NEXT-GENERATION FIRE SUPPRESSION TECHNOLOGY PROGRAM (NGP): TECHNICAL HIGHLIGHTS

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INTRODUCTION

The Department of Defense (DoD) is entering the third year of its Next Generation Fire Suppression Technology Program (NGP). The NGP goal is to demonstrate. by 2005, retrofitable, economically feasible, environmentally acceptable, and user-safe processes, tcchniques. and fluids that meet the operational requirements currently satisfied by Halon I301 systems in aircraft. ships, land combat vehicles. and critical mission suppon facilities. If successful, the NGP could eliminate DoD dependence on a harmful substance no longer in national production, minimize any readiness impacts that could result if Halon 1301 use restrictions were imposed in the future, and achieve these at greatly reduced cost.

The potential fire locations for which alternatives to Halon 1301 are sought include aircraft engine nacelles, dry bays. cargo bays. and fuel tanks; ground vehicle crew compartments; and shipboard machinery spaces and storage compartments (Figure 1). The hazards to be avoided include harm to people, thermal damage. post-fire corrosion. **loss** of visibility, and overpressure. Successful candidates must thus do well in the following: the fire suppression efficiency and reignition quenching, ODP, GWP, atmospheric lifetime. suppressant residue level, electrical conductivity, metals non-corrosivity and polymeric materials compatibility. long-term storage stability. low toxicity of the chemical and its combustion and decomposition products. speed of dispersion, and safety and occupational health requirements. To be cost-effective, the suppressant and storage/delivery systcm must be of light weight and low volume, as well **as** compatible with the host designs of existing platforms.

Points of contact and additional information on the strategy and status of the NGP can he found at the NGP web site: www.dtic.mil/ngp/.

PROGRAM STATUS

Support for the NGP comes from DoD funding and cost sharing from the participating laboratories. To date, most of the DoD support has come from the Strategic Environmental Research and Development Program (SERDP), with additional support from the Army Tank and Automotive Command (TACOM). To date. the NGP will have expended about 15% of the planned resources.

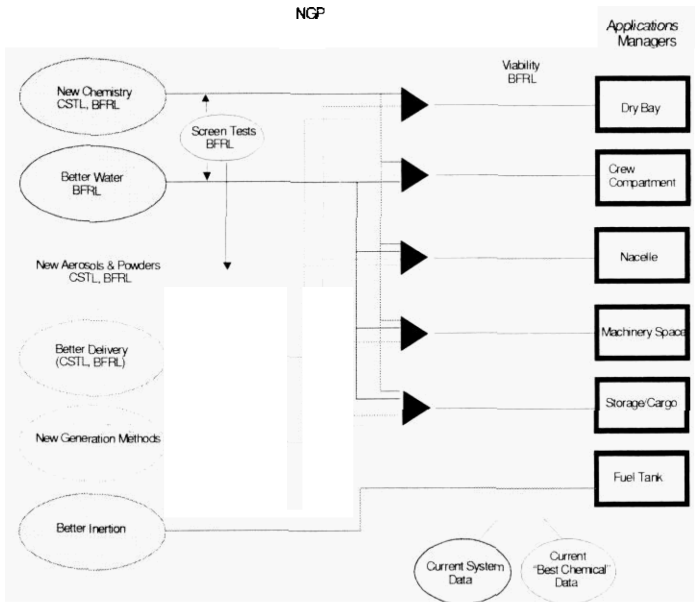

Figure 1. NGP research for retrofitable fire suppression technologies.

TECHNICAL HIGHLIGHTS

The achievements of the NGP research team have been numerous, significant and stimulating. The following describes the highlights.

New **Flame Suppression Chemistry**

An easy way to effect economical retrofit of a fire suppression system is with a new chemical that performs as well as CF_3Br, but without the environmental drawback. Limited searches have turned up a number of new chemicals for consideration, *so* it is likely that there are more worthy candidates. The NGP is developing both improved methodologies for doing the search as well as identifying candidates worthy of further consideration.

In the published literature on flame inhibition and suppression are a number of chemicals that are far more efficient at quenching flames than is CF_3Br. If any of these interfere with flame propagation chemistry in a manner different from the way Halon 1301 does. i.e., depleting the free radical (H, OH, O) pool that propagates combustion, this would provide additional guidance for the search through the world of chemistry.

- NGP laboratory studies with opposed flow diffusion flames have demonstrated a direct relationship between the degree of reduction of the OH concentration in the flames and suppressant efficiency for a range of additive chemistries. This measurement for a candidate chemical should enable rapid identification of similarity to or difference from Halon 1301 flame suppression.

- An NGP-developed reduced propane/air chemical kinetics mechanism will serve as the basis for understanding better the suppression activity of a chemical. Flame speed and species concentration predictions compare well with published data. A contract has been let to generate flame reaction rate data for additives of known high suppression efficiency.
- NGP research has developed two devices (an electrostatic atomization system and *an* inductively coupled plasma nebulizer) for seeding the air streams of laboratory burners with fine droplets of an additive compound. For several applications, water mists and other multiphase systems are under consideration. The ability to vary the droplet size makes it possible to study both chemical effects. after droplet vaporization, and the physical effects of the droplets.

Using published data, quantitative structure-activity relationships. and laboratory screening tests, NGP chemists have examined families containing thousands of chemicals to identify those with desirable properties: high fire suppression efficiency. short atmospheric lifetime, low toxicity, and boiling point sufficiently low that an extinguishing concentration can be achieved within a specified time following discharge.

- The presence of *a* bromine atom and **a** chemical feature that makes a molecule prone to rapid decomposition in the troposphere are a winning combination. Eight (8) bromolluoroalkcnes appear to have flame extinguishment concentrations not far from that of CF_3Br. Inhalation toxicity screening data for these compounds should be available soon. An additional 8 bromofluoroamines appear promising and have been targeted for synthesis or acquisition.
- **A** number of liquid and solid phosphorous-containing chemicals (PCC) are used as flame retardant additives in plastics. For many of those, the retardancy occurs in the gas phase. and PCCs thus merit serious consideration as fire suppressants. Moreover, the atmospheric lifetimes of these chemicals are expected to be sufficiently short (on the order of days) that thcy will not create any global environmental problems. NGP research indicates that lor most binding states of phosphorus, the flame suppression effectiveness is high and largely determined by phosphorus loading, so candidates can be selected on the basis of physical or toxicological properties. (There is a range of toxic potency, with a general tendency to increase *as* the oxidation state of the phosphorus decreases. Most PCCs also have high boiling points, so to be used *as* total-flooding agents, they would need to be carried on *a* powder or dispersed using a solid propellant gas generator.) Possible exceptions to this are the phosphorus nitrides, for which conflicting fire suppression efficiency data exist. Approximately a dozen PCCs are being examined more closely.
- Many organosilicon materials are stable, inert, and have low toxicities. Those with an oxygen linkage should have low atmospheric lifetimes. This suggests that adding bromine could provide a compound with good fire suppression capability while maintaining good environmental characteristics. Some fluorination is needed to reduce the boiling points. **A** small set of thcsc chemicals is being prepared for screen testing.
- Fluorinated amines and ethers are reported to be nonflammable and, in some cases, to act as fire extinguishants. Most have boiling points too high lor total-flooding use. However, NGP calculations on $C_4F_9OCH_3$ indicate an extinguishing concentration near that of Halon 1301, combined with **a** short atmospheric lifetime. This compound is EPA-approved for use as a solvent.
- This indication for $C_4F_9OCH_3$ is an example of a broader finding, that is, there are compounds that manifest reasonable flame quenching efficiency with little chemical interference in flame propagation. Examination of over 1500 potential thermal agents identified about 25 compounds that might be suitable as firefighting agents, and in fact some are already

being used as halon replacements. A variety of families including ethers, furans, amines, and straight-chain hydrocarbons are represented. Almost all are highly fluorinated.

Suppressant Screening Tests

Of the large number of chemicals to be considered in the search for replacement suppressants, many have been and will be discarded from further consideration based on available information. For the rest, screening tools are needed to enable rapid identification of those relatively few agents whose propriety should be investigated aggressively. These tools should be quick, inexpensive, and require little of the agent.

A measure of fire suppression efficiency is mandatory. The NGP has developed the first bench-scale suppression screen for comparing the flame extinction performance of both gases and liquids. The suppressant, added to the air flow past a cylindrical porous plug burner, sharply blows off the leading edge of the flame. The flow facility and the burner may also be made suitable as a screening tool for powders. Fabrication drawings and an operations manual are being prepared for distribution to interested laboratories.

A second apparatus is being developed for screening the effectiveness of a short burst of suppressant (such as would emerge from a solid propellant gas generator), both in quenching open flames and those stabilized behind an obstruction.

Of comparable interest is the development of a screening protocol and screening methods for the compatibility of agents with (1) people (toxicity). (2) materials used in the storage container for the agents and that the agent might contact after discharge, and (3) the environment. NGP research staff convened the experts in these fields, compiled a hierarchical roadmap through the maze of properties of interest, and identified the best screening tests for the key properties.

New and Improved Aerosol and Powder Suppressants

For some applications, clean (volatile) suppressants are not essential. While fine water mist and efficient powders have been the subjects of real-scale testing, the approaches to date have not met with universal success. As with gaseous and vapor suppressants. NGP research is directed at finding new approaches to condensed phase candidates and ways to improve the use of current suppressants.

Prior information about the effect of particle properties on flame suppression effectiveness has been obtained empirically. NGP research is determining the mechanics of how particles interact with flames. The alkali metal atoms released when sodium or potassium bicarbonate powders decompose in and near a flame participate in the chemical tie up of reactive flame radicals. The surface area of the powder particles controls the rate of release of these species into the flame and the subsequent decomposition and flame temperature reduction. The powder particle size and density dictate how closely the particles follow the flame gas velocity streamlines and thus how efficiently the particles reach the most chemically sensitive locations in the flame reaction zone.

In storage facilities and machinery spaces, the quenching of flames from liquid and solid fuels is of concern. NGP research has characterized the flame spread over polymethylmethacrylate (PMMA) as a surrogate **fuel.** The flame speed decreases as the opposing air speed increases, and the flame speed is greater over thinner samples than over thicker ones. Experiments are now underway with water droplets injected over these flames to provide correlations for the optimum drop sizes and velocities for effective extinguishment.

When a liquid droplet with high momentum impacts a burning liquid fuel surface, splashing of the fuel will likely occur. The splashing may generate satellite fuel droplets. which may create an additional fire hazard. There is no published information on this phenomenon. Measurements are in progress to provide a map of the velocity/drop size distributions that are capable of penetrating fires to reach the surface of the combusting material, and calculations are showing the magnitude of surface cooling that can he expected.

Interpreting most of these results and performing the model calculations require thcrmophysical property data for the tluids. A unique set of computer programs for estimating these properties is now operational. As the NGP examines new tluids, some not commercially available, and as solutions emerge as serious candidates (e.g., aqueous sodium lactate), these estimates will become pivotal.

The NGP is examining whether a highly efficient. but otherwise undesirable (e.g., high toxicity or atmospheric contamination) chemical can be stored and transported safely to the fire on an inert carrier. The criteria are stability of adhesion of the agent to the host powder at ambient temperatures, sufficiency of loading of the agent on the powder, and rapidity of release in the tlame zone.

- Guidance is emerging on the volatility of organometal complexes that are highly efficient suppressants, but often are toxic. Their relative volatility is dependent on the central atom, with the order of volatility generally being as follows: Al < Cu < Mo < Mn < Ni < Cr < Sn < Ti < Fe < Co < Sb < Pb < Ge. For the organic moiety. the order of increasing volatility was generally the following: oxalate < acetate < acetylacetate < methoxide < cthoxide < trifluoroacctylacctate < hcxatluoroacetylacetonate. Encapsulation of the compounds in matrices. such as alumina, decreased the volatility of the compound sharply. suggesting that it is unlikely that these would he very effective as fire suppressants.
- NGP researchers have examined the possibility of using dendritic ("tentacled") polymers as fire suppressants, perhaps with chemically active atoms bonded to the structure. Preliminary analysis shows that the "pure" dendrimers showed fire suppression effectiveness very similar to water, indicating that the polymer carrier is essentially inert and not detrimental to fire suppression properties. The dendrimer-alkali salt solutions were only about 20% more effective than pure water or **small** molecule salt controls.

Viability of New Suppression Technologies

The success of new NGP technologies requires (1) that the laboratory research replicate the suppression phenomena in real-scale fires and (2) that the NGP he able to demonstrate that candidate fire suppression methods are quenching flames as they would under the threats experienced in the field. Meeting both of these needs entails improved instrumentation in the test articles already owned by the military department laboratories.

Making these measurements of concentrations of fuel, oxygen, suppressant, and harmful combustion hyproducts during and after the fire suppression process requires groundbreaking advances in instrumentation. In many of these tests. the fire may be ignited by explosion of a shell, requiring both rapid data acquisition during a period of shock and vibration. High temperatures and rapidly changing flow patterns further complicate the measurements, Fortunately. industrial and academic researchers have developed new instrumental capahilities. NGP staff are building on these and adapting them to the harsh environments experienced during fires in aircraft, ships, and ground vehicles.

- For the first time, near-infrared tunable diode laser absorption spectroscopy (NIR-TDLAS) has been used for measurements during suppression of crew and engine compartment fires in ground vehicles. Oxygen concentrations have been measured during the 250 msec time-to-suppression of the fireball, providing the first glimpses of the mixing processes during this violent event.
- HF is a corrosive and toxic degradation product of any of the fluorinated fire suppressants (e.g., HFC-227ea and HFC-12.5) currently under consideration as replacements for Halon 1301. Excessive generation of **HF** is a principal deterrent to the deployment of these agents. The first in-situ, time-dependent measurements of the concentration of HF, its dissipation, and its amelioration by additives to the suppressant have now been recorded.
- Improving the spatial resolution of such measurements will require a fiber optic probe system capable of operation at elevated temperatures. NGP scientists have designed a probe for use at temperatures up to 1200 **K** in the presence of powder, smoke, and fine water mist. Using commercially available components where possible, a prototype design contains integrated diode laser fiber optics. Laboratory tests have shown that the probe provides an adequate signal for monitoring species concentration.

The NGP team has also developed a cell for use in measuring the high temperature ($\leq$ 1000 **K)** infrared properties of candidate suppressants. This information enables finding spectral lines for NIR-TDLAS detection and developing calibration curves for the temperature-dependent sensitivity of the measurements.

Measurement of the distribution of the suppressant is essential, initially to characterize the fire extinguishment process and later for certification of a suppression system. Since there are likely to be a multiplicity of candidate agents, with potentially different capabilities of being monitored. the NGP is developing two methods of detection, based on two distinct principles. It is expected that at least one of these will be suitable for each agent and each weapons system application.

- Laser-induced breakdown spectroscopy (LIBS) involves shattering the suppressant molecule and monitoring the breakdown products. NGP laboratory capability has established detection limits for Halon 1301 and several candidate halon alternatives.
- Improvements are being made to the prototype Differential Infrared Agent Concentration Sensor (DIRRACS) developed under a prior DoD program. A new design overcomes flow velocity effects on the measured concentration and on vibrations of the IR source and other optical components.

Better Suppressant Delivery

Fire suppression tests in the military departments' real-scale simulators show that Halon 1301 was so effective and inexpensive that extra suppressant was used to compensate for the engineering simplicity of the delivery and dispersion systems. In searching for retrofit alternatives for situations where storage weight and volume are limited, it is likely that some solutions will arise from improving the delivery system. This would enable use of an agent of only moderate efficiency.

Two principal reasons for overdesigning the Halon 1301 systems are the transient release of the suppressant and the presence of numerous obstructions or clutter. NGP engineers are determining the penalties imposed by these. They find that extinguishing concentration decreases with increasing injection period (longer residence time at proportionately lower concentration). The extinguishing concentration and injection period decrease as the air flow increases. At high flows, there is a minimum agent mole fraction below which no extinction occurs; there is a minimum injection period, below which the flame can not he extinguished, even at high concentrations. These rcsults will both quantify the potential gains from redesigning distribution systems and assist in screening for the effectiveness of candidate suppressants.

Replacement fluids must function within the cxisting distribution plumbing. Replacing the piping is a major cost in retrofit and is to be avoided. Thereforc one has to know how *a* new. multiphase chemical will behave in a long run of bent pipe. A new computer code for prediction of two-phase fire suppressant flows during discharge is now operational. It is derived from RELAP5, a computer program used to predict such flows, primarily for nuclear plant transient and accident analyses. It solves field equations for seven primary variables **as *a*** function of time and distance: pressure, phasic specific internal energies, vapor volumc fraction or void fraction. phasic velocities. and noncondensable quality. The modified code was successfully tested against previous expcriniental data for Halon 1301 dischargc. The code, portable to a variety of commonly used operating systems, will soon he modified to handle dissolved gas.

Construction of the facility to verify the suppressant flow and discharge predictions has been completed. The advanced instrumentation redefines the state-of-the-art in measurements of the instantaneous mass flow of fluid during transient discharge from the source vessel, fluid temperatures along the discharge pipe using film thermocouples with response times in the order of milliseconds, and the void fraction. using *a* capacitance sensing probe. Upon completion of the instrumentation, the apparatus will be tested under a wide range of operating conditions, generating parametric data for both Halon 1301 and HFC-227ea.

While several weapons systems incorporate a two-shot capability, there has always been reliance on the use of a singlc suppressant. One **of** the new concepts the NGP is exploring is the use of a dry powder ($NaHCO_3$ or $KHCO_3$) to suppress the fuel spray deflagration in **a** combat vehicle crew compartment, followed by *a* discharge of water mist to mitigate the inhospitable environment produced by the dry chemical discharge. Tests showed that the fireball could he extinguished near the 250 msec required and that modest quantities of water mist could effectively remove the dry chemical particles from suspension.

WHAT LIES AHEAD?

There is a broad spectrum of research yet to he performed if the NGP is to meet its goal of providing weapons platform managers with feasible alternative approaches for the retrofit of Halon 1301-based fire suppression systems.

- All of the currently selected candidate chemicals will undergo screening to identify those with truc potcntial. and the emerging subset will he subjected to more rigorous evaluation. The search for additional replacement chemicals (tluids and powders) will continue until the full range of possibilities has been considered.
- Research will begin on the use of novel ways of storing, generating and dispensing suppressants, such as solid propellant gas generators. Empirical tests have shown great potential for these. hut have also revealed serious flaws. e.g., excessive temperature. suppressant jetting, and compartment overpressure.

- The research effort into the science of agent and air distribution in the fire compartment will increase. This will provide information on the potential for minimal modifications to dispersion hardware.
- Data gathering and research will begin on retrofit technologies for fuel tank inerting. Ignition prevention or quenching phenomenology differs from flame extinguishment.
- Real-scale experiments with new suppression approaches will he carried out in the military department test fixtures, which will have been outfitted with enhanced measurement capability. These experiments will examine the variables involved in optimizing the new technologies, to verify the predictions from the models of fire suppression performance, and to identify what additional factors need research emphasis.
- The system for evaluating the relative desirability (total cost and performance) of changes to fire suppression systems and procedures will be completed. Input data for the best new technologies will be obtained, and comparative appraisals of the new technologies will be prepared.

Throughout the research, the NGP Technical Coordinating Committee will continue to maintain close contact with the platform managers and the testing and evaluation facilities in the military departments. As appropriate research questions arise, they will become the subjects of NGP investigation.