideline for Novec 612 fluid is 150 ppmV. On this basis, foreseeable use under normal operating conditions results in a large margin of safety between anticipated exposures and the exposure guideline. This margin of safety contrasts with the precautions needed when SO_2 (TWA = 2 ppmV) is used in cover gas applications. (Substantial investment in engineering controls and worker training and personal protection equipment must be considered with SO_2 due to its toxicity.)

Cover Gas Applications

When evaporated into a suitable carrier gas, Novec 612 fluid is an effective cover gas agent for the protection of molten magnesium. Typical processes where Novec 612 fluid provides excellent protection include various types of melting furnaces and casting operations, including:

- Open casting of ingots, direct chill casting, sand casting or investment casting
- High pressure die casting with hot or cold chamber melting furnaces
- Preparation of alloys from pure magnesium or other alloys
- Remelting of scrap from casting processes

Cover Gas Performance

Novec 612 fluid has been shown to protect pure magnesium or its alloys at melt temperatures from 650°C to 800°C (1170°F to 1450°F) in furnaces and during casting operations. Providing melt protection similar to SF_6, the Novec agent forms a thin, flexible surface film that prevents surface oxidation. Novec 612 fluid is significantly more reactive at melt temperatures and thus more efficiently utilized than SF_6. This efficiency allows it to be used at very low concentrations and nearly eliminates greenhouse gas emissions contributed by the cover gas agent.

U.S. EPA studies[4] of emissions from magnesium die casting and ingot casting operations have shown that Novec 612 fluid concentrations of only about 10% that of SF_6 are needed, and nearly all of the Novec 612 agent added is consumed in the process. GHG emissions are reduced by over 99%. Nearly all of the GHG emitted with Novec 612 formulations is the CO_2 carrier gas. The table shows data for a die casting and an ingot casting study where SF_6 and Novec 612 fluid were run in the same process and equipment.

Summary of Results from U.S. EPA Casting Studies

U.S. EPA Study	Cover Gas Agent	Use Rate[a]	Agent Emissions ($kgCO_2$ eq/hr)	Total[b] Emissions ($kgCO_2$ eq/hr)	Emission Reduction
Lunt Manufacturing Die Casting AZ-91D, Oct-07	SF_6 in CDA	0.3% @ 35 SLPM	384.6	384.6	
	Novec 612 Fluid in CO_2/CDA	0.03% @ 36 SLPM	0	2.1	99.5%
MagReTech Ingot Casting AZ-91D, Oct-08	SF_6/SO_2 (5/3) in CO_2/CDA (60/40)	1.1% @ 198 SLPM	1966	1967	
	Novec 612 Fluid in CO_2/CDA (80/20)	0.17% @ 189 SLPM	0.012	0.7	99.96%

CDA= Compressed Dry Air **a**=Agent Vol% **SLPM**=Std. Liters Per Minute **b**=Agent+Carrier Gas

Use of 3M™ Novec™ 612 Magnesium Protection Fluid in Casting Operations

The enhanced performance of Novec 612 fluid is directly related to its greater reactivity. Greater reactivity also means that it is best to upgrade components of the cover gas delivery system as needed rather than to use Novec 612 fluid as a simple drop-in replacement agent. Specifically, it will be beneficial to optimize cover gas formulation, agent concentration and flow rates, cover gas distribution over the molten metal and flow rate adjustments control during process operations.

- **Cover Gas Formulation:** Novec 612 fluid is added to a carrier gas stream with a gas bubbler apparatus or a precision pumping system. (Commercial gas mixers are available which are designed to work well with Novec 612 fluid. Information on these is available on request from 3M.) Dry carbon dioxide (CO_2) or dry nitrogen (N_2) with 5–10 volume % dry air (frost point <-40°C) are recommended as carrier gases.

  The lowest use rate of Novec 612 agent occurs with CO_2/dry air carrier gas. This combination also significantly reduces the production of white magnesium oxide residues in the casting area. Oxygen derived from dry air in the cover gas formulations also helps manage the production of unacceptable levels of carbon monoxide (CO), formation of high GWP perfluorocarbons (PFCs) and/or potentially hazardous degradation products.

- The concentration of Novec 612 in cover gas formulations is notably much lower than for any of the agents it replaces. The table below shows typical concentration ranges for magnesium casting and furnace operations with Novec 612 fluid and other cover gas agents. The greater reactivity of Novec 612 molecules and higher fluorine content (twice that of SF_6 and three times that of HFC-134a) allows it to form a protective film at very low concentration.

Properties	Novec 612 Fluid	SF_6	SO_2	HFC-134a
Boiling Point °C (°F)	49 (121)	-63 (-83)	-10 (14)	-26 (-15)
Typical Use Concentrations (volume %)	0.01–0.1	0.1–6.0	0.7–6.0	0.05–1.0

- **Gas Mixer:** Due to the low concentrations of Novec 612 fluid used in casting operations, it is recommended that the gas mixer used be capable of holding concentrations within a few percent of set points and not be affected by system upsets such as carrier gas line pressure variations or abrupt changes in volumetric demands for cover gas flow. Both can result in a wide concentration swing using older rotameter or fixed orifice based equipment.

- **Gas Distribution:** The low reactivity of SF_6 allows it to diffuse through the headspace of a furnace, produce an even distribution, and slowly react with the hot metal. The greater reactivity of Novec 612 fluid allows only diffusion over short distances before reacting with magnesium and requires physical distribution of the cover gas over the melt surface. Multiple gas ports and sometimes more extensive gas distribution system changes are required to produce a "shower" of cover gas while being compatible with melting furnace lids and casting processes. (Specific advice is available from 3M technical service.)

Data compiled from published information.

Not for specification purposes.

- **Cover Gas Flow Rate:** Increased cover gas flow rates produce a more even distribution when combined with a proportional decrease in Novec 612 fluid concentration. This approach also reduces emissions. The critical part of this approach is to keep the amount of Novec 612 agent delivered constant. The calculations below illustrate the relationship of concentration and flow rate with Novec 612 agent delivered.

Flow Rate	Concentration	Novec 612 Fluid Delivered
10 Liters/minute	500 parts Novec 612 Fluid/liter	5000 parts Novec 612 Fluid/minute
20 Liters/minute	250 parts Novec 612 Fluid/liter	5000 parts Novec 612 Fluid/minute
50 Liters/minute	100 parts Novec 612 Fluid/liter	5000 parts Novec 612 Fluid/minute

The high flow/low concentration approach produces better protection than the low flow/high concentration usually used with SF_6 systems because the gas distribution is improved significantly. In some cases the amount of Novec 612 agent required for protection is decreased with higher flow rates. Low concentrations also minimize the emissions.

Regulatory Status

Novec 612 fluid complies with the chemical notification requirements of the U.S.A. (TSCA), Canada (CDSL), Korea (KECI), Japan (METI) and China (CICS). It is registered in all these countries with no use restrictions.

3M Resources

Novec 612 fluid is supported by global sales, technical and customer service resources, with fully staffed technical service laboratories in the US, Europe, Japan, and Southeast Asia.

- **Replacement of Lost Cover Gas:** Hot cover gases in the headspace of a furnace are typically half the density of ambient air. When a furnace hatch is opened to add an ingot, to remove dross or take samples, headspace gas escapes quickly. This volume is replaced by ambient air which is comparatively wet and reactive with magnesium and the cover gas agent. This can significantly degrade protection if not replaced quickly.

  Traditionally the concentration of SF_6 was raised to compensate so that recovery is fast. The higher concentration was used as the set point for all process steps including during idle time. This practice adds cost that can be significant. In many cases the amount of cover gas agent needed to keep an idle furnace under control is about half that used during casting operations. More cover gas is only needed to offset the loss of cover gas volume.

  Increasing the flow rate of a 3M™ Novec™ 612 Magnesium Protection Fluid as a hatch is opened and continued for a period of time after the hatch is closed will overcome this operational issue while reducing cover gas agent use. Systems already in use for automatic ingot addition can be used to trigger the additional flow at little incremental cost.

Optimization of Novec 612 cover gas in specific systems and equipment using the recommendations above is very important to achieving good and robust melt protection, acceptable process economics, and minimal emissions.

Poor gas distribution, poor control of agent concentration, low flow/high concentration practices, and overprotection situations can result in degraded protection, unsatisfactory economics and the production of unwanted emissions such as high concentrations of hydrofluoric acid (corrosive and toxic), fluoro-olefins (toxic) and PFCs (extra GHGs).

References

1. N. Taniguchi, T.J. Wallington, M.D. Hurley, A.G. Guschin, L.T. Molina, and M.J. Molina, *Atmospheric Chemistry of $CF_3CF_2C(O)CF(CF_3)_2$*: Photolysis and Reaction with Cl Atoms, OH Radicals, and Ozone, **J Phys Chem A**, 2003, **107**, 2674-2679.
2. B. D'Anna, S.R. Sellevag, K. Wirtz, and C.J. Nielsen, *Photolysis Study of Perfluoro-2-methyl-3-pentanone under Natural Sunlight Conditions*, **Environ Sci Technol**, 2005, 39, 8708-8711.
3. Federal Register 2004, **69** (190), 58907; *Report of the Thirteenth Meeting of the Methodology Panel*, November 12-16, 2007, page 3 paragraph 9.
4. S.C. Bartos, *Characterization of Emissions and Occupational Exposure Associated with Five Melt Protection Technologies for Magnesium Die Casting, and Characterization of Cover Gas and By Product Emissions from Secondary Magnesium Ingot Casting, available at http://epa.gov/magnesium-sf6/resources.html. Additional information on SF_6 replacements is available on this website.*

The 3M™ Novec™ Brand Family

The Novec brand is the hallmark for a variety of patented 3M products. Although each has its own unique formula and performance properties, all Novec products are designed in common to address the need for safe, effective, sustainable solutions in industry-specific applications. These include precision and electronics cleaning, heat transfer, fire protection, lubricant deposition and several specialty chemical applications.

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