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FINAL REPORT

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June 1995

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FINAL REPORT

Project Sponsored by:	Defence Research Establishment Valcartier P.O. Box 8800 Courcelette, P.Q. G0A 1R0
	DREV Task No: 14/1-1992 (PRRN 22166)
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Executive Summary

The Defence Research Establishment Valcartier (DREV) has developed a number of pyrotechnic smoke producing devices for use by the Canadian armed forces. The successful operation of most of such devices involves the sublimation of a dye and dispersion of its vapour into the surrounding atmosphere where it condenses into a fine cloud of coloured particles. Sometimes, however, these devices unexpectedly burst into flaming combustion destroying the coloured smoke. DREV sponsored a research project at the Royal Military College of Canada (RMC) to investigate the factors that contribute to flaming tendencies of smoke mixtures in general and, in particular, of a white smoke composition incorporating cinnamic acid as the smoke producing agent.

During the first phase of the project, a detailed literature search was undertaken on various aspects of smoldering and glowing combustion in solids. The objective was to determine if this effort would provide guidelines for promoting flameless deflagration in smoke compositions. Smoldering combustion is generally a consequence of a heterogeneous reaction between a solid fuel and oxygen in the surrounding atmosphere and proceeds at very low burning rates. It is not possible to maintain such a form of reaction in smoke mixtures which carry their own fuel-oxidant combinations. During this phase, a theoretical analysis of the aerodynamics of a smoke puff generated by a smoke candle was also carried out to see the effects of the rate of burning of these candles on the subsequent dispersion of the smoke cloud generated. The analysis demonstrated that, from the point of view of perseverance of the smoke cloud, a rapid burning of the composition would be advantageous. The first report submitted on the project cover these topics.

In the next phase of the project, the performance of the new white smoke composition containing cinnamic acid formulated by DREV was analyzed in detail. It was concluded that the great propensity of this composition to flaming was due to the fact that cinnamic acid decomposes into large mole fractions of carbon monoxide and methane, both of which are combustible gases with self-ignition temperatures around the reaction zone temperatures. Any effort to curb the flaming tendency of this composition by reducing the reaction zone temperature is hampered by the fact that such a reduction also leads to slower burning and eventual extinction. A simple thermal analysis that shows the relation between the burning velocity and the reaction zone temperature was presented in the second report covering this phase.

In the final phase of the project, a number of attempts were made to see if the flaming tendency of the cinnamic acid composition could be controlled by other means. These included: (a) the use of other cinnamic acid compounds, (b) providing porous castings for the smoke candles, and (c) the use of flame inhibitors. Unfortunately, none of these efforts proved successful. A further set of experiments was conducted with a new white smoke composition based on ammonium chloride. These experiments demonstrated that a smooth burning candle producing copious amounts of nontoxic white smoke can be fabricated using the new composition. Further, a new binder, which available commercially as a glue, has been successfully tried in these experiments. This binder provides any degree of castability that is desired. It is very much easier to handle than the currently used hydroxy-terminated polybutadiene (HTPB) which in fact is a rocket fuel binder. The work done during the final phase of the project is summarized in the third and final report on the project.

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1. INTRODUCTION

The previous reports of this project [1,2] presented a detailed analysis of the factors contributing to the flaming tendency of the DREV white smoke composition. It was shown that the smoke producing compound used, trans-cinnamic acid, dissociates easily with the products containing large fractions of carbon monoxide and methane, both of which are combustible gases with spontaneous ignition temperatures below the temperature attained in the reaction zone of the burning smoke composition. Reducing the temperature of the reaction zone to alleviate the problem did not prove successful because it led to a decrease in the burning rate and, eventually, extinguishment. A theoretical analysis which demonstrated the relationship between the burning rate and the reaction zone temperature of the composition was also presented. As a consequence of these two conflicting factors, all attempts to control the flaming tendency of the original composition by varying the proportions of its ingredients were unsuccessful.

This report describes further work done in this direction in the final year of the project.

2. EXPERIMENTS WITH OTHER CINNAMIC ACID COMPOUNDS

The Handbook of Chemistry and Physics [3] lists as many as seventy-seven different compounds under the broad classification, cinnamic acid, with forty-seven of them derivatives of trans-cinnamic acid. The compound used in the DREV formulation is the following:

Chemical formula: $C_6H_5CH=CHCO_2H$

Formula Weight : 148.17

Melting Point : 135-6°C

Boiling Point : 300°C

Examining the list of compounds under the same classification, cinnamic acid, two compounds were found which are stated to sublime as smoke compositions are expected to. These are:

(a) 2-Nitrocinnamic acid (trans) (Aldrich Catalog No. N1,640-1)
Formula weight: 193.16
Melting point: 242-3 C
Boiling Point : Sublimes

(b) α ·Phenyl Cinnamic acid (Aldrich Catalog No. P2,200-1)
Formula weight: 224.26
Melting point: 134-5°C
Boiling point : Sublimes

A number of experiments were conducted substituting each of these compounds for the cinnamic acid in the DREV composition. Again, the results were unsatisfactory; the flaming tendency was still clearly present.

3. POROUS CASTINGS

It was felt that if it could be arranged that the cinnamic acid vapour formed near the reaction zone was provided with a quick and easy route to escape from the high temperature zone, the flaming tendency of the composition would be reduced. Such an egress would be provided for the vapour if the smoke composition could be formed into a porous casting. Porous castings of polymers are produced by two means, either mechanical or chemical. The mechanical method of producing porous castings consists of forcing an inert gas, such as nitrogen or carbon dioxide, through the polymer (binder) before it hardens during the curing process. Since this method requires an elaborate set-up and can be done only on a fairly large scale, it was decided to try the chemical method which uses 'blowing agents' that liberate an inert gas *in situ*.

Various manufacturers of such chemical blowing agents for polymers were contacted and samples were obtained from two manufacturers:

1. Uniroyal Chemical Company, Middlebury, Connecticut

   Chemicals: *Celogen* and *Kempore* blowing agents

2. Shell Chemical Company, Geismar, Louisiana

Chemical: *Neodal*

A number of experiments were conducted by mixing these chemical blowing agents in small proportions to the polymer (binder) of the smoke formulation before it was cured. However, it was found that these blowing agents evolve gases in sufficient quantities only at temperatures in excess of 150°C. This temperature is high enough for the Sugar-Potassium Chlorate fuel-oxidizer combination to start reacting [4]. In one case, the smoke formulation ignited spontaneously in the oven when cured at this temperature. These experiments were therefore abandoned.

4. FLAME INHIBITORS

As pointed out in the literature survey conducted in connection with this project [1], there are a number of compounds which suppress flaming of reactive mixtures. The most frequently used such compounds are the antimony-halogen compounds such as antimony trichloride and antimony tribromide. These compounds enter the flame chemistry via a series of reaction steps to neutralize the chain carriers as in the sequence

$$Hbr + OH \rightarrow H_2O + Br$$

$$Hbr + O \rightarrow OH + Br$$

$$Hbr + H \rightarrow H_2 + Br$$

$$Br + H + M \rightarrow Hbr + M$$

$$Br + HO_2 \text{ -> } Hbr + O_2$$

These compounds thus act as 'radical traps' and slow down the reaction rate.

Experiments were conducted with both antimony trichloride ($SbCl_3$) and antimony tribromide ($SbBr_3$). It was found that antimony trichloride was not effective in reducing the flaming tendency at all. The flaming tendency could be reduced by antimony tribromide; however, the proportion of antimony tribromide required to do so was fairly large. This chemical in excess of 5% of the total weight of the composition had to be added to suppress flaming, which is excessive. Further, with such high proportions of antimony tribromide, the colour of the smoke evolved turns dirty brown due to the presence of a large concentration of bromine gas which is a product of dissociation of antimony tribromide.

It is concluded therefore that even though these antimony-halogen compounds may be effective as flame retardants in fires involving cellulosic material, they cannot be used in pyrotechnic smoke mixtures.

5. AMMONIUM CHLORIDE AS A WHITE SMOKE PRODUCING AGENT

Since all attempts to develop a successful white smoke composition based on cinnamic acid compounds proved to be of no avail, attention was turned to see if other compounds could be found to work satisfactorily as white smoke producers.

Most of the white smoke compositions mentioned in the literature are based on zinc and hexachloroethane (HC) combinations. The products of the pyrotechnic reaction are zinc chloride and carbon which produce a greyish white smoke which is stated to be somewhat toxic. It was noted that ammonium chloride has been mentioned as a white smoke producing agent in some old literature [5]. The smoke produced is said to be nontoxic. It was therefore decided to conduct experiments to test the suitability of ammonium chloride for use in white smoke formulations.

The experiments with ammonium chloride proved to be successful almost from the first attempt. After a few trials, the following formulation was evolved which burned well and uniformly producing copious amounts of white smoke.

New White Smoke Formulation

Component	Weight Percent
Ammonium Chloride	42
Potassium Chlorate	28
Sugar	14
Binder	15
Iron Oxide	1

The rate of burning of a pyrotechnic composition is of course dependent on the particle sizes of its ingredients. In the present case, with an average particle size of about 50 μm of the ingredients, the burning rate was about 0.5 mm/s. The rate can be decreased by the addition of a 'cooling agent' such magnesium carbonate as required. On the other hand, the burning rate can be increased with the addition of small amounts of aluminum powder to the composition. The progress of the reaction front is smooth and uniform and there was no interruption in the burning until the entire composition was consumed. There was absolutely no flaming tendency.

Figures 1 and 2 are photographs of small specimens of this formulation burning inside a fume hood. Figure 1 shows a cylindrical specimen of about 3 cm in diameter burning with evolution of white smoke while Figure 2 shows burning of the same composition enclosed in a cylindrical cardboard tube.

Variants of the basic formulation given above can be employed in different applications. It may be recalled that a theoretical analysis presented in a previous report [2] shows that a fast burning composition produces a dense puff of smoke with little dispersion. Such a puff will be visible for a longer period than the puff from a slower burning composition that produces a larger less dense puff.

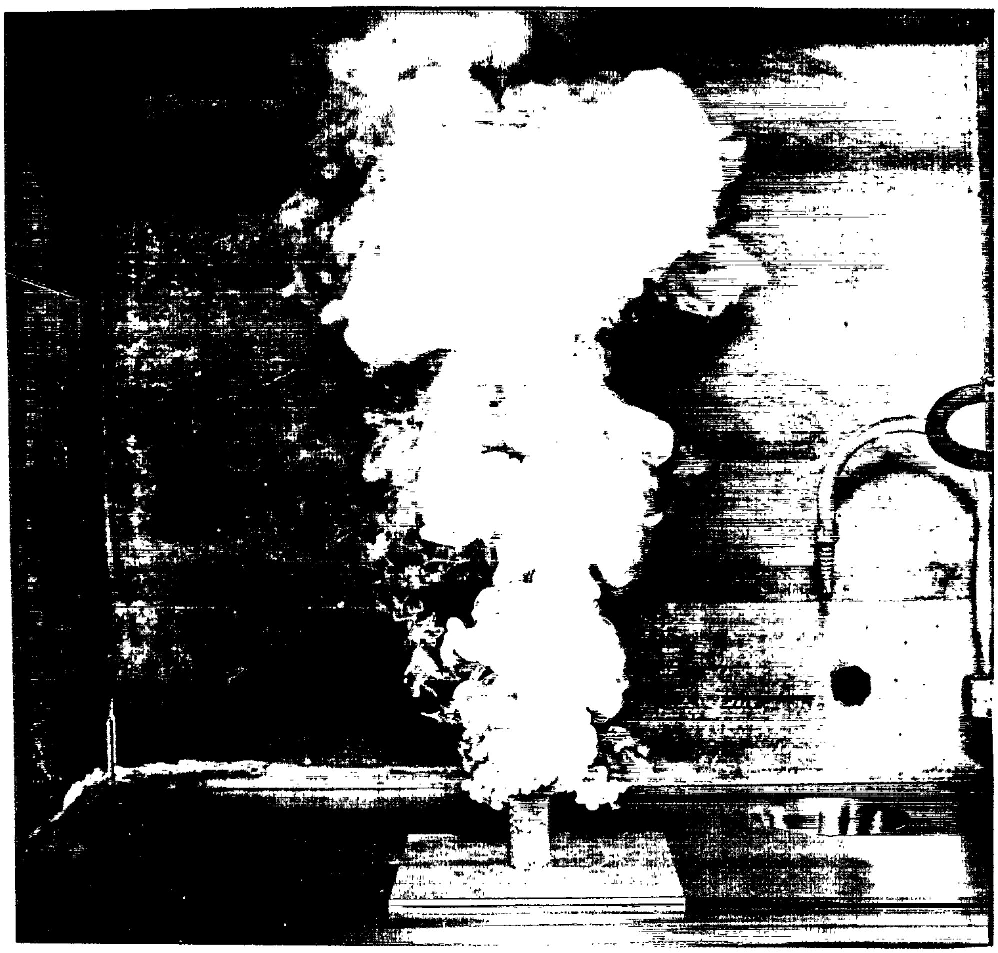

Figure 1: Candle Made With Ammonium Chloride Smoke Formulation Burning in the Open

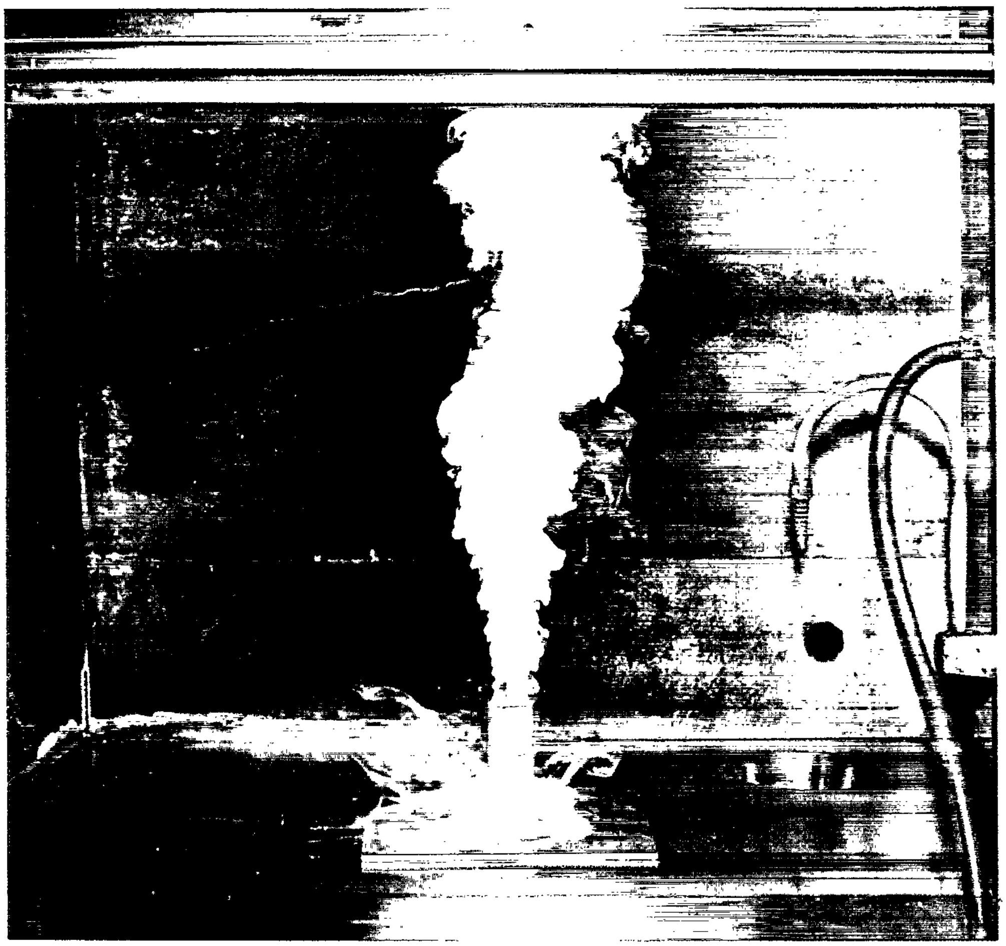

Figure 2: Ammonium Chloride Smoke Formulation Burning Inside a Cardboard Cylinder

6. NEW BINDER

The binder currently employed by DREV in their smoke compositions - HTPB polymer with curing and plasticizing agents - though successful, is cumbersome to use on a small laboratory scale as it requires careful mixing and curing. It was therefore decided to explore the possibility of using commercially available premixed polymeric adhesives as binders for these formulations. After a few trials, it was found that a commercial adhesive marketed under the name "Two-Coat Rubber Cement" by LePage's Limited, Brampton, Ontario, constitutes an excellent binder for these applications. This adhesive is a solution of a mixture of polymers in a petroleum-based solvent. Typical properties of this product are listed below:

Colour	clear, colourless
Form	viscous liquid, 11% solids
Base	natural rubber
Specific Gravity	0.70
Viscosity	2,900-3,200 cps @ 10 rpm/24°C
pH	not applicable, non-acidic and non-corrosive

This binder can be mixed easily with the other ingredients of the formulation and the mixture dries to a rubbery solid a few hours. There is no need for curing in an oven as with the HTPB binder. The castability of the smoke composition can be improved by thinning the mixture with the solvent. The ease of handling and processing this binder makes it worthy of serious consideration by DREV for use in all its smoke formulations.

7. CONCLUSIONS.

1. Smoke formulations containing cinnamic acid compounds have a marked flaming tendency which is difficult to control. The reason is that these compounds dissociate into carbon monoxide and methane which are combustible gases.
2. Antimony-halogen compounds which are effective flame retardants in fires involving cellulosic material are not effective with these compounds.
3. Ammonium chloride is an excellent white smoke producing agent. The smoke produced is said to be nontoxic; however, this has to be verified by clinical trials. The rate of burning of smoke formulations based on ammonium chloride can be controlled as desired. The rate can be decreased by the addition of inert agents such as magnesium carbonate or increased by the addition of fine aluminum powder.
4. A commercially available premixed polymer adhesive makes an excellent binder for use in castable pyrotechnic smoke compositions.

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