

EXTINGUISHING IN-FLIGHT ENGINE FUEL-LEAK FIRES

WITH DRY CHEMICALS

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SUMMARY

When fuels leak onto surfaces of an operating engine they can ignite when engine case temperatures exceed 540°C (1000°F). As aircraft flight speeds are increased, engine case temperatures, bleed air temperatures, maximum air velocities, and fire extinguishant storage temperature requirements also increase, making the task of extinguishing fuel-leak fires in flight even more difficult. We have undertaken to find new fire extinguishants that are more effective than the CF₃Br, CF₂Br₂, and CF₂ClBr now in use. Besides testing commercially available dry chemicals, such as NaHCO₃, KHCO₃, KCl, and KC₂N₂H₃O₃ (ICI Monnex ©), we have tried to develop and test new dry-powder fire extinguishants. Specifically, our interest has been in developing new dry-powder extinguishants that, when discharged into a jet engine fuel-leak fire, would stick to the hot surfaces. Moreover, after putting out the initial fire, these extinguishants would act as anti-reignition catalysts, even when the fuel continued to leak onto the heated surface.

INTRODUCTION

Previous fire extinguishment tests with Halons like CH₃Br, CH₂ClBr, CF₃Br, and CF₂ClBr have shown that the minimum Halon concentration in the gas phase above a liquid pool or spray fire required to extinguish the fire at first increases with increased airflow at low flow rates but then decreases at still higher flow rates. In both situations, however, the total weight of extinguishant required to put out the fire increased with increasing airflow (refs. 1, 2). To counter this, an increase in the Halon discharge rate by increasing the stored nitrogen pressure or by increasing the extinguishant discharge temperature will decrease the total weight of Halon required for complete extinguishment (refs. 3, 4). The reduced weight effectiveness of Halons with increased airflow has induced Gravinor, the manufacturer of the Concorde nacelle fire extinguishing system, to install a pair of airflow-reducing flaps upstream of the compressor; the flaps reduce the nacelle airflow to a minimum before Halon is discharged after an engine fuel-leak fire has been detected (ref. 5).

The longer fuel-leak fires burn before extinguishment is begun, the harder they are to extinguish; also, long-burning fires can start up again once the extinguishant is exhausted because the surroundings are then hot

enough to reignite the fuel (refs. 6-8). Therefore, we have devised an experimental procedure for rating the effectiveness of fire extinguishants in controlling fuel-leak fires. In this technique, the effectiveness of an extinguishant is measured in terms of the delay between initial extinguishment and reignition; throughout the test fuel continues to drip on the heated surface until reignition occurs.

This program was sponsored by Wright-Patterson AFB, but most of the experimental work was done in the facilities of the Chemical Research Projects Office of Ames Research Center. The program was conducted with the assistance of Professors A. C. Ling, L. A. Mayer, and D. J. Myronuk, San Jose State University, and their students.

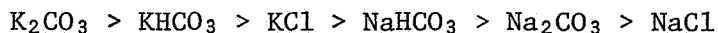
TEST PROCEDURES

Static Test

The initial experimental setup devised by Altman and Myronuk is shown schematically in figure 1 and in actual operation in figure 2. The fire was started by dripping JP-4 fuel onto a heated semicylindrical stainless steel surface. The surface was heated to a temperature between 700°C and 900°C by a Nichrome heating element placed below the curved surface. The ambient air in the cavity above the stainless steel surface was also heated by a combination of hot-surface radiation and gas convection to a temperature below that of the hot surface; however, we made no attempt to control this process. One of the two parameters used to rank the effectiveness of fire extinguishants was the hot-surface temperature, which was imprecisely determined by an uncalibrated Chromel-Alumel thermocouple. The thermocouple was welded to the semicylindrical surface at a point close to that where the fuel drop made initial contact with the hot surface.

To further describe the experimental procedure, suppose that the steady-state temperature of the hot surface was a nominal 700°C, as determined from the recorded emf output of the thermocouple. The dripping of the JP-4 fuel was then started, and very soon after the first fuel drop hit the hot surface, the temperature of the surface dropped, to, say, 650°C (because of fuel evaporative cooling). Shortly thereafter, the thermocouple temperature began to rise because the fuel drops had burst into flame. When the nominal temperature had returned to 700°C a given weight of dry chemical fire extinguishant was discharged onto the plate in the same area where the drops had first landed. If the flame was extinguished, the continuous stream of nonburning fuel drops striking the hot surface induced further evaporative cooling and the temperature dropped again. Because the fire extinguishing powder now blanketed the thermocouple-to-surface weld, the nominal temperature rose again when the drops burst into flame, although to a temperature higher than 700°C; the higher temperature was a result of the insulating effect of the powder blanket. The time from first extinguishment to second reignition, the so-called reignition delay time, was the prime measurement used in ranking the effectiveness of the dry chemical fire extinguishants.

Some of the reignition time delay results obtained from an initial survey of commercial and reagent dry chemicals made from Na- and K-bicarbonate, carbonate, and chloride, etc., on a 775°C hot surface are given in figure 3. The rank order obtained



is about the same as that reported by other investigators (refs. 9-13). Our experiments with two different particle size distributions of KHCO_3 and K_2CO_3 , all made from reagent chemicals, demonstrated that reduction in particle size increased the reignition time delay just as it increased fire extinguishant weight effectiveness. In agreement with these earlier investigations, the data in figure 3 also show that given the effectiveness of any sodium salt, the analogous potassium salt always seemed to be still more effective. We were, however, surprised to observe the special effectiveness of K_2CO_3 and $\text{NaAl}(\text{OH})_2\text{CO}_3$; as a result, we undertook the preparation of a commercial dry chemical from K_2CO_3 with an additive to reduce the spontaneous hydration and also developed an alternative method of preparing Na- and K- $\text{Al}(\text{OH})_2\text{CO}_3$ by heating dry powder mixtures of $\text{Al}(\text{OH})_3$ and Na- or K- HCO_3 in a CO_2 atmosphere (ref. 14).

Van Tiggelen et al. (ref. 15) separate fire extinguishants into two classes: (1) those that interfere with the flame chemical reactions and (2) those that cool the flame, that is, change the mechanism of flame propagation rather than merely reduce the overall rate of chemical reaction. Since, as mentioned in the description of our experimental procedure, the presence of fire extinguishing powder altered the hot surface heat-transfer properties, we also tried alumina, Al_2O_3 and silicic acid, H_2SiO_3 , as reignition delay "baseline" test materials; alumina because no chemical change would be expected and silicic acid because it could decompose to yield only water and SiO_2 . At least in amounts of 7 g or less these possible flame temperature reducers were no less effective than the poorest chemical flame reaction interference agents, NaHCO_3 , Na_2CO_3 , NaCl , $\text{NH}_4\text{H}_2\text{PO}_4$, or $\text{KC}_2\text{N}_2\text{H}_3\text{O}_3$ (ICI Monnex ©).

The initial fire test apparatus was modified somewhat as shown in figure 4 in order to better control the fuel flow rate and make the reignition delay results more reproducible (ref. 14). Some of the results obtained with this newer apparatus (designed by Professors Ling and Mayer) are given in figure 5. We were, of course, pleased to see that the commercial K_2CO_3 preparation was the best of the lot of commercial dry chemicals. Because early experimental work at WPAFB (ref. 16) had demonstrated that the most weight-effective Halon was one containing iodine, that is, CH_3I , we tried to develop a dry chemical iodide. Of such iodides tested - SnI_2 , KI , NAI , and ClI_4 - ClI_4 was ineffective in delaying reignition even at 700°C; all the other iodides turned out to be less effective at 900°C than the commercial dry chemicals. The other tin salts listed in figure 5 were tried to see whether the increased effectiveness of SnI_2 over ClI_4 had something to do with the tin. Sodium tungstate, Na_2WO_4 , with and without water, was tested because Lewis and Von Elbe (ref. 17) cited some experimental data on the greater effectiveness of Na_2WO_4 over that of KCl as a surface coating

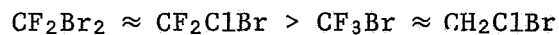
on glass in removing H free radicals. Obviously, the effect of water release from Na_2WO_4 dihydrate in delaying hot-surface reignition is as great as the chemical effectiveness of Na_2WO_4 by itself.

Figure 6 shows some of the results obtained with other experimental dry chemicals. Obviously, Na- and K- $\text{Al}(\text{OH})_2\text{CO}_3$, sodium and potassium dawsonite, are superior to Na- and K-bicarbonate. Since either of the dawsonites can be considered to be an addition product of boemite, AlOOH , and the appropriate alkali metal bicarbonate, the effectiveness of K-dawsonite (KD) might then be expected to be some mole-fraction weighted sum of the effectiveness of KHCO_3 and AlOOH . But the effectiveness of KD is clearly greater than the effectiveness of any combination of KHCO_3 and AlOOH . Boron trioxide, B_2O_3 , was tested because it melts at 450°C to form a glass; however, it seems to be no more effective than Al_2O_3 , and a mixture of KD and B_2O_3 is even less effective than pure KD. We conclude this section by noting that the effectiveness of both mechanical and preheated mixtures of KI with either Al_2O_3 or KD seems superior to that of either constituent, particularly at the higher temperatures, but further discussion is deferred until the presentation of the effect of airflow rate on extinguishment effectiveness.

Dynamic Test

A schematic of the dynamic fire test facility designed by Professor Myronuk and Richard Fish of ARC, is shown in figure 7. The test section downstream of the blower contains a stainless steel surface heated to 800°C - 900°C . Ambient air flowed over the surface at rates from 6 to 36 m/sec and JP-4 fuel was leaked onto the surface at a rate of $250\text{ cm}^3/\text{min}$. As in the static testing, once a steady hot-surface temperature was obtained at a given airflow rate, the fuel leak was initiated and made to ignite on the hot surface within 1 sec. After ignition a specific mass of extinguishant was discharged within 1 sec onto the heated surface, and, with the fuel leak uninterrupted, the time between initial extinguishment and reignition was recorded as the prime parameter of extinguishment effectiveness. The other variables were airflow rate and hot-surface temperature.

Because of their potential toxicity we could not obtain static reignition delay time data with Halon extinguishants. Therefore, our first objective was to obtain dynamic results with these materials in order to establish a baseline; some of the results are given in figure 8. To explain the data tabulation, all four of the Halons tested extinguished the fuel-leak fire at an airflow rate of 6 m/sec and did prevent its reignition for 2 sec; however, 39 g of CH_2ClBr were required but only 21 g of CF_2Br_2 . In all these tests the fire reignited after 2 sec because the Halon was being continuously diluted by the airflow after the first second of discharge time. When the airflow was increased to 36 m/sec, even more Halon extinguishant was required to keep the fire from reigniting for as long as 20 sec - 40 g of either CF_2Br_2 or CF_2ClBr and 60 g of either CF_3Br or CH_2ClBr . Twenty seconds is the upper limit of the reignition delay time reported because when the fire was kept from reigniting for a longer time the hot-surface temperature declined significantly as a result of fuel evaporative cooling. From data such as this we rank these extinguishants as follows:



A similar procedure was then carried out with commercial dry chemicals; these results are given in figure 9. As shown in figure 9, the extinguishment effectiveness of these chemicals was ranked as follows:

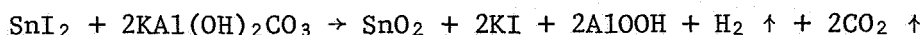


Potassium carbonate, K_2CO_3 , is reported to be more than three times as effective as Na_2CO_3 or KCl in fire extinguishment and Na_2CO_3 is reported to be about twice as effective as Li_2CO_3 or NaHCO_3 (ref. 15). Since the best of the commercial lots reported in figure 9 was Ansul's K_2CO_3 , Li- and Na-carbonate dry powders prepared from reagent chemicals were also tested as an exercise in varying the alkali metal element in the carbonate; the results are shown in figure 10. The parallelism between the recorded literature effectiveness and ours indicates that increased reignition delay time is directly related to extinguishment effectiveness. Figure 10 also shows that while the effectiveness of pure KD is nil at an airflow rate of 36 m/sec, a 2:1 mixture of KD and KCl by weight increased the weight effectiveness of KCl three to five times. The results were similar for a 9:1 mixture of KD and KI when compared with the results for pure KI . Since both KCl and KI are volatile at these temperatures, the increase in KI and KCl effectiveness in these mixtures with KD could be due to the creation of a diffusion barrier for the gaseous alkali halide molecules by the KD or to the creation of some new chemical compound between the alkali metal halide and KD thus reducing the volatility of both the alkali metal halide and decomposition products of KD.

To shed some light on these alternatives, a mixture of alumina and KI having approximately the same KI content as the mixtures of KI with KD was tested. Since no reignition delay resulted over the entire airflow range with even twice the total mass as the KD plus KI mixture, the diffusion barrier idea seems incorrect. Still another way of testing this idea is to try to increase the stickiness of KD, for if KD makes either the KCl or KI stick to the hot surface longer, thereby increasing the effectiveness, then increasing the stickiness of KD should increase its own effectiveness to something like its static effectiveness, shown in figure 6. For this test a mixture of KD with 10% B_2O_3 was prepared, but as shown in figure 10 it was no more effective than pure KD, even though some evidence of glass formation was apparent because the steel surface was very difficult to clean.

As for the possibility of some new chemical compound between KCl or KI and KD being produced by the hot surface when mechanical mixtures of alkali metal halides and KD are tested, an intimate mixture of KI and the starting materials for making KD was heated as if to make KD. Since no chemical reaction is expected between KI and either of the KHCO_3 or $\text{Al}(\text{OH})_3$ materials for making KD, the preheated mixture should show similar fire extinguishing properties to those of the mechanical mixture of KI and KD given in figure 10. Various such mixtures of the precursors of KD with 5% to 18% KI were heated as if to make KD; their reignition delay time properties, which are tabulated in figure 11, do not seem to be significantly different from those of a mechanical mixture of KI and KD.

In a separate study, we have shown that heating SnI₂ with the precursors of KD, that is, KHCO₃ and Al(OH)₃, yields KI, AlOOH, and SnO₂ by the following gross reaction:



An infrared investigation of the solid after it was heated demonstrated the presence of SnO₂, KI, and AlOOH, and the entire disappearance of SnI₂ and KD when the starting mole ratios of SnI₂ to KD-precursors were 1:1 or 1:2. As expected, KD remained when the SnI₂-to-KD-precursors were 1:4. For all three samples of the KD·SnI₂ end product reported in figure 11, the KD is in great enough excess to give a product containing SnO₂, AlOOH, KD, and KI. Further experimental work is necessary to determine why the fire extinguishment effectiveness of this material is better than that of the KD·KI preparations.

CONCLUSION

Certain dry chemicals developed and tested in our laboratories seem to have greater weight effectiveness than the Halons in current use for controlling fuel-leak fires, particularly in the presence of high airflow rates. However, the experimental variables and their role in the results obtained are insufficiently understood and the understanding of fire extinguishment has not been advanced much by this study. A further discussion of the many uncertainties is, therefore, deferred until more detailed publication in a scientific journal.

The applicability and effectiveness of these materials, namely potassium dawsonite mixed mechanically with KCl or KI, in controlling engine nacelle fires have yet to be demonstrated. However, we plan to participate further in such a test activity that will be conducted at the FAA Technical Center in Atlantic City, New Jersey, in the not too distant future.

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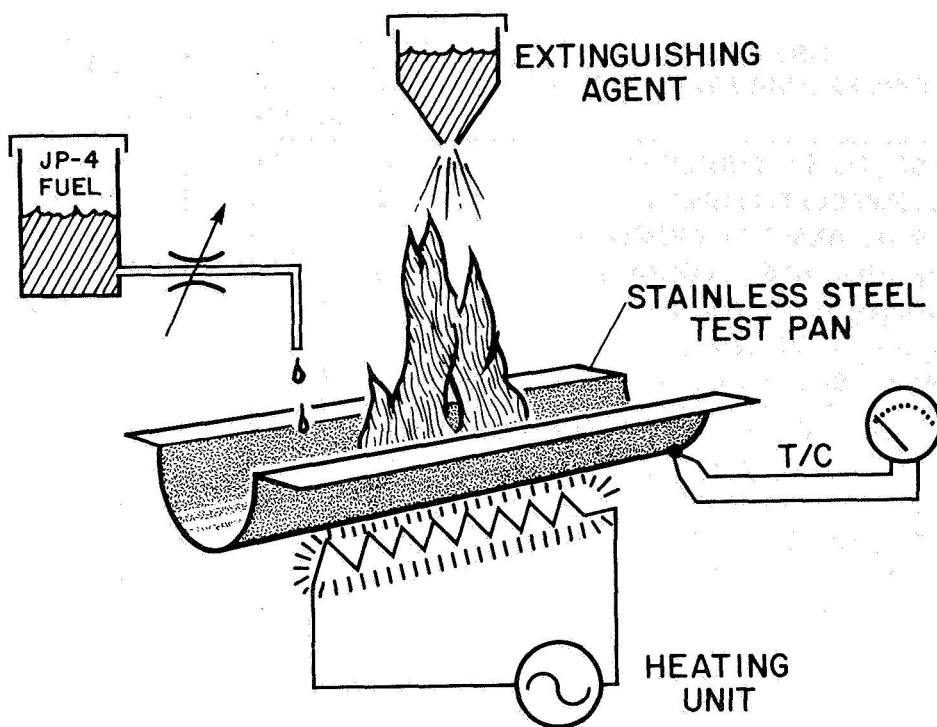


Figure 1.- Static nacelle fire test facility (schematic).

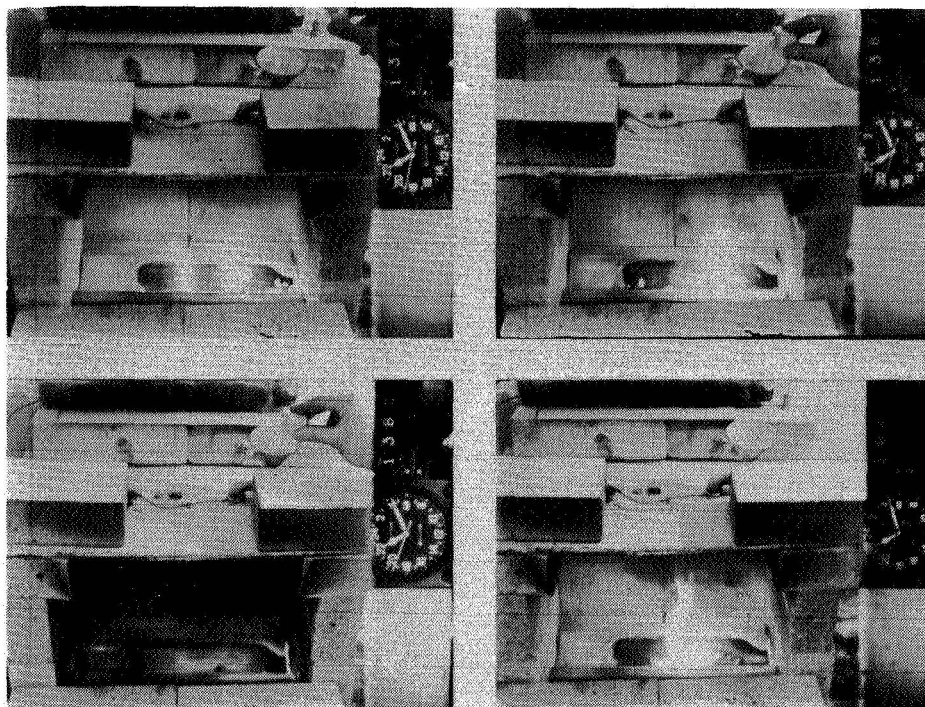


Figure 2.- Static nacelle fire test facility (actual).

DRY CHEMICAL FIRE EXTINGUISHANT POWDER	SAMPLE SIZE, grams		
	2.5	5	7.5
	SECONDS TO REIGNITE		
KHCO ₃ (ANSUL PURPLE K*)	30	100	220
KCl (PYROCHEM SUPER K*)	3	17	70
NaHCO ₃ (ANSUL DRY POWDER*)	3	4	8
NH ₄ H ₂ PO ₄ (ANSUL FORAY*)	3	2	2
KC ₂ N ₂ H ₃ O ₃ (ICI MONNEX*)	2	2	2
Na ₂ CO ₃ (ANSUL NaX*)	1	1	1
NaCl (ANSUL MET-L-X*)	0	0	2
NaAl(OH) ₂ CO ₃ (KAISER DAWSONITE)	40	125	340
K ₂ CO ₃ (REAGENT POWDER)	20	300	NO IGN.
K ₂ CO ₃ (REAGENT GRANULAR)	12	38	260
KHCO ₃ (REAGENT POWDER)	40	60	200
KHCO ₃ (REAGENT GRANULAR)	15	40	150
Al ₂ O ₃ (REAGENT ALUMINA)	2	2	15
H ₂ SiO ₃ (REAGENT SILICIC ACID)	2	2	12

*THESE ARE COMMERCIAL EXTINGUISHANTS

Figure 3.- Average time for reignition of JP-4 fuel drip on 775°C hot surface.

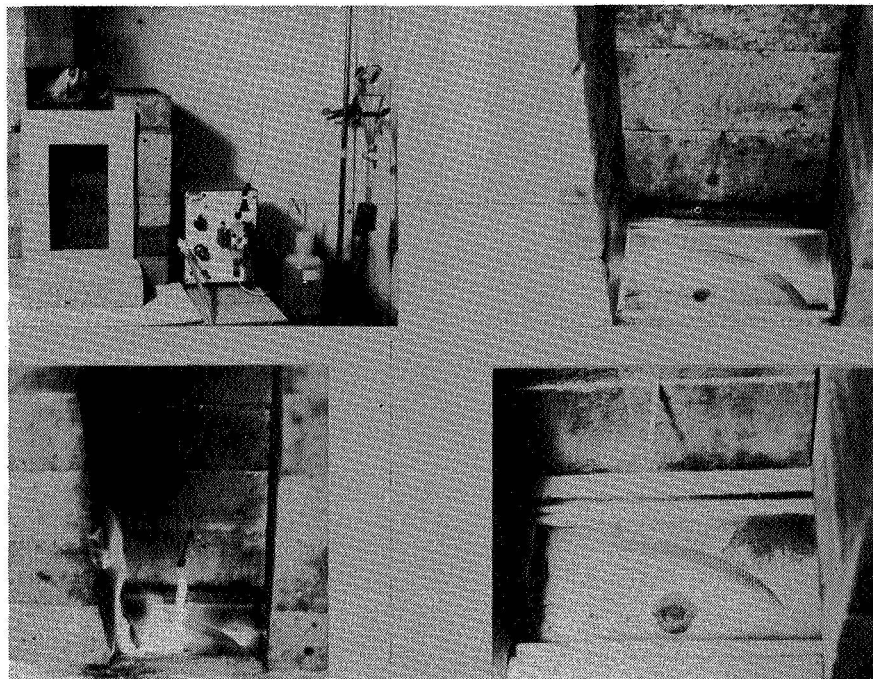


Figure 4.- Modified static nacelle fire test facility.

DRY CHEMICALS	DELAY TIME, sec	
	700°C	900°C
K ₂ CO ₃ (ANSUL PREP)	150 ± 80	—
KHCO ₃ (ANSUL PURPLE-K)	69 ± 20	7 ± 4
KC ₂ N ₂ H ₃ O ₃ (ICI MONNEX)	55 ± 30	7 ± 2
KCl (PYROCHEM SUPER-K)	33 ± 4	—
NaCl (PYROCHEM BCD)	33 ± 15	5 ± 2
(NH ₄)H ₂ PO ₄ (ANSUL FORAY)	12 ± 2	—
(NH ₄)H ₂ PO ₄ (PYROCHEM TUW-156)	8 ± 3	—
SnI ₂ (68% I)	380 ± 80	2 ± 2
KI (76% I)	>900	2 ± 2
NaI (85% I)	600 ± 60	3 ± 2
Cl ₄ (98% I)	NONE	—
SnCl ₄ • 2H ₂ O	26 ± 3	—
SnO	15 ± 5	—
Na ₂ WO ₄ • 2H ₂ O	17 ± 2	—
Na ₂ WO ₄	8 ± 2	—

Figure 5.- Reignition delay time for JP-4 fuel drip on hot surface with 10 g of commercial and experimental dry chemicals.

DRY CHEMICALS	DELAY TIME, sec	
	750°C	900°C
NaAl(OH) ₂ CO ₃ †	296 ± 50	6 ± 3
KAl(OH) ₂ CO ₃ †	153 ± 15	10 ± 4
Al(OH) ₃	100 ± 30	3 ± 2
AlOOH†	48 ± 35	NONE
Al ₂ O ₃	28 ± 12	NONE
B ₂ O ₃	5 ± 3	2 ± 1
H ₃ BO ₃	10	—
KD + B ₂ O ₃ (10%)	62 ± 28	6 ± 2
K ₃ AlF ₆	14 ± 5	—
Al(OH) ₃ + SnI ₂ (7% I)	204 ± 20	8 ± 1
Al(OH) ₃ + KI (8% I)	233 ± 56	—
Al(OH) ₃ • KI (7% I)	72 ± 3	8 ± 1
AlOOH • KI (7% I)	131 ± 7	15 ± 4
Al ₂ O ₃ • KI (7% I)	>900	50 ± 12
KAl(OH) ₂ CO ₃ + SnI ₂ (6% I)	520 ± 52	51 ± 3
KAl(OH) ₂ CO ₃ • SnI ₂ (6% I)	419 ± 61	50 ± 2
KAl(OH) ₂ CO ₃ + KI (7% I)	500 ± 90	13 ± 4
KAl(OH) ₂ CO ₃ • KI (7% I)	>900	50 ± 14

+ MECHANICAL MIXTURE
• MECHANICAL MIXTURE PREHEATED BEFORE TEST (WEIGHT PERCENT IODINE IN MIXTURE)
† PREPARED AT ARC FROM REAGENT CHEMICALS

Figure 6.- Reignition delay time for JP-4 fuel drip on hot surface with 10 g of experimental dry chemicals.

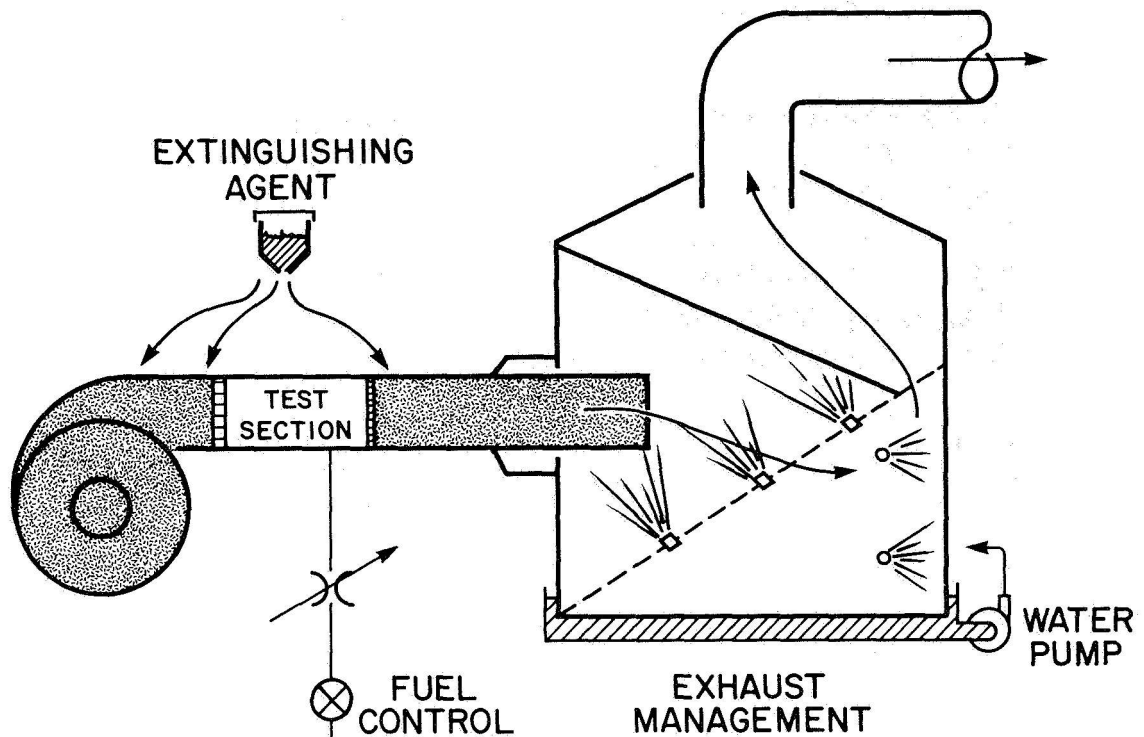


Figure 7.- Dynamic nacelle fire test facility.

HALON	GRAMS	DELAY TIME, sec, AT VARIOUS AIRFLOWS, mps	
		6	36
1202 CF_2Br_2	21	2	-
	40	-	20
1211 CF_2ClBr	24	2	-
	40	-	20
1301 CF_3Br	35	2	-
	60	-	20
1011 CH_2ClBr	39	2	-
	60	-	20

EXTINGUISHMENT EFFECTIVENESS

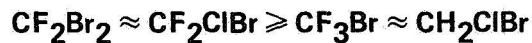


Figure 8.- Reignition delay time versus airflow rate for JP-4 fuel drip on 800°C hot surface for various Halon extinguishants.

DRY CHEMICALS	GRAMS	DELAY TIME, sec, AT VARIOUS AIRFLOWS, mps	
		6	36
(ANSUL PKP)	30	20	2
	50	—	20
KHCO ₃ * (ANSUL X)	20	20	<1
	30	—	20
NaHCO ₃ * (ANSUL +50C)	30	20	0
	50	—	<1
KC ₂ N ₂ H ₃ O ₃ * (ICI MONNEX)	10	2	0
	20	20	20
KCl* (PYROCHEM SUPER - K)	30	<1	0
	50	—	20
K ₂ CO ₃ * (ANSUL PREP)	8	0	20
	20	2	20
	30	20	—

*800°C
EXTINGUISHMENT EFFECTIVENESS
K₂CO₃ > KC₂N₂H₃O₃ > KHCO₃ > NaHCO₃ > KCl

Figure 9.- Reignition delay time versus airflow rate for JP-4 fuel drip on hot surface with commercial dry chemicals.

DRY CHEMICALS	GRAMS	DELAY TIME, sec, AT VARIOUS AIRFLOWS, mps	
		6	36
Li ₂ CO ₃ †	30 - 40	<1	0
Na ₂ CO ₃ †	30 - 40	<1	0
KAl(OH) ₂ CO ₃ * ("KD")	30	20	0
KD + KCl (32%)*	10 - 20	2	20
KI†	40	<1	0
KD + KI (10%)*	20	3	20
Al ₂ O ₃ + KI (9%)*	40	0	0
KD + B ₂ O ₃ (10%)*	20	20	0

*800°C
†900°C
+POWDER MIXTURE

Figure 10.- Reignition delay time versus airflow rate for JP-4 fuel drip on hot surface with experimental dry chemicals.

DRY CHEMICALS	GRAMS	DELAY TIME, sec, AT VARIOUS AIRFLOWS, mps	
		6	36
KD • KI (5%)	20	1	<1
	25	20	—
KD • KI (9%)	15	<1	20
KD • KI (18%)	20	<1	20
Al ₂ O ₃ • KI (9%)	40	0	0
KD • SnI ₂ (5%)	15	20	20
KD • SnI ₂ (10%)	15	20	20
KD • SnI ₂ (20%)	10	20	20

• MECHANICAL MIXTURE PREHEATED BEFORE USE

Figure 11.- Reignition delay time versus airflow rate for JP-4 fuel drip on 800°C hot surface with experimental dry chemicals.