PROJECT ADMINISTRATION DATA SHEET

Project No. A-3191
Project Director: Dr. T. L. Starr
Sponsor: Amerex Corp; Trussville, Al

Date 3/18/82

Type Agreement: P. O. No. 24181-M
Award Period: From 3/9/82 To open (Performance) (Reports)
Sponsor Amount: $2,000
Cost Sharing: Contracted through: GTRI/GPfX
Title: Fire Extinguisher Compounds Decomposition

ADMINISTRATIVE DATA

1) Sponsor Technical Contact:
   David Ellison
   Amerex Corp.
   Box 81
   Trussville, AL 35173
   205-655-3271

2) Sponsor Admin/Contractual Matters: same

Defense Priority Rating: none
Security Classification: none

REstrictions
See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval — Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with N/A

COMMENTS:

COPIES TO:
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Project File
Other

FORM OCA 4:781
SPONSORED PROJECT TERMINATION SHEET

Date 9/8/82

Project Title: Fire Extinguisher Compounds Decomposition

Project No: A-3191

Project Director: Dr. P. L. Starr

Sponsor: Amerex Corp.

Effective Termination Date: OPEN

Clearance of Accounting Charges: 

Grant/Contract Closeout Actions Remaining:

[X] Final Invoice and Closing Documents

[ ] Final Fiscal Report

[ ] Final Report of Inventions

[ ] Govt. Property Inventory & Related Certificate

[ ] Classified Material Certificate

[ ] Other ______________________

Assigned to: EMSL (School/Laboratory)

COPIES TO:

Administrative Coordinator
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Legal Services (OCA)
Library

EES Public Relations (2)
Computer Input
Project File
Other __________
Mr. David Ellison
Amerex Corporation
P. O. Box 81
Trussville, AL 35173

Dear David:

April 22, 1982

I am enclosing my report on the decomposition products from your dry fire extinguisher materials. The additional experiment we discussed with the sulfate material and charcoal again produced no detectable sulfur dioxide.

Concerning the extinguishing mechanism for these materials, my suggestions that the ammonia serves to quench the free radical reactions and the phosphate polymerized to shield the fuel appear to be substantially correct. In support of this, let me quote Dr. Richard Tuve in Principles of Fire Protection Chemistry,

"The mechanism of flame quenching by monoammonium phosphate (multi-purpose), with concurrent deposition on Class A material of a coating of glassy metaphosphoric acid, probably involves union of active H atoms or OH radicals with NH₃ radicals during dissociation of the NH₄ evolved upon decomposition of the compound in the flame. The phosphoric acids remaining from the decomposition may then dehydrate fully to the anhydrous glassy metaphosphoric acid, HPO₃. This postulated mode of action has not been fully investigated."

Since the ammonium sulfate does not polymerize like the phosphate, it can not be expected to provide the same extinguishing capability. Your observation that the 100% sulfate will extinguish wood fires but not heptane fires cannot be easily explained by this mechanism. This only serves to emphasize that too little is known about the fundamental mechanisms of fire extinguishing.

I hope these results meet your needs. Feel free to call me if you have any questions.

Sincerely,

Thomas L. Starr
Energy and Materials Sciences Laboratory
Investigation of Dry Fire Extinguisher Decomposition Products

Performed for: Amerex Corporation, Trussville, Alabama
by: Engineering Experiment Station,
Georgia Institute of Technology

Contract no: A-3191

Background

Dry fire extinguishers consisting primarily of monoammonium phosphate (MAP) are widely used in this country. New formulations containing up to 50% ammonium sulfate are now being tested and may be placed on the market in the near future. The purpose of this limited investigation is to determine if this change in formulation introduces a significant new health hazard to the use of this type of fire extinguisher.

Conclusion

No significant new hazard was found resulting from the use of ammonium sulfate in dry fire extinguishers. As compared to the present formulation using MAP, the acid produced is somewhat more corrosive and a greater amount of ammonia may be formed.

Discussion

In examining hazards associated with fire extinguisher materials, it must be kept in mind that (1) a fire itself is a serious hazard and produces many toxic gases and (2) the present MAP formulation is known to produce large amounts of ammonia in use.

Materials produced in a fire, from combustion of the fuel or from decomposition of the extinguisher substance, are dispersed for various
distances away from the fire. We can divide the area around a fire into three zones as illustrated in figure 1. The hot zone nearest the fire will contain the non-volatile combustion and degradation products. The condensation zone, where the temperature is cooler, will contain those products that are volatile at the fire temperature, but are liquids or solids at normal temperatures. The gas zone will include those products that are gaseous at normal temperatures.

A wood fire, for example, could distribute char and ash in the hot zone, water and polyaromatic hydrocarbons in the condensation zone, and carbon dioxide and carbon monoxide in the gaseous zone.

A combination of experimentation and review of the chemical literature leads us to the conclusion that the decomposition products and their distribution are similar for these two product formulations. Both will produce a strong acid in the condensation zone and ammonia in the gaseous zone. However, some differences do exist in the specific composition and concentration of the decomposition products.

For the two materials, the initial decomposition upon heating is:

\[
\begin{align*}
\text{NH}_4\text{H}_2\text{PO}_4 & \rightarrow \text{NH}_3 + \text{H}_3\text{PO}_4 \\
\text{MAP} & \quad \text{ammonia} \quad \text{phosphoric acid} \\
(\text{NH}_4)_2\text{SO}_4 & \rightarrow 2\text{NH}_3 + \text{H}_2\text{SO}_4 \\
\text{ammonium sulfate} & \quad \text{ammonia} \quad \text{sulfuric acid}
\end{align*}
\]

In both cases, a strong acid is produced which will deposit in the condensation zone. Sulfuric acid is more corrosive and more volatile (would deposit in a somewhat wider area) than phosphoric acid, but generally, the results of two decompositions are similar. Ammonia is produced in both cases and is carried to the gaseous zone. The amount of ammonia
produced by the sulfate will be somewhat greater than by the phosphate due to the stoichiometry of the reactions.

Subsequent reaction of these initial degradation products in the flame is complex and poorly understood. One particular reaction for the phosphate is known to be important:

\[ \text{H}_3\text{PO}_4 \xrightarrow{\Delta} \text{H}_2\text{O} + \text{HPO}_3 \xrightarrow{\Delta} (\text{HPO}_3)_x \]

The polymerized phosphate glass produced by this reaction helps to extinguish the flame by coating and isolating the fuel, and, in addition, reduces the amount of acid carried to the condensation zone. No comparable reaction for the sulfate exists.

Review of the chemical literature suggests that sulfur dioxide could be produced by further reaction of the sulfuric acid in the presence of a reducing agent, such as metal or carbon (char):

\[ \text{H}_2\text{SO}_4 \xleftrightarrow{\text{H}_2\text{O} + \text{SO}_3} \]

\[ 2 \text{SO}_3 + \text{C} \xrightarrow{} 2\text{SO}_2 + \text{CO}_2. \]

However, in experiments performed in this laboratory, no sulfur dioxide was detected under conditions that simulate contact with hot char in a fire. While some sulfur dioxide might be formed by decomposition of the sulfate material under some conditions, we do not believe that this would present a significant new hazard considering the much larger quantities of ammonia already known to result from the formulations.

**Experimental**

A number of experiments were performed to define the nature of the decomposition products from the different extinguisher formulations.
The basic apparatus, illustrated in figure 2, was designed to simulate the decomposition and distribution of materials in an actual fire. A small amount of sample (2-10 mg) was heated in a section of glass tubing. The volatile decomposition products were drawn into a condensation trap maintained at room temperature. The non-condensing gases were then drawn through a gas detection tube. Detection tubes for ammonia and sulfur dioxide (Dräger AG, Fed. Rep. of Germany) were used alternately for each formulation. These tubes can measure 7-70 μg ammonia and 3-125 μg sulfur dioxide in a gas stream. After each decomposition, the condensation trap was washed with distilled water and the pH measured. The results, shown in Table 1, were similar for all formulations: acid is condensed in the trap, ammonia is formed in substantial quantity, and no sulfur dioxide is detected.

In an additional experiment, approximately 50 mg of material was decomposed in 125 ml sample bulb. Analysis of the gas by gas chromatography/mass spectrometry (GC/MS) did not detect sulfur dioxide.

Table 1. Decomposition of fire extinguisher materials

<table>
<thead>
<tr>
<th>Formula</th>
<th>%MAP</th>
<th>% ammonium sulfate</th>
<th>condensate</th>
<th>NH₃</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>95</td>
<td>----</td>
<td>acid</td>
<td>&gt; 70 μg</td>
<td>N.D.</td>
</tr>
<tr>
<td>15</td>
<td>45</td>
<td>50</td>
<td>acid</td>
<td>&quot;</td>
<td>N.D.</td>
</tr>
<tr>
<td>18</td>
<td>75</td>
<td>20</td>
<td>acid</td>
<td>&quot;</td>
<td>N.D.</td>
</tr>
<tr>
<td>15 + charcoal</td>
<td>--</td>
<td>---</td>
<td>----</td>
<td>---</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

N.D. = not detected

Thomas L. Starr
Energy and Materials Sciences Laboratory
April 22, 1982
Figure 1. Fire emission distribution zones

Figure 2. Decomposition experiment