ADVANCED STREAMING AGENT PROGRAM

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Due to the lower efficiency or uncertain regulatory outcome of first-generation streaming agent replacements for flightline use (150-lb. wheeled, the U. S. **Air** Force (WL/FIVCF, Tyndall AFB) has embarked on a search for superior performing, environmentally acceptable streaming agents. These agents are termed "second-generation" or advanced streaming agents. This paper will describe the **Air** Force Advanced Streaming Agent Program.

Recently, several **Air** Force groups met to discuss the need for clean streaming agents for flightline use (Tyndall AFB, April 18-19, 1994). At this meeting, several conclusions were reached: 1) most near-term streaming candidates have limited production lifetimes due to ODP or GWP; 2) none of the near-term candidates are as effective as Halon 1211; **3)** some of the near-term candidates are more toxic than Halon 1211; and 4) all of the near-term candidates are more expensive. Consequently, **Air** Force decided that no near-term candidate is completely acceptable and that the **Air** Force will retain Halon 1211 until a suitable replacement becomes available.

A suitable halon replacement must satisfy criteria in four categories: effectiveness, environmentally acceptability (low ODP and GWP), toxicity, and cleanliness. Selection criteria have been suggested for advanced streaming agents (Table 1).

TABLE 1. ADVANCED STREAMING AGENT SELECTION CRITERIA

CATEGORY	CRITERIA
ODP	<0.05
GWP	near zero
Atmospheric Lifetime	< 1 year
Extinguishing Concentration	similar to Halon 1211
Boiling Point	> 10 °C
Melting Point	< 60 °C
Vapor Pressure	- 1 kPa @ 0 °C
Materials Compatibility	Non-corrosive @ 85 °C
Stability	< 1 % decomposition per year @ 85 °C
Toxicity	Acute toxicity endpoint LOAEL concentration

The objective of the Advanced Streaming Agent Program is to develop and evaluate advanced streaming agents with equal or greater fire suppression/extinguishment capability than Halon 1211. The advanced streaming agent(s) negligible, if any, global environmental impacts [Ozone Depletion Potential (ODP)/Global Warming Potential (GWP)] compared to Halon 1211. The outcome of the program will be a recommended Advanced Streaming Agent (ASA) for military procurement and a set of specifications and other data that any manufacturer deciding to engage in ASA manufacture can utilize. The overall program encompasses a four-year effort. The program is divided into four phases initiating with the identification of candidates that meet the requirements of an ASA, and then proceeding into a rigorous testing effort designed to generate more specific information on the most promising candidates. Detailed information is comprised of physical properties analysis, chemical stability, tire suppression effectiveness, toxicological evaluation, materials compatibility testing, and operational validation of the recommended agent. The last step is the development of a military specification of the product. Current funding addresses work up through the Laboratory Scale Testing, which is designated as Phase I, and work that determines the feasibility of one highly promising, previously identified streaming agent candidate (Phase II Candidate A), A Workplan that describes tasks needed to complete the entire four-year program has been developed. Figure 1 shows the relationship between the phases. Note that more than one potentially promising candidate may be identified in Phase I, but at different times during the project; therefore, the candidates may enter into Phase II in a staggered fashion. Early identification of likely promising candidates and accelerated funding for Phases III and IV may result in a shorten overall program term.

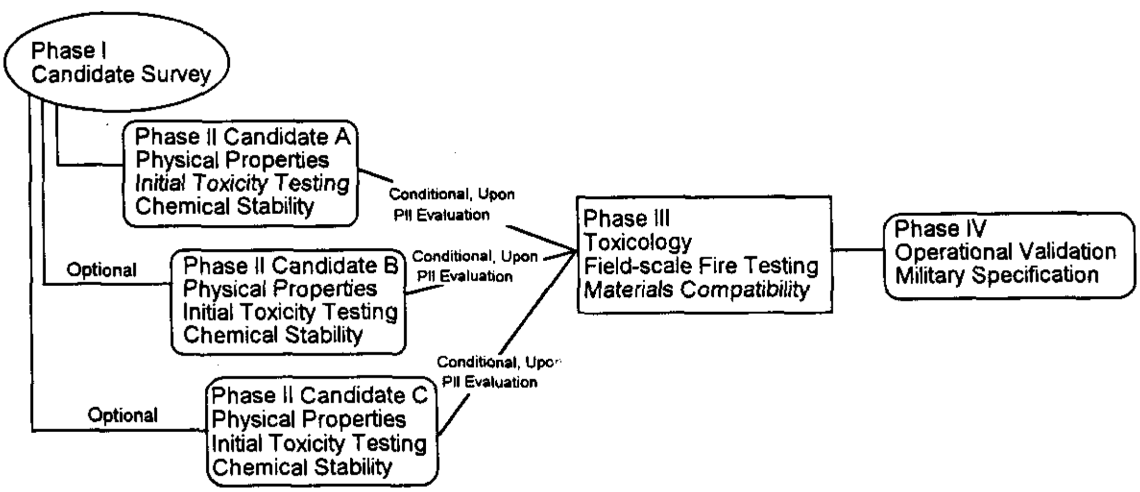

Figure 1. Schematic Relationship of Workplan Phases

PHASE I - ADVANCED STREAMING AGENT PROGRAM

Phase I addresses identification of ASA candidates and testing these candidates up to laboratory scale. This phase is designed to identify a relatively large number of candidates that are to be evaluated predominantly from available or predicted data. In addition, initial fire suppression properties are derived. Phase I covers the following tasks:

Task 1. Expert Panel and Workplan Development

Task 2. Survey Candidates and Fire Suppression Mechanisms

Task 3. Manufacturability and Synthesis Assessment

Task 4. Global Environmental Impact Assessment

Task 5. Preliminary Toxicity Evaluations

Task 6. Initial Laboratory Testing

The final product of Phase I will be a written, camera-ready, final report summarizing the selection criteria and analyses, information on all candidates considered, test performance and results, comparisons of replacement agents with Halon 1211 and conclusions. Finally, recommendations will be made on the ASAs for replacing Halon **1211** that should be evaluated in subsequent phases of the program.

TASK 1 - EXPERT PANEL AND DEVELOPMENT OF WORKPLAN

Task 1 is divided into two parts. The first part was the establishment of a panel of experts who will provide advice on the work to be performed and review the progress of the project. The second part is the development of a Workplan which describes the work needed for a four-year program to develop and evaluate ASAs for military use.

Establishment of Expert Panel

The panel, which is composed of approximately ten members in addition to **NMERI** personnel, was contacted at the initiation of the project and meets approximately every six months to provide advice on work to be performed and to review project progress. The panel review includes technical approach, data collection procedures, interpretation of results, and environmental, regulatory, and safety issues that may have an impact on agent viability. The first objective of this panel was to provide input to Air Force on the criteria that will be used to select chemicals that will enter Phase II. The criteria and their weights are especially important because they are the primary means by which the down selection of agents for further testing is to be accomplished.

Panel members were chosen from the areas of global environmental issues, toxicology, fire suppression technologies, and chemical synthesis and manufacturing. In addition, representatives from the other military services and the U. S. EPA were invited to participate. Other experts may be consulted as required.

Workplan Development

Although Phase I only covers work up through Laboratory Scale Testing, NMERI developed a Workplan for the entire process of testing an ASA through fielding of a new agent The Program Workplan contained descriptions of all required activities and milestones for a projected four-year effort, with particular emphasis on the Laboratory Scale Testing.

TASK 2 - SURVEY CANDIDATES AND FIRE SUPPRESSION MECHANISMS

Task 2 is designed to identify the chemicals that will be investigated throughout the remainder of the effort. Consequently, this is perhaps the most important task in the entire program since it identifies chemicals to be investigated throughout the remainder of the effort. The task commenced with a review of fire suppression mechanisms and development of predictive algorithms that could be used to estimate the fire suppression capability of compounds. Simultaneous with this review, a set of selection criteria against which all the candidates will be evaluated later in the project was established. An initial list of chemical candidates was then developed ("Broad List"). Information on the Broad List of chemicals is currently being collected or predicted focusing on items pertaining to manufacturability, toxicity, environmental issues, physical/chemical properties, and other relevant information. The data on the chemicals will be compared to the selection criteria in a Weighted Attributes Candidate Assessment Matrix (WACAM). Those chemicals or chemical families which best meet the selection criteria will be selected for further evaluation and testing at laboratory scale.

TASK 3 - MANUFACTURABILITY AND SYNTHESIS ASSESSMENT

In Task 3, the manufacturability of candidate streaming agents is being assessed. The initial step is to determine the availability of chemicals from current commercial sources. If commercial sources are not identified, synthetic mechanisms will be proposed. Using advice from the expert panel member(s) on manufacturability, the proposed synthetic routes will be scrutinized and the scale-up potential will be determined. The manufacturability assessment will include estimates of agent cost, production requirements, and time required for production

TASK 4 - ENVIRONMENTAL IMPACT REVIEW

Available information on global, terrestrial, and aquatic environmental characteristics will be collected on the broad list of chemicals. Data on atmospheric lifetimes, ODP, GWP, and environmental fate will be collected or, since most compounds will not have this information known, estimates will be made, if possible. Environmental fate will also be considered at this stage only to provide an indication about whether the specific candidates may pose other environmental problems related to classical terrestrial and aquatic environmental concerns.

TASK 5 - PRELIMINARY TOXICITY EVALUATION

NMERI will perform a preliminary toxicity assessment of the ASA candidates. The assessment will commence by compiling all available toxicological information on the broad list of candidates. In cases where no information is available, estimates of toxicological indices will be made for selected individual compounds. These estimates will be made using available toxicity data by performing either qualitative or quantitative structure activity relationships. This evaluation is needed to avoid expenditures of time or money on developing compounds that could not ultimately be used. The work will be coordinated with EPA, Air Force, and other toxicologists in addition to the Project Officers. Extensive coordination will be done with Armstrong Laboratory (AL/OET) at Wright-Patterson Air Force Base during the entire project since they serve as the primary Air Force expert on these issues. Concerns expressed by the Air

Force, EPA, and other sources about the appropriate toxicity endpoints will be considered in the initial assessments of candidates' toxicities. NMERI will use the toxicity information during the WACAM process to down select the candidate list.

TASK *6* - INITIAL LABORATORY TESTING

Development or Refinement of Cup Burner Method for Room-Temperature Boiling Chemicals

Many of the ASA candidates have boiling points at or near room temperature. Previous experience has shown that with room temperature boiling point agents, it is difficult to obtain reliable and reproducible cup burner values for comparison with other compounds. **NMERI** has developed a cup burner technique to measure the fire suppression effectiveness of room temperature boiling point compounds. However, at best the reproducibility of this method is to within 10 to 15 percent. Additional experimentation has been performed and the initial version of a more refined technique has been developed. This new technique will be further developed to increase the quality of cup burner values for room temperature boiling point compounds. Method development will commence well before candidate agents have been identified for testing.

Initial Flame Suppression Testing

The cup burner fire extinguishment concentration value when normalized against weight and volume is recognized as an acceptable means of comparing halon replacements. Therefore, cup burner values will be determined for the compounds identified during this effort. However, it is also recognized that the cup burner value is not exclusively appropriate for defining and ranking streaming agents.

Development of Laboratory-scale Streaming Agent Test Method

As previously mentioned, it was determined during earlier research that the cup burner value is not always an appropriate parameter for ranking streaming agent replacement candidates. Streaming agent variables not taken into account by the cup burner method include: agent discharge container, nozzles, techniques of the firefighter personnel, flow rates, discharge pattern, varying discharge rate as container volume changes, container fill density, and timing of the test. Limited earlier research efforts focused upon the development of a laboratory-scale streaming test procedure designated the Laboratory-Scale Discharge Equipment (LSDE). The LSDE consisted of a discharge cylinder, solenoid valve, and various nozzles. Nozzle patterns and flow rates (influenced by pressure) were the apparatus variables which most affected result, other than the agent itself. Several compounds were tested with the LSDE and results showed that the cup burner extinguishing concentration was of limited value in ranking streaming agents. Nonetheless. problems were encountered with the LSDE. One such problem was that agent decomposition byproducts were not very well contained and damage occurred to the laboratory fume hood and associated equipment. There was also the danger of these decomposition gases entering and contaminating the laboratory work area. The LSDE experimental technique and results will be revisited during this task and the positive attributes of the experiment will be further refined. **A** laboratory-scale streaming agent method which provides for acceptable emissions control will be developed. Method development will commence early in the project. Baseline testing will be performed using Halon 1211, HFC-123 (FE-232), and FC-6-1-14 (PFC-610). The baseline data will be compared to the available large-scale fire suppression data on these agents.

Testing Candidates in Streaming Test Method

Compounds from the Broad List will be evaluated using the experimental test methodology developed as mentioned above. Results will be used to determine an appropriate fire suppression effectiveness ranking for the selected compounds. Compound which are obviously ineffective in this test will be excluded from larger-scale testing.

Evaluation of Combustion Products using FTIR

While developing the laboratory-scale streaming agent test, decomposition byproduct measurements will be incorporated into the test method. The NMERI Fourier Transform Infrared (FTJR) Spectrometer will be the main analysis apparatus of choice. Decomposition byproduct generation as a function agent application rate, fire size, and fuel will be monitored and reported.

FINAL REPORT

A camera-ready final report which documents the findings of the entire Phase I effort will be assembled. The results of the fire suppression mechanism and candidate surveys will be presented along with the information compiled during the manufacturing and synthesis assessment, environmental review, and toxicity evaluation. The procedures taken during the laboratory evaluation will be documented along with the results of the fire suppression and decomposition testing. The final report will also document a WACAM which down selects to approximately three to five most promising advanced streaming agent candidates recommended for assessment in Phase II. Phase II work will be initiated as candidates are identified. This is likely to occur before the completion of the Phase I final report.

PHASE II

The objective of Phase II of the Advanced Streaming Agent Testing Program is to determine specific data that will establish critical information about highly promising candidates identified in Phase I. Additional physical or chemical property determinations, agent stability, and initial acute toxicity are the focus of this phase. It is anticipated that the best three to five candidates down selected to in the last task of Phase I will progress to Phase II (Figure 2). The outcome of Phase II will determine which, if any, candidates will progress to Phase III.

TASK 1 - PHYSICAL/CHEMICAL PROPERTY ANALYSIS

For candidates that are lacking data on certain physical properties that are necessary for thorough feasibility evaluation, these properties will be determined in this task. For example, room temperature density measurements and vapor pressure between approximately -60 and 160°F will be measured in addition to the evaporation rate at ambient temperature for liquid agents.

TASK 2 - CHEMICAL STABILITY

The chemical stability of candidates will be evaluated as it relates to shelf-life by conducting a series of *6* month stability tests at 80 and 170^{o}F with both the neat agent and the agent pressurized to 360 psi with nitrogen. Samples will be removed weekly for infrared analysis and monthly for analysis of solids and other potential chemical species not analyzable by IR.

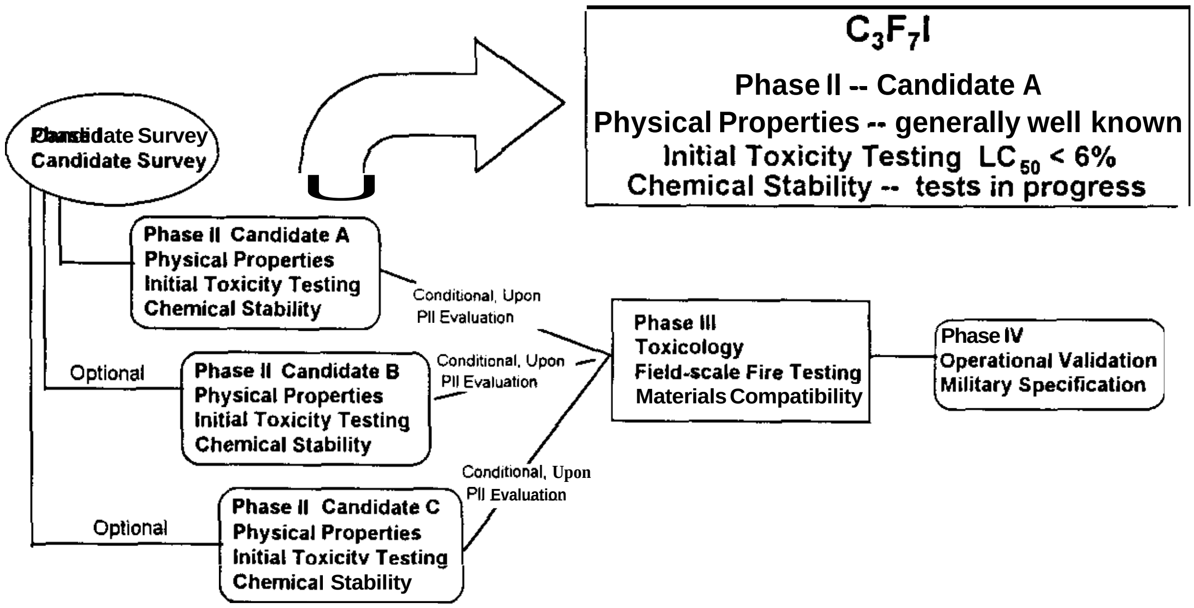

Figure 2. Program Schematic Identifying Phase II Candidate

TASK 3 - TOXICOLOGY

For candidates lacking known acute toxicity information, a number of toxicological tests will be performed in coordination with Armstrong Laboratories. In order to preliminarily assess the acute toxicity of a candidate in a cost effective manner, a modified limit test will be performed. This modified limit test is an adaptation of the U.S. EPA's acute inhalation "Limit Test" as described in 40 CFR Ch. I(7-1-09 Edition) §798.1 150. Since agents are likely not to be available in substantial quantities the modifications allow for the test to be performed in rats by nose-only inhalation for 15 minutes at a concentration approximately twice the extinguishment concentration as determined by the cup burner or other appropriate tests. The test animals are then observed for 14-days after which sacrifice and gross necropsy are performed. For candidates that may be cardiac sensitizers, the lowest and no observable effect levels for cardiotoxicity will be determined through coordination with Armstrong Laboratories.

PHASE III

Phase III of the Advanced Streaming Agent Program addresses work that will be required to further evaluate and field the ASAs qualified under Phase II. Since agent requirements and cost outlays are high for Phase III, only candidates that have successfully passed all the test requirements in Phase II will be carried through Phase III. The work in Phase III commences by progressively increasing the scale of fire suppression testing in an outdoor scenario until the ASA has demonstrated extinguishing ability on 150-ft^2 pool fires and three-dimensional flowing fuel fires. Phase III tasks also investigates the toxicological properties of the candidate(s) and their compatibility with materials which they will come in contact.

PHASE IV

Once the agent or agents have demonstrated large-scale fire suppression capabilities, materials compatibility and toxicological acceptance, a series of tests will be undertaken which will assist in defining the operational conditions under which the agent will function. This will include defining fire fighter exposure scenarios and combustion product assessment under real world conditions and operational fire scenarios which are likely to be encountered by the military. The final effort is the development of a military specification for the agent(s) that will ultimately be used in the military inventory.

CONCLUSIONS

In conclusion, the Advanced Streaming Agent Program is underway at NMERI. The four-year program is composed of four phases, which progress in a semi-staggered fashion. The phases commence with candidate identification and proceed through progressively larger fire size testing and agent validation protocols. The planned final product at the end of the entire four-year effort is an advanced streaming agent that is equivalent or superior to Halon 1211 in performance, but without the detrimental global environmental impacts.