THE ULTIMATE HALON REPLACEMENTS ARE IN SIGHT

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Introduction

We have identified a small set of clean firefighting agents that we beliwe includes the agents that will replace halons for the far term Careful development of screening criteria, candidate lists, collection and estimation of properties, plus calculation of properties of blends using a new software program we have developed, have revealed a number of agents that appear to meet all the desired criteria for halon replacements. We have identified a set of approximately a dozen agents that are particularly attractive. These agents are proprietary and patents (containing government rights clauses) are pending. Although the agents require further validation work before deployment, at the present time there is no reason to rule out these chemicals as ultimate halon replacements.

What is an Ideal Halon Replacement?

What properties would the ideal halon replacements have? They should be highly effective three-dimensional fire and explosion suppression and inerting agents, with weight and liquid storage volume requirements comparable to those of Halons 1211 and 1301, They must have appropriate physical properties for the application; Halon 1211 replacements should be deliverable as low-boiling liquids; Halon 1301 replacements as gases. All agents should represent minimal or no health hazard, with the lowest possible toxicity. In addition, the combustion products of the agents should be no more toxic than those of halons in current use. The agents should pose no environmental hazard; this means having an ozone-depletion potential (ODP) of zero and global warming potential (GWP) near zero, plus rapid breakdown to harmless products in the environment, while not presenting a volatile organic compound (VOC) problem. The agents should evaporate cleanly and should be electrically nonconductive. The agents should have no adverse effects on materials or components, including long-term durability; they should also be available at low cost and in bulk. The agents should be suitable for use with existing equipment (perhaps with minor modifications such as new nozzles and O-rings) so that the large existing investment in firefighting equipment can be preserved. These ideal criteria represent very stringent requirements, and even Halons 1211 and 1301 do not meet them all.

A clean firefighting agent can be either a single (neat) chemical or a blend of two or more chemicals. Mixing chemicals can allow optimization of properties such as freezing point, vapor pressure, extinguishing ability, and cost. If the agent is a blend, the vapor pressures of the components should ideally be similar so that the blend will not change composition significantly during evaporation; this greatly simplifies the logistics of handling. For example, systems that have leaked or have been partially discharged can be topped up without requiring draining the residual agent or chemical analysis to determine the composition of the residue. Azeotropic blends are particularly attractive because they do not change composition at all on evaporation.

Approaches to Agent Selection

Two distinct approaches can be taken to the development of halon replacements. The first, which we call the near-term strategy, consists of screening readily available bulk chemicals with fully investigated properties to determine which come closest to meeting the desired criteria. This approach can also be called a "bottom-up" approach; taking the small universe of available bulk chemicals and determining which are most acceptable. This approach has the advantages that any chemicals found acceptable are available soon, relatively inexpensive, and do not require a great deal of development work. The disadvantages of this approach are the very limited range of candidates considered and the fact that candidates chosen may be marginally acceptable for some applications, but are far from ideal or generally applicable. Properties on which major compromises are commonly made include effectiveness and toxicity. Another disadvantage of the near-term strategy is that a substantial investment in new equipment may be required which may become obsolete as superior technologies are developed.

The second approach, which we call the long-term strategy, consists of a "top-down" approach. In this approach, the properties of an "ideal" agent are specified by examining data on existing halons and other firefighting agents. Once the selection criteria have been determined, the full range of all possible chemical structures is screened for candidates. This approach has the advantage that it can yield outstanding firefighting agents, which may be widely useful and may even be superior to current halons. They may also be "drop-in" replacements in existing equipment with only minimal changes (such as new O-rings). This long-term approach has the disadvantages that it is more labor-intensive and requires a longer commitment and more development work. We favor the long-term approach because we consider the investment required very small compared to the great potential rewards.

Currently Available Halon Replacements

Most halon research to date has followed the "near-term" strategy. Interest in near-term alternatives has focused on hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), hydrobromofluorocarbons (HBFCs), perfluorocarbons, and inert gases such as nitrogen, argon, and carbon dioxide. However, all of these chemicals have potentially serious drawbacks as firefighting agents. Hydrofluorocarbons, though having zero ODP and low toxicity, are only moderately effective extinguishants and thus often require large system volumes. Some HFCs also require high-pressure systems. For the purpose of this discussion, a highly effective extinguishant is defined as one that extinguishes an n-heptane fuel fire in a cup burner below 5% concentration by gas volume. A moderately effective agent extinguishes a similar fire at 5% to 12% concentration, and a poor extinguishant requires over 12%.

HCFCs are only moderately effective extinguishants, have nonzero ODPs, and face phaseout under the Montreal Protocol. Some HCFCs have shown undesirable toxicity. The hydrobromofluorocarbons proposed commercially to date, although effective extinguishants and fairly nontoxic, have unacceptably high ODPs. Perfluorocarbons are moderately effective extinguishants, extremely nontoxic, and have zero ODP, but have very long atmospheric lifetimes and high global warming potentials (GWPs). Inert gases are poor extinguishants and require high storage volumes; they may also pose a danger of asphyxiation in occupied areas because of the high concentrations required.

Although several agents have been proposed as replacement total-flooding or streaming agents, none of those currently undergoing large-scale testing are nearly as effective extinguishants as Halons 1211 or 1301. The alternative chemicals proposed require much greater system volumes and/or weights. For applications where weight and volume are not seriously limited, some of these agents may be suitable, particularly for unoccupied areas. However, none are especially attractive for applications where excellent fire and explosion suppression are needed or serious constraints on system volume and weight apply. For example, highly effective, rapidly dispersable agents are needed to ensure safety in operations that handle large volumes of petroleum products. As further examples, aircraft face serious constraints on both system volume and weight, while tanks, ships, and submarines are constrained primarily by volume.

Our Approach to Agent Selection

The general approach used to find the ETEC agents is described in reference 1. A systematic, rational screening process was applied encompassing all known and many unknown chemicals. There are approximately 11 million chemicals reported in the literature: 8 million organic (carbon-containing) and 3 million inorganic. All of these chemicals were screened, as were other structures not reported in the literature that we considered potentially attractive as firefighting agents. Any metal-containing chemical (inorganic or organometallic) was ruled out because it would not be clean. In addition, any chemical with a boiling point over 60°C was eliminated because it would not have sufficient volatility for rapid knockdown and rapid evaporation. Agents meeting all other selection criteria and having boiling points between -85°C and 0°C were classed as candidate total flooding agents, while those with boiling points from 0°C to 60°C were classed as candidate streaming agents. Chemicals having highly unstable or highly toxic functional groups were ruled out. These undesirable functional groups included, for example, -N=C=O, >NI, -SH, and $-POF_2$.

The AZEO Program

In order to more accurately predict the properties of pure chemicals and blends, ETEC has developed a proprietary computer program, called AZEO, that calculates several properties and predicts azeotrope formation and composition. Mathematical modeling in this program is based upon the theory of corresponding states and uses a third order virial equation of state. AZEO uses the well-documented Soave modification of the

Redlich-Kwong (SRK) equation of state (EOS), specifically fitted to small halogenated hydrocarbons (Refs. **2-7).** The SRK EOS was chosen in preference to the Carnahan-Starling-De Santis (CSD) EOS for two reasons: (1) the SRK EOS is superior to CSD in modeling vapor-liquid properties, and (2) the SRK EOS requires fewer parameters as input. The required inputs for SRK for each chemical are molecular weight, normal boiling point, critical temperature, critical pressure, and Pitzer acentric factor. The Pitzer acentric factor is calculated at the normal boiling point as a function of the critical pressure, critical temperature, and molecular weight. AZEO has built-in estimation algorithms for critical temperature and pressure in case those values are unavailable. The Pitzer-Curl method is used to calculate mixture cross correlation coefficients. The thermodynamic properties calculated by AZEO as functions of temperature include vapor pressure, specific vapor volume, liquid density, liquid enthapy, enthalpy of vaporization, vapor enthalpy, entropy of the liquid, entropy of vaporization, and entropy of the vapor, specific heat of the vapor at constant pressure and constant volume, specific heat of the liquid at constant pressure.

CSD requires significantly more input parameters than SRK, and these parameters are often not known for far-term candidate agent. Because it requires less input data, the SRK EOS is more suitable than CSD for far-term candidate agents. The SRK method provides an accuracy of within **2%** in calculated thermodynamic properties. This accuracy is quite adequate for initial screening of far-term candidate agents. The CSD EOS is more accurate than SRK and should be used when the properties of a compound are well studied and higher accuracy is required.

AZEO works for up to five-component mixtures and allows a choice of units. It identifies probable azeotropes, near-azeotropes, and non-azeotropes. For azeotropes and near-azeotropes, it gives the approximate azeotropic composition. The AZEO program reproduces the composition and properties of all known azeotropes tested (such as R-500 **and R-502)** within 1% accuracy. It calculates vapor pressure curves and gives enthalpies of vaporization and specific heats of liquid and vapor as functions of temperature. Typical output from AZEO (for Halons 1301) is shown in figure 1. The properties of one of our replacement agents are shown in Table . AZEO is only a tool **for** initial screening to identify attractive blends and possible azeotropes; all results obtained from AZEO must be validated by laboratory measurements.

THERMODYNAMIC DATA FOR FILE NAME pure1301 05-10-1993

Temp.	Pressure	Volume	Density		Enthalpy		Entropy	
		Vapor	Liquid	Liquid	Latent	Vapor	Liquid	Vapor
		Vg	1./Vf	Hf	Hfg	Hg	Sf	Sg
Degrees F	Psia	Ft3/lbm	Lb/cu.ft		BTU/Lb		BTU/Lbm-Deg R	
-40.0	6.3306	3.5171	59.872	0.000	51.429	51.429	0.00000	0.12245
-30.0	8.4510	2.6846	58.955	2.053	50.594	52.647	0.00478	0.12244
-20.0	11.1078	2.0784	58.017	4.407	49.748	54.155	0.01002	0.12308
-10.0	14.3927	1.6299	57.058	6.721	48.890	55.611	0.01494	0.12358
-0.0	18.4043	1.2932	56.076	8.996	48.016	57.011	0.01956	0.12394
10.0	23.2482	1.0371	55.071	11.232	47.126	58.358	0.02390	0.12417
20.0	29.0371	0.8398	54.039	13.430	46.215	59.645	0.02799	0.12427
30.0	35.8894	0.6861	52.979	15.590	45.287	60.878	0.03183	0.12425
40.0	43.9296	0.5649	51.890	17.714	44.332	62.046	0.03544	0.12411
50.0	53.2881	0.4685	50.769	19.801	43.351	63.152	0.03885	0.12385
60.0	64.1002	0.3911	49.613	21.851	42.339	64.191	0.04205	0.12347
70.0	76.5059	0.3283	48.419	23.866	41.297	65.163	0.04506	0.12298
80.0	90.6502	0.2770	47.184	25.846	40.214	66.059	0.04790	0.12237
90.0	106.6818	0.2348	45.903	27.790	39.090	66.880	0.05057	0.12165
100.0	124.7544	0.1997	44.571	29.698	37.919	67.618	0.05309	0.12080
110.0	145.0251	0.1704	43.183	31.572	36.694	68.267	0.05545	0.11983
120.0	167.6548	0.1457	41.730	33.411	35.409	68.820	0.05768	0.11873
130.0	192.8081	0.1248	40.204	35.214	34.051	69.265	0.05978	0.11749
140.0	220.6539	0.1070	38.591	36.981	32.609	69.590	0.06174	0.11609

Property =	Constant +	....* T +	....* T**2 +	....* T ** 3	Std Dev
Psat	1.85217E+01	43.598E-02	4.0007E-03	2.2744E-05	0.11108
Hf	8.99311E+00	22.476E-02	-1.7228E-04	-4.1380E-08	0.03587
Hg	5.69976E+01	13.690E-02	-2.4043E-04	-6.6922E-07	0.03508
Hfg	4.80045E+01	-87.864E-03	-6.8152E-05	-6.2784E-07	0.01106
Sf	-6.52668E-01	28.861E-04	-3.9904E-06	1.9412E-09	0.00008
Sg	-1.61819E-03	49.337E-05	-4.2694E-07	-1.1377E-10	0.00008
Sfg	1.35175E+02	-42.409E-02	7.9899E-04	-6.2831E-07	0.01106
Vg	1.34517E+00	-32.995E-03	3.5417E-04	-1.3356E-06	0.05643
Mens	5.60650E+01	-99.079E-03	-1.0437E-04	-5.5377E-07	0.01168
Cpvap	-1.71934E-02	58.506E-05	-6.0496E-07	0.0000E+00	0.00008
Cpliq	-4.00886E-01	13.846E-04	-1.0243E-06	0.0000E+00	0.00024

USE CAUTION EXTRAPOLATING ABOVE AND BEMW ENDPOINTS

Sf, Sfg, Sg, Cpvap, & cpliq Use T in Deg R
All others use T in Degrees F

Figure 1. Output from AZEO Program for Halon 1301

Physical and Chemical Properties

The agents identified are blends containing modified fluorocarbons. The modified fluorocarbons are relatively high molecular weight and have boiling points between -60°C and 50°C. The lower-boiling, more gaseous agents (BP -60°C to 0°C) are outstanding candidates for Halon 1301 replacements. The higher-boiling, more liquid agents (BP 0°C to 60°C) are outstanding candidates for Halon 1211 replacements.

Firefighting Effectiveness

Several components of the ETEC agents have been tested in cup burners and show extinguishment concentrations in the range of 1.8% to 3.5% by gas volume for n-heptane fuel fires. These values are in the same range as those obtained for Halons 1211, 1301, and 2402. For accurate comparison, firefighting effectiveness must be compared on relative weight and volume bases as well as on cup burner concentrations. A comparison of interpolated effectiveness (by gas volume, weight, and liquid storage volume) of selected new blended agents with the effectiveness of current halons is shown in Table 1.

TABLE 1. EXAMPLES OF EFFECTIVENESS OF NEW AGENTS COMPARED TO HALONS 1301 AND 1211

AGENT	GAS VOLUME % TO EXTINGUISH n-HEPTANE FIRE	RELATIVE WEIGHT	RELATIVE LIQUID STORAGE VOLUME
Halon 1301	2.9	1.0[a]	1.0[a]
Halon 1211	3.2	1.0[b]	1.0[b]
ETEC F-1	3.1	1.40[a]	0.88[a]
ETEC S-1	2.2	1.01[b]	0.93[b]

a. total flooding agents are compared to Halon 1301
b. streaming agents are compared to Halon 1211

Environmental Considerations

The ETEC agents have zero ODP because they contain no chlorine or bromine. In addition, they photolyze rapidly in the troposphere, giving them very short atmospheric lifetimes and minimal global warming potentials. Because of the short atmospheric lifetime, only a vanishingly small fraction of the material released will survive to reach the stratosphere. It will be desirable to investigate the effects of the breakdown products of the agents in the troposphere.

Toxicity Considerations

The limited information available regarding the acute toxicity of the agents is highly encouraging. For several agents the mice 2-hr LC_{50} is known to be greater than 250,000 ppm by weight. Additional acute, chronic, and subchronic toxicity testing will be needed. Acute toxicity testing can be conducted under an accelerated schedule in about 90 days. Because the combustion products of the ETEC agents are similar to those from current halons, the toxicity of these combustion products is also expected to be similar.

Remaining Validation Work

The remaining validation work consists of additional testing in five areas: effectiveness (laboratory and large-scale), toxicity, long-term stability, materials compatibility, and tropospheric reactions.

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