A NOVEL NEW CLASS OF LOW GWP COMPOUNDS AS IN-KIND CLEAN AGENT ALTERNATIVES TO HFCS AND PFCS

Paul E. Rivers
3M Specialty Materials

INTRODUCTION

Choosing a halon alternative is proving to be a rather complex one for the end user charged with the responsibility of effectively yet responsibly protecting critical assets and assuring continuity of operation. What remains elusive to this day is the proper balance of four key considerations: extinguishing performance, acceptable toxicity profile, advantageous environmental characteristics, and commercial viability. Drawbacks in any of these reduce the desirability of the extinguishing alternative under consideration.

BASIC RESEARCH: A WORK IN PROGRESS

The complexity is evident, for example, in the US Naval Research Laboratory's process to choose an approach in search of a streaming replacement for Halon 1211 [1]. The philosophy heretofore had been to search for a replacement that would have all the positive attributes of Halon 1211 but without the negative environmental impact. Attractive as that philosophy was, the fatal flaw inherent was that without success in identifying an alternative, the only option was to return to square one—using Halon 1211 as the benchmark, the resultant choice became Halon 1211 itself. The question then became, was it really necessary to find a clone of Halon 1211? An alternative systems engineering approach was put forth using the notion that multiple technologies could be employed to replace Halon 1211 in its historic applications. Those technologies could be in-kind and not in-kind, either clean or dirty, and may exist in any of the three physical states. Basically, NRL is using a performance-based approach, again, with the ultimate goal being to provide the proper balance for performance, toxicity, environmental acceptability, and marketability.

For much of the 1990s, significant effort has been put forth in the Advanced Agent Working Group (AAWG) and the Next-Generation Fire Suppression Program (NGP) to discover the elusive "drop-in" replacement for halon. The direction their in-kind replacement research has taken has resulted in the identification of potentially effective materials that are liquid at normal ambient temperatures. To date, Mather and Tapscott **[2]** have identified several liquid tropodegradeable brominated olefins that appear to have performance and environmental advantages, and with preliminary low level toxicity testing indicating the materials may be acceptable for short duration exposure. But. questions remain concerning their longer-term exposure effects, their stability and commercial viability. Gann **[3]** has also reported on high boiling alternatives that are being explored as alternatives, some commercially available and some rather exotic, that show varying degrees of effectiveness but an undetermined balance of the aforementioned four criteria: performance, toxicity, environmental acceptability, and marketability.

PRESSURE ON EXISTING COMMERCIAL TECHNOLOGY PLATFORMS

Fire protection engineers designing active suppression today need a wide array of technologies available to them. When considering gaseous agent alternatives, over a dozen clean agents have surfaced in the past decade that are commercially available today. Many are in-kind HFC and PFC replacements. HCFCs are also included. but their use is limited and is presently either banned or is on a phaseout schedule. Significant pressure in the past year has been placed on users and producers of HFCs and PFCs in all categories of end use, not just halon replacement due to the long atmospheric lifetime and high global warming potential of these compounds.

That pressure is leading *to* a revision presently in process of the existing voluntary codes of practice—VCOPs—in the UK to further restrict use of CFC and halon replacements. The UK agreements were developed in the mid 1990s between the UK Department ofthe Environment, Transport and the Regions (DETR), and industry groups. It is *also* lead to VCOPs in other EU countries, Australia, and others. A new fire protection VCOP spearheaded by the US HARC was just completed this year with USEPA and fire protection industry groups in the US directly participating. The common theme in all of these is an "essential use" litmus test precluding use of high GWP compounds unless no other alternative agent or method of protection is technically feasible.

At a recent HARC board of directors meeting [4], Stephen Andersen, PhD (co-chair of the UNEP Technical Advisory Assessment Panel, USEPA Director of Strategic Climate Projects, and a co-founder of HARC) presented a concise view of the direction industry should take in the use of high GWP fire protection materials. The viewpoint is that, irrespective of where one's opinion falls on the issue of climate change, industry self-discipline will he vital to minimize promulgation of future regulatory requirements. The message was, "Industry should control their own destiny." To do this, several criteria must be considered:

- Set a goal of zero emissions for HFCs and PFCs
- Improve manufacturing processes
- Promote best practices with respect to use of HFCs and PFCs, i.e., VCOPs
- Recover and destroy unusable agents
- Seek and welcome new alternatives

DISCOVERY OF A NEW ENVIRONMENTALLY ADVANTAGEOUS CLASS OF COMPOUNDS

3M recently discovered what appears to be a class of compounds that have utility as halon replacements. Having utility in satisfying some of the above environmental criteria put forth by Dr. Andersen positions this class of compounds, for which 3M has patent position. as a potentially viable replacement technology for HFCs and PFCs in certain fire protection applications. These materials have been shown to be effective in extinguishing standard fire test scenarios. The material tested via in-house acute studies exhibits low toxicity characteristics when compared to cup-burner extinguishing concentrations and the expected end use. These materials exhibit outstanding environmental attributes, and it appears they are conimercially viable for the halon replacement market. The materials that show promise are high boilers, ranging from as low as 0 °C to as high as 100 °C. So far, three molecules have been shown in laboratory screening tests to have the potential for the aforementioned balance of extinguishing performance, acceptable toxicity profile, advantageous environmental characteristics, and commercial viability. Table 1 shows the range of boiling points. Commercialization is targeted for early 2001 for at least one of these compounds. Sample quantities for testing will be available in the second half of 2000.

TABLE 1. AGENT PERFORMANCE COMPARISON.

Compound	Boiling Point °C	Cup-burner Vol% (propane)	Mass Ratio Size to 1211	Comments
Halon 1211 CF_2ClBr	-3.4	3.6	1.00	NFPA 12B 1975 Ed. shows 3.9% heptane value
L-I6140 3M Proprietary	20-30	xx	2.19	
L-15566 3M Proprietary	40-50	xx	1.86	
L-I6141 3M Proprietary	70-80	xx	2.03	
FC-5-1-14 $CF_3CF_2CF_2CF_2CF_2CF_3$	56.0	4.0	2.21	3M [illegible]ptane nun[illegible]er is 4.1%

APPLICATION

The fire protection end use for this class of compounds, expected to have the best initial effectiveness, is as a streaming agent, in manual handheld application, or perhaps flight line suppression. Initial experimental tests run have shown effectiveness on standard UL 711 pan fires with standard halon extinguishing hardware. For example, fire tests in two pan fire scenarios, the UL 2B and the 5B, using L-15566 as the extinguishing agent have been conducted. Tests were run with 2-in (5.08-cm) in-depth heptane fuel on 4-in (10.16-cm) of water with a 6-in (15.32-cm) freeboard in standard UL pans. Pre-bums were 1 min, and fresh heptane was used in accordance with methods used by UL. Because this is a technique dependent application, the unforgiving type of fire in the UL scenario will not extinguish if the agent is marginal. This is especially true with clean agents, so to extinguish these fires is significant (Table 2).

Although the initial obvious application for this class of compounds is in streaming, utility in hazards requiring flooding and local application protection may become evident as development work continues. For example, in a standard UL 1254 test scenario, utilizing a 4-m^3 enclosure, L-15566 has effectively extinguished a 2B pan fire with a system designed for gaseous agent delivery. With the exception of the use of directional spray nozzles as a replacement for the gas nozzles, the system was not optimized. Further work on nozzle delivery could yield flooding-like performance or utility in local application with one of the identified materials.

It should be noted that potential has been shown for this class of compounds in other industrial applications as alternatives to HFCs, PFCs, and HCFCs. Trials are underway and details of that work will **be** the subject of a future paper(s).

TABLE 2. STREAMING TRIAL COMPARISON: FC-5-1-14 AND L-15566.

Test	Agent	Fire type	Preburn (sec)	Exting. Y/N	Discharge time (sec)	Agent discharge (kg)	Flow mte (kg/sec)
4	FC-5-1-14	UL 2B Pan	60	Y	2.6	2.03	0.78
6	L-15566	UL 2B Pan	60	Y	3.5	2.59	0.74
X	FC-5-1-14	UL 5B Pan	60	Y	3.2	2.53	0.79
13	L-15566	UL 5B Pan	60	Y	3.x	2.87	0.76

PROPERTIES, TOXICITY, AND MATERIALS COMPATIBILITY

Preliminary screening tests for materials tested show similar properties to PFCs in terms of stability, solubility of water, and compatibility with typical materials used in fire protection systems. Further tests are underway. The L-15566 material, for which the most work has been performed to date, has properties similar to FC-5-14 as shown in Table 3.

TABLE 3. PROPERTIES COMPARISON.

	L-15566	FC-5-1-14	HFC-227ea	HFC-236fa	IFC-1311	HCFC-Blend B
Molecular Weight	>250	338	170.03	152.04	195.91	150.7
Boiling Point °C	40-50	56	- 16.4	-1.4	-22.5	27
Physical State @ 25 °C	Liquid	Liquid	Gas	Gas	Gas	Liquid
Exting. Conc. % heptane	xx	4.1	6.5	6.3	3.6	6-7
"propane		4.0*				
Vapor pressure @ 25 "C kPa	32.6	31.0	457.1	272.4	439.2	77.0
Liquid density g/ml @ 25 °C	1.60	1.68	1.68	1.36	2.1	1.48
LC-50 4 hour acute inhal. %	>10 **	>30	>80	>X0	-16.0	3.2
** in-house whole body mouse		(@ sat.)				
NOAEL/LOAEL% vlv	TBD	17/>17	9.0/10.5	10.0115.0	0.2/0.4	1.0/2.0
		(@ sat.)				

From a toxicity standpoint, at this time, these materials arc considered suitable for the anticipated target streaming market. In-house acute inhalation tests with mice give confidence thc formal acute inhalation studies for L-I5566 scheduled for a Q2-2000 completion at the Huntington Research Centre (UK) will show a 4-hr acute of at least 100,000ppm. Since the range of formal toxicity testing additional to the 4-hr acute, that is, cardiac sensitization, chronic inhalation, etc., is yet to be completed. the decision to offer this material for occupied spaces is pre-mature if local application or flooding capabilities become apparent.

ENVIRONMENTAL COMPATIBILITY

The biggest differentiation these compounds have from those materials commercialized today **is** the lack of apparent environmental impact. According to Molina et al. [5], the uv absorption spectrum for L-15566 indicates a lifetime against photolysis of less than one month, which will give a corresponding global warming potential of less than 10. Table 4 shows **a** comparison of L-15566 with other commercially available clean agents. Tests are underway for the other molecules, but the basic mechanism for breakdown is present for all molecules in this class.

TABLE 4. ENVIRONMENTAL COMPARISON.

Agent	ODP	ALT (yrs)	GWP (100 yr. ITH)	SNAP (Yes/No)
L-15566	0	<0.08	<10	No
FC-5-1-14	0	2600	9000	Yes
HFC-227ea	0	36.5	3800	Yes
HFC-236fa	0	209	9400	Yes
FIC-1311	0.0001	0.005	<1	Yes
HCFC Blend B	0.014	1.4	120*	Yes

* Based on HCFC-123 only—contains PF-methane, **a** PFC.

CONCLUSION

Choosing a halon alternative requires one to consider the proper balance of four key considerations: fire extinguishing performance, the toxicity profile, the environmental characteristics, and commercial viability of the candidate. Drawbacks in any of these reduce the desirability of the extinguishing alternative under consideration. Increasing pressure to limit the use of HFCs and PFCs to applications only where they are essential has given impetus to the search for alternative technologies.

A new class of 3M compounds for which 3M has patent position is presently under development with commercialization targeted for early 2001. These compounds have a wide range of boiling points, which can provide a candidate agent for halon replacement applications, particularly in streaming, where HFCs, PFCs, and other alternative technologies have been used to date.

REFERENCES

1. Naval Research Laboratory, NRL/MR/6180--99-8411, "U.S. Navy Halon 1211 Replacement Plan Part II - Halon 1211 Requirements Review," Nov. 1, 1999, pp. 6-9.
2. Mather, J. D., and Tapscott, R. E., "Tropodegradeable Halocarbons and Main Element Groups," *Proceedings*, Halon Options Technical Working Conference, Albuquerque, NM, pp. 132-135, 1999.
3. Gann, R. G., "Next Generation Fire Suppression Technology Program (NGP): Technical Highlights," *Proceedings*, Halon Options Technical Working Conference, Albuquerque, NM, pp. 88-90, 1999.

4. Andersen, Stephen, USEPA Director of Strategic Climate Projects, Presentation at the Halon Alternatives Research Corporation Board Meeting, March *2, 2000.* (Copy on file with the author).

5. Guschin, Andrei G., Molina, Luisa T., Molina, Mario J., Department of Earth, Atmospheric and Planetary Sciences, "Atmospheric Chemistry of L-15566, etc.," prepared for 3M Specialty Materials Laboratory, p. 4, July 1999.