3M™ Novec™ 612 as a Substitute for SF_6 in Magnesium Processing: Experience to Date in Varied Casting Operations

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Abstract

3M™ Novec™ 612 Magnesium Protection Fluid is part of the family of 3M™ Novec™ Fluid products designed as replacements for ozone depleting substances (ODSs) and materials with high global warming potentials (GWPs). This paper will outline the properties that differentiate this product as a sustainable replacement for SF_6 as a cover gas in magnesium casting. In addition to the process understanding gained from commercial use, substantial understanding has been gained from trials in a wide variety of casting operations. These trials have led to an optimization of cover gas delivery to minimize both costs of conversions and greenhouse gas emissions. A more thorough understanding of the data generated to date will position Novec 612 fluid as a viable replacement not only for SF_6 but also for HFC-134a and SO_2. It is also important to note the recent commercial availability of Novec 612 fluid in Europe in accordance with the REACH Directive.

Introduction

Novec 612 fluid is part of the family of 3M™ Novec™ Fluid products 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. Although the U.S. Environmental Protection Agency (EPA) had set a goal of eliminating its use in magnesium casting by the end of 2010, the industry is still progressing towards that goal.

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) is still used in casting processes, its use presents unique challenges due to concerns over toxicity and corrosion.

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 less than SF_6, while enabling a 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, 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 is also 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.

Environmental, Health, and Safety

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 result 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.)

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 96% when used to replace HFC-134a.[4] 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%.

Table 1 shows a comparison of measured emissions in one study[4] from a small cold chamber die casting furnace. Since cover gas agents can be used with a variety of carrier gases only the emissions due to cover gas agents are included in this comparison.

Table 1: Comparison of Cover Gas Agent Emissions

	Flow Rate (SLPM)	Start Conc. (ppmV)	Meas. Emission* (kg CO_2e/hr)	% SF_6 Emission
SF_6	35	3000	370	
HFC-134a	40	4200	9.9	2.7
	40	3600	6.7	1.8
Novec 612	36	400	0.34	0.09
	36	300	0.02	0.01
	36	200	0.25	0.07
	36	150	0.16	0.04

*Emissions due to cover gas agent only converted to CO_2 equivalents

Cover Gas Performance

3M™ Novec™ 612 Magnesium Protection 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.

A large range of molten magnesium processes have been tested at industrial scale as can be seen in Table 2. These include a broad range of alloys, melt temperatures, and process conditions with generally good results. Some operations proved more challenging to protect with Novec 612 fluid due to high temperatures (sand casting) or high dross levels (remelting). Initial studies with these applications, with less than optimal gas delivery, indicate that Novec 612 fluid is capable of producing good, economically acceptable protection.

Table 2: Studies/Trials of Novec 612 Magnesium Protection Fluid in Processes Using Molten Metal

Casting Process	Alloy	Concentration (ppmV)	Carrier Gas	Temperature (°C)
Part Casting				
Cold Chamber Die Casting	AZ91, AM50, AM60, AZ31, AJ62	200-600	CO_2/dry air	680-700
Hot Chamber Die Casting	AZ91, AM-50	150-400	CO_2/dry air	670-690
Sand Casting	AZ91E, WE42	2500-3300	CO_2/dry air	750-810
Investment Casting	AZ91E	2000-3000	CO_2/dry air	750-800
Bulk Casting				
Ingot	Pure, AM50, AZ91	500 - 5000	CO_2/dry air	660-790
Direct Chill	Pure	1000 - 5000	CO_2/dry air	660-790
Melt Operations				
Alloy Preparation	AM50, Specialty	500 - 2000	CO_2/dry air	<700
Metal Refinement	Pure, Alloys	500 - 2000	CO_2/dry air	<700
Scrap Remelt	AZ91, AM50	1000 - 2500	CO_2/dry air	<700

Use of Novec 612 Fluid in Casting Operations

The performance of Novec 612 fluid is directly related to its greater reactivity than SF_6 under melt conditions. This means that cover gas practices need to be changed from what has been done with SF_6. First, it is best to upgrade the cover gas delivery system rather than to use Novec 612 fluid as a simple drop-in replacement for SF_6. Specifically, it is best to review and optimize cover gas formulation (agent concentration and carrier gases), flow rates, cover gas distribution over the molten metal and flow rate control during process operations.

Novec 612 fluid is best added to a carrier gas stream with a gas bubbler apparatus. (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. Nitrogen/dry air mixtures generally require higher concentrations of Novec 612 fluid than a CO_2/dry air carrier gas. CO_2/dry air also significantly reduces the production of white magnesium oxide dust in the casting area. Oxygen derived from dry air in the cover gas formulations is required to form the protective film and it helps manage the production of unacceptable levels of carbon monoxide (CO) and the formation of high GWP perfluorocarbons (PFCs) and/or potentially hazardous degradation products.

The concentration of Novec 612 fluid in cover gas formulations is notably much lower than for any of the agents it replaces. Table 2 shows typical Novec 612 fluid concentration ranges for magnesium casting and furnace operations. The greater reactivity of the Novec 612 fluid molecule and higher fluorine content (twice that of SF_6 and three times that of HFC-134a) allow it to form a protective film at very low concentration.

Another consequence of the higher reactivity and low use concentrations of Novec 612 fluid is that losses of headspace gases need to be more carefully monitored and controlled. 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 the cover gas is not replaced quickly.

Traditionally, the concentration of SF_6 was raised to compensate for lost cover gas. This higher concentration became the set point for all process steps including idle time. This practice adds cost that can be significant, since the amount of cover gas agent needed to keep an idle furnace under control is about half that used during casting operations. Additional cover gas is only needed to offset the loss of cover gas volume. In most cases, increasing flow rate rather than concentration is a more effective means of maintaining protection during these open operations.

Increasing the flow rate of Novec 612 fluid when a hatch is opened and continuing that increased flow for a period of time after the hatch is closed will compensate for lost gas and will reduce cover gas use. Systems already using automatic ingot addition can be used to trigger the additional flow at little incremental cost.

Finally, uneven gas distribution, poor control of 3M™ Novec™ 612 Magnesium Protection Fluid concentration, a low flow/high concentration scheme, 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).

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

Cost Analysis Relative to SF_6 and Other Alternatives

The cost of converting from SF_6 to an alternative cover gas includes a consideration of both conversion costs and costs associated with ongoing operations. Conversion costs associated with transition to Novec 612 fluid or HFC- 134a are estimated to be approximately $6500 annually when amortized over 10 years. Conversion costs for SO_2 are approximately $9000 over the same amortization schedule. The difference in conversion cost for SO_2 is primarily due to the additional capital for gas mixing, distribution and industrial hygiene. (Retrofitting costs were modeled after the 2009, Schwarz and Gschrey report to the European Commission with updated equipment costs estimates.)[5]

The primary considerations associated with ongoing operating costs of SF_6 alternatives are gas consumption, agent cost, and licensing fees. There is no licensing fee associated with the use of Novec 612 fluid, so that variable was not included in the following analysis. Table 3 provides an estimate of operating costs for the various alternatives relative to SF_6 (Again, modeled based on data in the Schwarz and Gschrey report).[5] This analysis is most relevant for die casting operations. Cost of alternatives relative to SF_6 will be somewhat higher for operations such as sand casting or remelt operations where higher concentrations are likely to be used.

Table 3: Operating Cost Analysis for SF_6 Alternatives

Cover Gas Agent	Use Concentration[a] (ppmV)	Flow Rate (SLPM)	Use Rate[b] (pound/hr)	Agent Cost[c] ($/pound)	Ratio Agent/ SF_6	Ratio with Royalty Estimate[d]
SF_6	2000	20	0.031	13		
HFC-134a	2000	20	0.022	6.5	0.3	1.0
SO_2	16000	20	0.011	1.6	0.4	0.4
Novec 612	250	40	0.017	20	0.8	0.8

a = Typical use concentration and flow rate from Schwartz and Gschrey Report to EU Com

b = Concentration* flow rate • 60 min/hr • (1 L/ 1,000,000 ppmV) • (1 mole / 24.5 L) • (grams/mole) • (1 pound/454 grams)

c = Agent costs from Schwartz and Gschrey Report to EU Com

d = Royalty estimate from Schwartz and Gschrey as 2.23 times SO_2 cost

The combined conversion and operating costs of Novec 612 fluid make it a very attractive substitute for SF_6 in most casting operations. Many casting operations may be able to achieve an overall cost reduction from conversion to Novec 612 fluid.

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. As of December, 2010, Novec 612 fluid has also been notified for use in Europe in accordance with the REACH Directive.

Summary

Novec 612 fluid is now commercially available globally, including Europe. Novec 612 fluid strikes a balance of properties not offered by other potential replacement technologies. Novec 612 fluid is low in toxicity, substantially reduces greenhouse gas emissions relative to SF_6 and HFC-134a, and is likely to be the most cost effective replacement for SF_6 in most casting operations.

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5. W. Schwarz and B. Gschrey, *Service contract to assess the feasibility of options to reduce emissions of SF_6 from the EU non-ferrous metal industry and analyse their potential impacts, Progress Report*, April, 2009.

The 3M™ Novec™ Brand Family

The Novec brand is the hallmark for a variety of patented 3M compounds. 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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