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TECHNICAL REPORT AFATL-TR-74-92 THE INFRARED SIGNATURE OF PYROPHORICS AD921319 **AEROS**³ACE TARGETS BRANCH AIR-TO-AIR MISSILES AND TARGETS DIVISION RORMAR MAY 1974 9 1974 AUC <u>GGGUU</u> B FINAL REPORT: January 1973 to May 1974 Distribution limited to U. S. Government agencies only; this report documents test and evaluation; distribution limitation applied May 1974 . Other requests for this document must be referred to the Air Force Armament Laboratory (DLQT), Eglin Air Force Base, Florida 32542. AIR FORCE ARMAMENT LABORATORY AIR FORCE SYSTEMS COMMAND . UNITED STATES AIR FORCE EGLIN AIR FORCE BASE, FLORIDA

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above 200 watts/steradian/gram/second and (4) had an ignition time between 5 and 20 milliseconds. A second series of tests were performed with a co-flowing airstream created by releasing air into the vacuum chamber through a choke. These tests demonstrated the significant effect of airflow on the radiant intensity of unchoked exhaust plumes. A chemical equilibrium computer program was used to gain insight into other parameters affecting infrared radiation. Plume temperatures and the distribution of significant exhaust species were computed as a function of mixture ratio.

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PREFACE

The work reported herein was conducted in-house at the Air Force Armament Laboratory, Eglin Air Force Base, Florida, in support of Program Element Number 62602F under Project Number 19210301, entitled "Infrared Plume Simulation Technology." The work was conducted by Dr. D. B. Ebeoglu, Lt C. W. Martin, and Mr. D. F. Fink. Dr. K. E. Harwell, Professor of Aerospace Engineering at Auburn University, contributed to the project as a consultant. The work was performed during the period of 1 January 1973 to 1 May 1974. Experiments were conducted jointly with Dr. N. M. Rosenberg and Mr. K. E. Vickery of the Air Force Cambridge Research Laboratory (AFCRL/LKC), L. G. Hanscom Field, Massachusetts, to determine the infrared signature characteristics of pyrophoric materials.

Parts of the effort described in this report have been reported in three papers authored jointly with AFCRL and presented outside the laboratory. The first entitled, "Infrared Emission from Liquid Pyrophorics" was presented to the 11th Infrared Information Symposium (IRIS) on Targets and Countermeasures, 10 - 11 April 1973 at White Oak, Maryland. The second, entitled "Pyrophorics as IR Decoys" was presented to the Air Force Systems Command Science and Engineering Symposium, 12 - 14 October 1973, at Kirtland Air Force Base, New Mexico. The third, entitled "The Infrared Signature of Pyrophorics in Static and Dynamic Environments" was presented to the 12th IRIS Symposium on Targets and Countermeasures, 3 - 4 April 1973 at Fort Monmouth, New Jersey. These have been or are being published by the respective sponsor organizations.

This technical report has been reviewed and is approved.

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JOHN W. JOHNSON, Acting Chief Air-to-Air Missiles and Targets Division

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SECTION I

INTRODUCTION

A series of laboratory experiments were conducted to study the infrared signature of pyrophoric materials at high altitudes and at subsonic air velocities in order to evaluate their potential application as infrared sources for aerial targets. Pyrophorics were burned in large vacuum chambers at static conditions to determine ignition characteristics and to study the infrared signature as a function of altitude. The vacuum chamber simulated the earth's atmospheric pressure up to a height of 60,000 feet. Airstreams were introduced into the vacuum chamber through a choke to impinge on the burning pyrophorics. Air velocities up to 300 feet per second were created and the infrared radiation intensity was measured as a function of air velocity.

Infrared signatures were determined for six pyrophorics mixtures that have acceptable freezing points (i.e., below -67°F, the minimum temperature up to an altitude of 65,000 feet) with the exception of triethyl boron (TEB) whose fumes posed a potential health hazard. Pyrophorics mixtures were atomized in a mixing nozzle by nitrogen at a pressure of about 100 psia. Ignition occurred spontaneously with the air in the vacuum chambers at all altitudes. The spectral distribution of the infrared signatures were measured during static ambient experiments together with intensity in two bands, generally 2.5 to 3.3 microns and 4 to 5 microns. All the data were taken at 30-degree and 90-degree aspect angles as measured from the tail.

The pyrophorics mixtures consisted of: (1) Triethyl aluminum (TEA), (2) Diethyl aluminum chloride (DEAC), (3) Diisobutyl aluminum Hydride (DIBAH), (4) Tri-n-propyl aluminum (TNPA), (5) 90 percent trimethyl aluminum (TMA) and 20 percent TEA (by weight), and (6) 60 percent diethyl aluminum Hydride (DEAH) and 40 percent TEA (by weight).

Kerosene was used to provide the comparison infrared performance of a conventional hydrocarbon. A computer program (Reference 1) developed at the National Aeronautics and Space Administration (NASA) was used to calculate mole fraction distribution of exit species and temperatures for all the pyrophorics as well as the kerosene.

Reference:

^{1.} Gordon, S. and McBride, B. J., <u>Computer Program for Calculation of Complex Chemical Equilibrium Compositions</u>. Rocket Performance. Incident. and Reflected Shocks and <u>Chapman-Jouquet Detonations</u>, NASA SP-273, NASA-Lewis Research Center, Cleveland, Ohio, 1971.

SECTION II

EXPERIMENTAL CONDITIONS

The experiments were conducted at two similar vacuum chambers located at the Armament Development Test Center (ADTC) at Eglin AFB, Florida, and at the Naval Weapons Center (NWC), China Lake, California. Figure 1 shows the experimental arrangement of the Air Force Chamber (Reference 2). The flow system used for the pyrophorics experiments is shown in Figure 2. The acronym TMA is used for simplicity to mean pyrophorics; the same system was used for all the mixtures.

The combustion geometry chosen was that of an exhaust plume, since the primary objective was to determine the infrared performance of pyrophoric materials as extended sources for subscale target drones. In order to create a plume, a mixing nozzle was used to mix nitrogen with and atomize the pyrophorics mixtures. Flow rates were chosen so that the plumes created would fall entirely within the field of view of the radiometers within the limited confines of the vacuum chambers used.

Pyrophoric mass flow rates ranged from 1 to 5 grams per second. Nitrogen at 100 psia was used to pressurize 5-gallon. or larger, bottles containing the pyrophorics. A separate nitrogen line at approximately the seme pressure and having a flow rate approximately one-tenth that of the liquid fuel was used to atomize the mixture via a mixing nozzle. Mass flows were measured with a turbine flow meter as well as glass flow meters. Quartz crystal pressure transducers and charge amplifiers were used to monitor pressure. Kerosene was used to purge the system via vent lines going outside the facility.

The mixing nozzle which resulted in the most effective atomization of the pyrophorics mixtures is shown in the top right hand corner of Figure 2. Other mixing nozzles either did not create an adequately fine spray (producing several jets instead of a plume) or became rapidly clogged with Al₂O₃ deposits around the exit plane. Both problems would have precluded any kind of accuracy in relating the infrared radiant intensity to mass flow rate. The mixing nozzle was connected in reverse to usual practice to prevent clogging. Normally, liquid fuel would enter into the small central section of the nozzle.

In addition, it was found necessary to fashion a 'flameholder' around the mixing nozzle during the co-flowing air experiments. This device, which is shown in two views in Figure 3, permitted enough air to ignite the pyrophorics while serving to deflect the forces of the airstream. Figure 3 also shows the settling chamber and exit port of the blow down system at the NWC facility.

Reference:

2. Long, J. F., Ebeoglu, D. B. and Harwell, K. E., <u>Infrared Plumes Simulation Test Facility</u> <u>Handbook</u>, AFATL-TR-74-15, Eglin AFB, Florida, January 1974 (Unclassified).







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SECTION III

EXPERIMENTAL RESULTS

1. IGNITION TIME MEASUREMENT

The time required for a given pyrophorics mixture to ignite after contact with the atmosphere was determined at static ambient conditions simulating altitude to 60,000 feet. The technique used is illustrated in Figure 4.

A laser beam was made to intersect the exit plane of the mixing nozzle perpendicular to its axis. Radiation from the beam was collected by a photo diode and displayed on a scope. The commencement of atomized flow of the pyrophorics through the mixing nozzle attenuated the laser beam and established the time of contact with the atmosphere. The subsequent spontaneous combustion of the pyrophorics was detected as an increase in the photodiode signal above that produced by the laser beam. The time required for the output to go from the attenuated level to its maximum then gave the ignition time. The ignition rate can be determined from the slope.

A typical scope trace is shown at the bottom of Figure 4. The data show ignition time to vary between 5 and 10 milliseconds for all the pyrophorics tested.

2. SPECTRAL RADIANT INTENSITY

The relative spectral radiant intensity distribution in the 2 to 5 micron band for the six pyrophorics materials investigated is shown in Figures 5 through 10. Figure 11 shows the spectrum of a typical conventional hydrocarbon, kerosene, obtained in the same manner. The spectra all show that the radiation emitted in the 2 to 5 micron band is produced solely by CO_2 , which is emitting in a band centered around 4.2 microns, and H_2O and CO_2 , together emitting the band centered around 2.8 microns. These data were taken with an interferometer spectrometer placed approximately perpendicular to the plume axis at a distance of 7 feet from the plume. The field of view of the instrument covered a circle with a diameter ranging between 0.4 and 1.5 inches on the plume. All the data shown were taken around a point about 12 inches from the nozzle. Due to the close proximity to the plume, the characteristic CO_2 atmospheric absorption gap is not evident in the data.

Radiating species, other than CG_2 and H_2O , are not immediately identifiable. They could be emitting in and around the two major radiating bands but are clearly not dominant. No greybody radiation was apparent in the radiation spectrum resulting from the combustion.

Except for TNPA, which might have been inhibited by the atomizing nitrogen, the pyrophorics and kerosene have spectra that do not differ greatly. TNPA appears to show the emission spectrum of methane. The flame did not resemble that produced by the others at visible or infrared wavelengths, although combustion occurred at altitudes from sea level up to 60,000 feet. However, other infrared data¹, obtained with a direct release of this material at sea level, show it to have a radiant intensity similar to the other materials investigated. The combustion of TNPA would thus appear to be quite sensitive to the nitrogen used to atomize it or to the release geometry.

¹Personal Communication, Avco Systems Division, Wilmington, Massachusetts, September 1973.



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3. RADIATION FIGURE OF MERIT

In order to obtain a quantitative comparison of infrared performance, the radiant intensity measured by the radiometers was normalized to a radiation figure of merit, J, by dividing watts/steradian, J, by the mass flow rate of liquid fuel. In the case of countermeasures, this must be regarded strictly as a relative unit which can be used to assess the merit of one mixture over another. The absolute value of the figure of merit for any countermeasure will depend on additional major factors including weight and volume of the released amount, aerodynamic drag on the canister used, flight velocity and choice of additives.

Table 1 summarizes the average figures of merit observed at 30,000 feet static altitude, at an aspect angle of 30 degrees from the tail and over three infrared bands. The 4 to 5 micron data encompasses the CO₂ band and the 2.5 to 3.3 micron data covers a large portion of the H_2O band. The data show no discernible change in total radiation with variations in altitude between sea level and 60,000 feet in the absence of a wind stream.

TABLE 1. AVERAGE FIGURE OF MERIT OF SOME PYROPHORIC MATERIALS AT 30,000 FEET				
MATERIAL	Figure of Merit (watts-sec/ster-gm)			
IR BANDS	3.9 μ - 5.05μ	3.6 µ - 4.5 µ	2.5 µ - 3.3 µ	
Kerosene	97	126	94	
TMA/TEA	115	278	228	
DEAC	170	225	147	
DEAH/TEA	174	295	196	
TEA	183	311	237	
TNPA	0.3	1.07	2.11	

Greybody radiation did not appear to be associated with the combustion. Direct greybody radiation superimposed on plume CO₂ and H₂O radiation is shown in Figure 12 for a steel place placed in a propane/oxygen exhaust plume. None of the pyrophorics spectra exhibited this type of radiation spectrum.

The major differences to be found between the infrared signature of the pyrophoric and the kerosene are simply: (1) The total radiation emitted in a given band, and (2) the relative amount of CO_2 versus H_2O radiation. Combustion of the fuel occurs with the ambient oxygen in the atmosphere in all cases. It can be concluded that pyrophorics produce approximately twice as much infrared radiation intensity per unit mass flow rate as that produced by kerosene under these circumstances.



The figure of merit produced by using nitrogen to atomize a liquid fuel, however, is not a maximum. The condition for producing maximum radiation was explored further in a later experiment. In this case, kerosene was atomized and mixed with oxygen rather than nitrogen and the O/F ratio was varied. It was determined that the figure of merit for the kerosene is inversely proportional to the O/F ratio for both radiating infrared bands as shown in Figure 13. J becomes larger either if the oxygen flow rate is decreased or if the kerosene flow rate is increased.

These data then show that kerosene is capable of a higher figure of merit than that shown in Table 1 if it is burned at more favorable O/F ratios. They also indicate that an inert gas, rather than nitrogen, would be a better choice for an atomizer in any application where it might be necessary and where maximum radiant intensity is sought. It is postulated that the figure of merit for any of the pyrophorics will exhibit similar dependence on O/F ratio as shown in Figure 13 for kerosene.



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SECTION IV

EFFECT OF A CO-FLOWING AIRSTREAM

The effect of a co-flowing airstream of even moderate velocity on the plumes created by the mixing nozzle is quite severe. Figure 14 shows sequential photographs depicting the significant reduction in plume volume going from static conditions to co-axial airstream velocities of 100 feet per second and 300 feet per second. At the higher air velocity, the flame is almost extinguished.

Infrared radiant intensities were measured for air velocities up to 400 feet per second up to an altitude of 40,000 feet. Figure 15 shows the variation of the figure of merit with the velocity of an airstream applied co-axially behind the nozzle. At 190 feet per second, the infrared intensities were about 25 times larger than at static conditions. At 120 feet per second, intensities were reduced by a factor of 5-6 and a reduction of 2-3 was observed at 60 feet per second.

It is quite clear, from these results, that low velocity exhaust plumes would have very limited use as infrared simulation sources in aerial targets. Exhaust gases traveling at velocities lower than the co-flowing airstream are rapidly dispersed and cooled, emitting little or no infrared radiation. A flameholder helps in maintaining external combustion over a relatively short distance from the exit plane. It is doubtful, however, that a flameholder could be devised to act as a shield over a significant length of plume.

It appears, therefore, that the plume exhaust velocity must be nigher than (or at least equal to) that of the co-flowing airstream if the plume is to maintain its integrity and thus radiate over a significant volume. On the other hand, previous data have shown that the highest radiation, under static altitude conditions, is produced by unchoked (or subsonic) exhausts. The following conclusions can thus be reached: (1) Unchoked exhaust plumes cannot be used as infrared simulation sources in supersonic aerial targets. (2) Unchoked exhaust plumes might be used as infrared simulation sources in subsonic targets at low target velocities. Careful trade-offs must be made, in this instance, between gas velocities over the plume volume, simulator chamber pressure, and target mission altitude/velocity profiles. (3) The optimum relationship for infrared simulation between airstream and exhaust gas velocities under choked conditions is not fully known. Expansion ratios for choked plumes to be used in supersonic targets can only be selected when this relationship is determined.



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STATIC PLUME

- MIXING NOZZLE WITH FLAME HOLDER PYROPHORICS MIXTURE
 - 20 40 THOUSAND FT ALTITUDE



Figure 14. Effect of Co-Flowing Air on an Unchoked Exhaust Plume





SECTION V

ANALYTICAL EVALUATION

A chemical equilibrium program (Reference 1) developed at the NASA-Lewis Research Center, Cleveland, Dhio, was used to determine some of the analytical foundations for their relative performance of the pyrophorics materials. This computer program was used to predict exhaust gas temperature and the mole fraction of exit species as a function O/F ratio using equilibrium chemistry and assuming frozen conditions.

Figure 16 shows that over the range of stoichiometric O/F ratios between 2.66 and 3.40 given in Table 2, the maximum difference in temperature is 1.6 percent among pyrophorics and 4 percent between the hottest pyrophoric, TMA, and kerosene. It also shows that the combustion temperature at any O/F ratio is inversely proportional to the stoichiometric ratio.

TABLE 2. STOICHIOMETRIC RATIOS

Material	O/F
ТМА	2.66
80% TMA/20% TEA	2.72
DEAH	2.79
60% DEAH/40% TEA	2.89
TEA	2.94
TNPA	3.07
TIBA	3.15
Kerosene	3.40

These plumes, however, are not the result of combustion near stoichiometry. Judging from the yellowish-red colors of the kerosene and pyrophorics plumes observed in these investigations, combustion occurs at a relatively low O/F ratio. The plume produced by the mixing nozzle is also entirely created by afterburning combustion with the ambient oxygen supplied through diffusion and entrainment. The analytical program does not treat these mechanisms and thus the calculations cannot be used to obtain a direct estimate of the exact effect of the ambient oxygen, the true O/F ratio, nor the effect of temperature on radiant intensity.

The effect of temperature can only be deduced by relating the experimental data to the analytic temperature prediction. Figure 14 predicts the kerosene combustion temperature to be approximately one-half that of any pyrophoric material up to an O/F ratio of about 0.6. Table 1 shows that kerosene, at worst, has an infrared figure of merit 60 percent smaller than pyrophorics in either the H_2O or the CO_2 band. This would indicate that the true O/F ratio is less than 0.6 and that the figure of merit has a temperature dependence that is at most linear.



Figure 16. Computed Variation in Combustion Temperature with O/F Ratio for Pyrophoric Materials

The mole fractions of the exit species were also calculated to obtain better insight into the mechanism of infrared radiation. Figure 17 shows the distribution of CO, CO₂, and particulate carbon as a function of O/F ratio for DEAC. The distribution of exit species is similar for the other materials investigated, including kerosene. Figure 17 shows that carbon is produced in increasing quantity as O/F is decreased. The production of CO and CO₂ as a function of O/F ratio does not show any trends that are reflected in the experimental observations. H, H₂, OH, and H₂O production as a function of O/F ratio were also computed and also show similar lack of agreement with measurements.

The experimentally determined relationship between CO_2 and H_2O production and O/F ratio were illustrated in Figure 13. Two possible mechanisms can be postulated to explain the data. The first is that the infrared radiation is created as the direct result of particulate carbon production. This theory requires intermediate processes, not treated by the computer program, that would culminate either in the production of CO_2 and H_2O or in the enhancement of radiation from these species. Blackbody, or greybody, radiation from hot carbon particles was not apparent in the spectral data.

The second possible mechanism is that CO_2 and H_2O are created by non-equilibrium processes and as the result of the combustion of unburned fuel with the ambient oxygen. Unburned atomized liquid fuels which have been visually observed in all the experiments are not, unfortunately, treated by the analytical program. It becomes quite obvious, therefore, that verifiable analytical models are required. Present programs do not realistically treat the processes that lead to maximum infrared radiation from plumes. Until such programs can be established, extrapolations will have to be made experimentally.



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SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

The objective of the experiments described in this report was to determine the infrared performance of pyrophorics materials as candidate extended sources for infrared simulation devices in aerial targets. A kerosene/oxygen mixture was used as the basic direct comparison datum since the degree of atomization could be duplicated using the same mixing nozzle. The infrared data was also compared against that produced by the combustion of other chemicals. These comparisons were made using the same experimental geometry, the same infrared instrumentation, and more significantly, the same gas dynamics conditions.

It can be concluded that pyrophoric materials offer a higher radiation than all the other materials tested under the same conditions. The data indicate a figure of merit above 200 watts-seconds/steradian-gram, in the 4 to 5 micron band and also in the 2.5 to 3.3 micron band with no airflow. The infrared signature from pyrophorics is not affected by altitude changes from sea level up to 60,000 feet.

All the data were taken with subsonic exhaust plumes. Thus, they all exhibit the advantages and disadvantages peculiar to unchoked flows. A very high infrared figure of merit is produced under static conditions; however, under the influence of even modest airflows, the figure of merit drops by several orders of magnitude. These characteristics are peculiar to unchoked flows and are independent of chemistry. The present data on the infrared performance of the pyrophoric materials can thus only be compared against plumes created under similar conditions. In this case, only the kerosene/oxygen mixture and the other sources shown in Table 3 provide valid subjects for comparison (Reference 3).

The infrared signature data presented in this report are all relative. Further refinements are necessary to obtain maximum radiant intensity from pyrophoric materials in absolute terms. It is recommended that pyrophorics be atomized with oxygen (using an external mixing nozzle) to obtain the infrared performance as a function of O/F ratio, as described in this report for the kerosene/oxygen mixture. It is further recommended that chambered combustion be investigated with this mixture using sonic and supersonic exit nozzles to obtain absolute infrared performance under choked conditions.

It is recommended that verified analytical infrared performance prediction programs be established to permit realistic extrapolations to be made outside the laboratory. Major fundamental processes that give rise to infrared emission have now been identified experimentally. These should be incorporated into computer models so that maximum infrared signatures can be predicted accurately.

The effects of airstreams on both choked and unchoked flows should be determined precisely and a modified matrix (as in Table 1), with air velocity as a parameter, should be developed. Chemical parameters postulated to have direct effects on radiation (such as temperature, particulate carbon, and unburned fuel) as well as indirect effects, (such as stoichiometric ratios and non-hydrocarbon compounds), should be explored parametrically.

Reference:

3. Ebeoglu, D. G., <u>Fundamental Parameters Affecting Plume Infrared Radiation</u>, AFATL-TR-74-84, Eglin AFB, Florida, April 1974 (Unclassified)

	Pops Rocket (NH ₄ ClO ₄ /Zr/C)	Sea Level (watts-sec/ster-gm)	60,000 Feet (watt s-sec/ster -gm) 0.4
-	Rocket (kerosene/oxygen)	1.0	
Mer [Ramjet (JP4)	1.6	
Cheked	HAST Hybrid Rocket (Polymer/IRFNA)	4.8	
E Flow	Siurry Flameholder (NaNo ₃ /HEPTANE/Mg)	20	20
choki	Ram Rocket (Plexiglas)	97	
Š	Injector Nozzle (kerosene/oxygen)	250	250
	Mixing Nozzle (Pyrophorics)	300	300

TABLE 3. MAXIMUM FIGURES OF MERIT (STATIC CONDITIONS)

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