

“BLACK WIDOW” THERMAL ABSORPTIVITY- ENHANCED DRY CHEMICAL POWDER – RECENT EVALUATIONS IN VARIOUS FIRE PROTECTION APPLICATIONS

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INTRODUCTION

Dry chemicals and other extinguishing chemicals have been enhanced by numerous means over the years. In the field of dry chemicals, the patent literature alone reveals numerous techniques of enhancement to improve their performance. With all these various techniques of improving the performance of such dry chemicals, there has been no means observed in the literature of improving such performance by controlling the extinguishant's interaction with the thermal radiation emitted from a fire.

A special class of enhanced dry chemical fire extinguishant formulations have been recently derived, based upon the principle of enhancing the powder particle's absorptivity of the infrared radiation released from a flame. This theoretical hypothesis led to the development of various dry chemical embodiments that have been observed to feature significant improvements in efficiency and firefighting performance in a range of various fire extinguishing types of tests performed over a recent period, by various groups and agencies, in comparison to more conventional dry chemical powders. These evaluations included portable extinguisher, ballistic dry bay and other types of fire scenarios, with improvements observed over this wide array of fire structures. Various alternative methods of producing this absorptivity enhancement in powders have all exhibited this improvement to varying degrees. Some of the derivatives may also feature other secondary enhancements that improve delivery, and persistence near the flame front.

FUNDAMENTAL THEORY OF “BLACK WIDOW” RADIATION EXPLOITATION

Fires, and in particular liquid fuel pool fires of interest, have multiple simultaneous mechanisms occurring, which in turn sustain the fire and dissipate its thermal energy. One of the key, but least understood mechanisms is thermal radiation. Thermal radiation released by the reaction zone in the fire transports heat to the liquid pool below, to promote vaporization and the introduction of fuel vapor into the reaction zone to sustain the fire. Since radiation is released in all directions (omnidirectional), it also radiates heat away from the fuel and the fire. This loss of heat must be replaced by the exothermic chemical reactions in the reaction zone to maintain sufficient heat to support and sustain the rate of chemical reaction. Friedman [1] states that in Class B fires such as pool fires, radiation is the primary means of providing energy feedback to continue to vaporize the fuel, and thus the rate of burning, as well as the spread of fire to nearby

combustibles. It is stated that if there is a "cooler smoke or fog droplets" between the flame and its (combustible) target, it will reduce the intensity of the radiation on the target. It is also shown in Figure 1, taken from this reference, that the percentage of heat lost due to radiation varies between 9% and 43%, with liquid fuels of interest near the higher end. It is stated [1] that "loss of heat by radiation causes a lower temperature in the flame, which slows down the chemical oxidation reactions", which obviously supports the goal of weakening or extinguishing the fire. Only limited data is available on radiation effects as they pertain to fire, due to the complexities of analyzing and calculating the direction and extent of heat losses, their deposition on surrounding structures (dependent on their spatial location relative to the fire) and their re-radiation back to the fire, radiation losses and generation within the surrounding hot air itself, and the respective rates of radiation emittance, absorption and reflection from each of the constituents. Most research has focused on the radiation-based heat deposition on surrounding combustible structures (such as walls and curtains), and the minimum radiative heat flux required to result in their ignition and sustained fire. This mechanism can result in the spread of the fire to these surrounding structures from the original site of the fire, and can lead to a runaway fire spread condition that is beyond the means of fire personnel or fire extinguishing equipment to control and eventually vanquish.

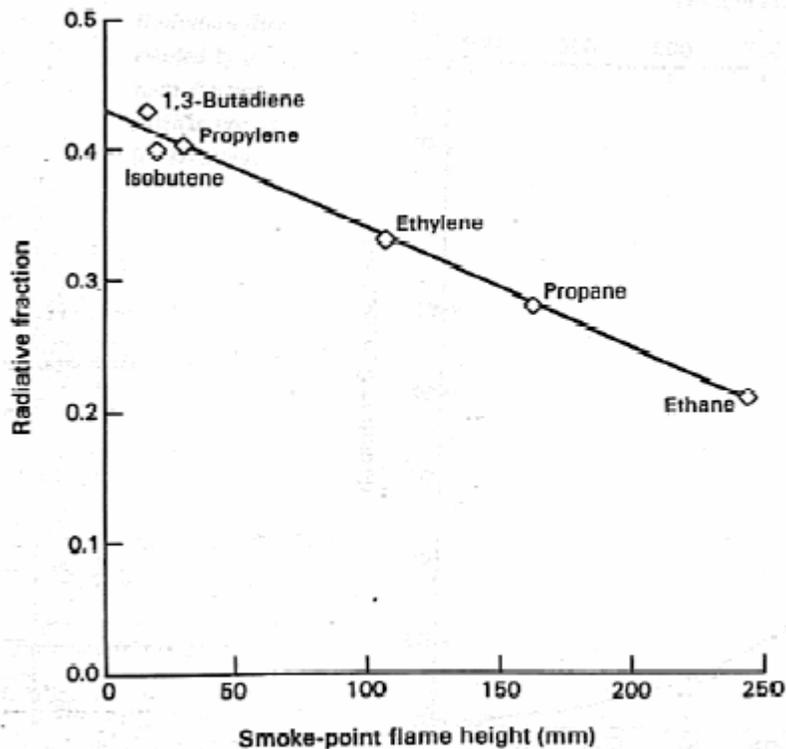


Figure 1.

Fraction of radiative heat losses for different fuels.

The amount of thermal radiation produced by a flame or fire is also affected by factors such as the optical thickness and temperature of the fire (influenced by the fuel burned, the degree of oxygen mixedness and other factors), and in particular the degree of black soot produced by the flame or fire. The black soot particles can not only emit heat (since they are reactive carbon

particles that can oxidize in an exothermic fashion), but also rob the reacting fire zone of its heat due to its absorption of radiation from the fire. Since many “real world” fires such as pool fires have inefficient fuel/air mixing and inefficient burning, these fires are very “sooty”, and these effects of heat loss and radiation absorption are significant. The effects of these factors on the radiative output from a flame is shown in Figure 2, taken from Friedman [1].

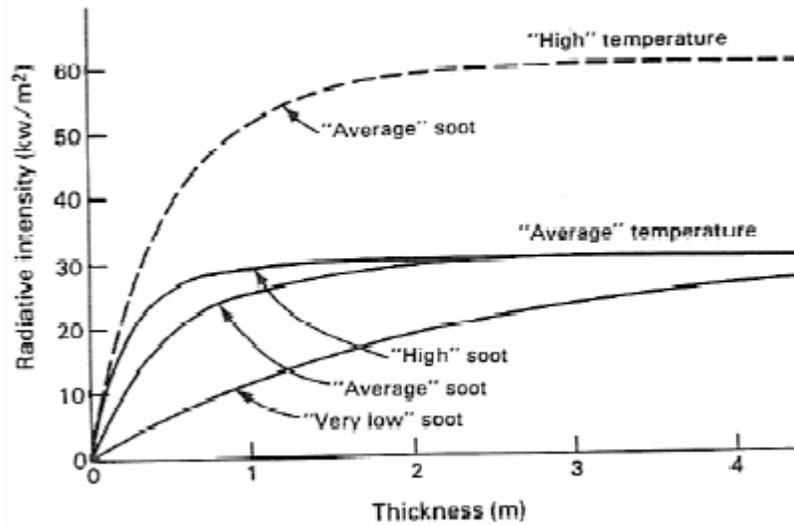


Figure 2. Radiation intensity effects of temperature, flame thickness, soot levels.

Radiation also affects the performance of dry chemical fire extinguishing particles when they are introduced into the fire region. Such particles can be a sink for the heat released by the fire, to cool it below its sustainment temperature. Chemically reactive dry chemicals, such as sodium and potassium bicarbonate, also decompose when exposed to heat, to release carbon dioxide and metal ions to interrupt the fire reaction chemically as well as smother it. Also in the previously cited book by Friedman [2], in a section entitled "Dry Chemical Agents", it is stated that "the effectiveness of any of these agents depends on the particle size. The smaller the particles, the less agent is needed as long as particles are larger than a critical size (Ewing et al., 1975). The reason for this fact is believed to be that the agent must vaporize rapidly in the flame to be effective (Iya et al., 1975). However, if *extremely* fine agent were used, it would be difficult to disperse and apply to the fire." The cited reference also discusses the high performance of a dry chemical marketed under the name "Monnex", due to its ability to decompose, "causing a breakup of the particles in the flame to form very fine fragments, which then gasify rapidly." It also states that "it seems clear that the effective powders act on a flame by some chemical mechanism, presumably forming volatile species that react with hydrogen atoms or hydroxyl radicals."

Unfortunately, dry chemicals commonly in use typically are white or near-white in visible color. This state results in a high degree of radiative heat reflection from each particle (like little mirrors) back to the fire zone or to the liquid fuel source, and minimal heat absorption by the particles themselves. This promotes the robustness of the fire, and slows the rate of decomposition of the particles themselves, reducing the rate of heat extraction from the fire, and

the generation of fire-inhibiting decomposition products to mix into the reaction zone. As a result, particles in the region above or near the fire zone may not break down (and are thus of very little effectiveness), and will deposit in the air or surrounding area.

If the dry chemical particles could be modified, either on their outer surface only or through their thickness, such that they absorbed a greater degree of the thermal radiation, less heat would be reflected back to the fire to maintain the fire, the particles would decompose faster to release their chemical ions and decomposition products to chemically interrupt the fire to a greater degree, and even particles some distance from the fire zone might be of service by extracting additional heat from the fire, and possibly prevent the ignition of surrounding combustible materials by reducing the transmission of infrared radiation from the fire to them. If the dry chemical particles were changed to a color more conducive to thermal radiation absorption (with less reflectivity), such as a flat black, then this desired behavior would be greatly enhanced. In their book, Incropera and DeWitt [3] discuss the effects of surface color on radiative absorption in the chapter entitled "Radiation: Processes and Properties". Figure 3 (taken from this reference) shows the coefficients of absorptivity and reflectivity for various material surface types and colors. For opaque materials, the sum of the coefficients of absorptivity and reflectivity equal one; a highly absorptive surface is correspondingly less reflective, and vice versa. One can see that the curve corresponding to the reflectivity (at a given wavelength) of "white paint" surfaces shows that as high as 90% of radiative energy at wavelengths at or below 1 micrometer is reflected, with only 10% absorbed, and at least 80% is reflected at wavelengths up to 2 micrometers. In comparison, "black paint" surfaces consistently absorb about 97% or more across the wavelengths, and reflect only about 3%.

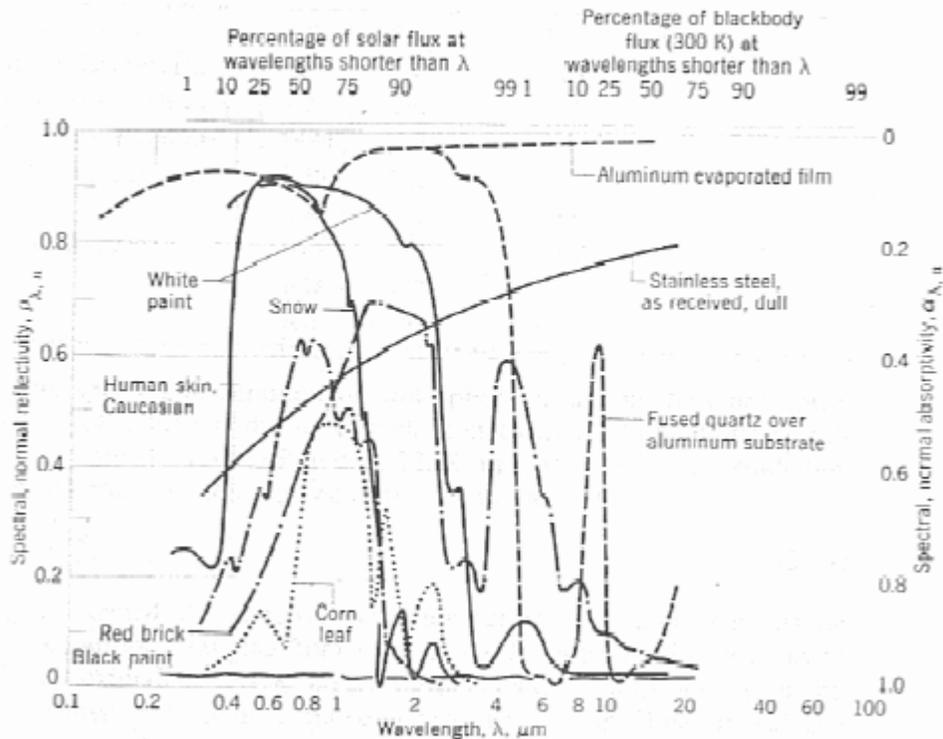


Figure 3. Thermal Absorptivity Vs. Wavelength for Various Materials.

Hydrocarbon fires have been characterized with regard to their electromagnetic spectrum emissivity, as a function of the radiant intensity at various wavelengths. Figure 4 from Reference [4] reveals the spectral signature of a hydrocarbon flame. Figure 5, which illustrates optical emissions from JP-4 burning at 35,000 feet, shows that its signature of emissivity is very similar to a black body at 1800 K.

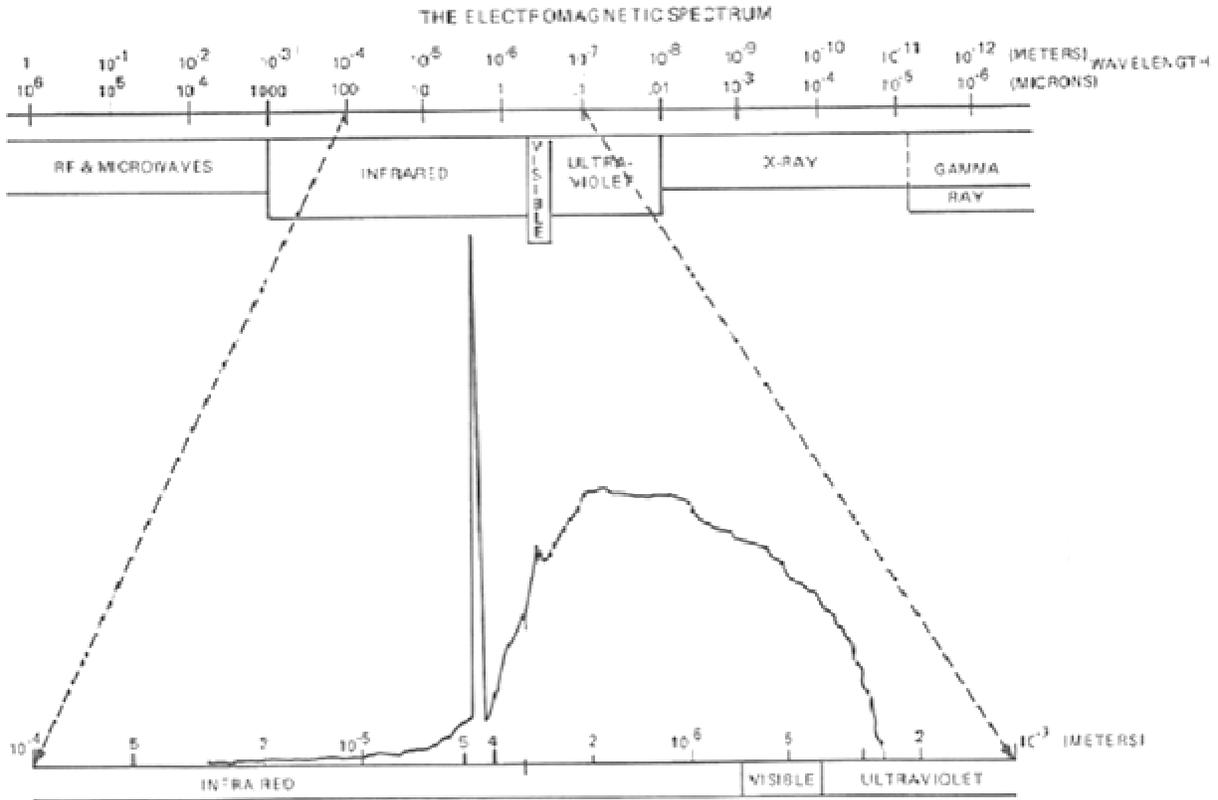


Figure 4. Electromagnetic spectrum for hydrocarbon fires.

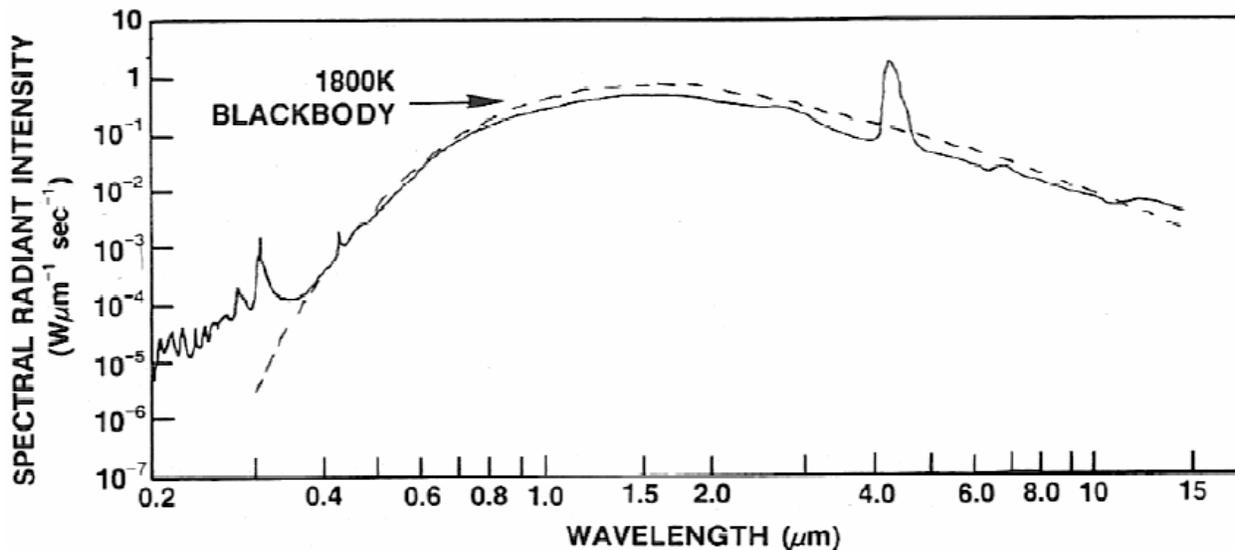


Figure 5. Optical signature – JP-4 fire at 35,000 feet.

Table 12.1 from reference [3] can be used to determine an estimate of the percent of total emissive power released from a flame at a given temperature, up to a given wavelength. For a flame temperature of 1800 K as cited above, for wavelengths up to 3 microns, approximately 68% of a black body's emissive power is represented (which is relatively consistent with Figures 4 and 5 above). Similarly, 40% of its total power is emitted at wavelengths up to 2 microns, and 4% up to one micron. From Figure 3, one can observe that white colored objects such as white paint reflect approximately 90% of radiation up to 1 micron, 80% at 2 microns, and 40% at 3 microns. From this data, one can estimate the percentage of total fire radiation reflected at wavelengths up to 3 microns, at a pro-rated amount of 43.6%. Alternatively, black paint reflects 3% of impinging radiation, which for radiation up to 3 microns would equal about 2%. This is a significant difference in the percentage and overall amount of radiation reflected when white and black objects are exposed to hydrocarbon fires.

Accordingly, black surfaces will absorb versus reflect a substantially larger portion of the radiation released by a flame. Such particles will extract heat from the fire zone much more efficiently, and decompose much more rapidly, much like particles of much smaller size, while maintaining favorable "throw" characteristics of larger particles during discharge. They will inhibit the transport of heat to the liquid fuel source, and break down in areas farther from the center of the reaction zone, to create a more concentrated cloud of metal ions and inert gas molecules induced into the fire. Such particles will thus replicate the well-known combustion-inhibiting behavior of soot particles, which deprive reaction zones of the heat they need to sustain efficient combustion, such as in engines. Unfortunately, soot particles are carbon-based, which can react exothermically and add heat to the fire in some cases. With this concept, a non-combusting (in fact, combustion-inhibiting) material would exhibit this radiative heat-extraction behavior - the best of both worlds.

As a result, any means that could improve the thermal absorptivity of the particles would "supercharge" the performance of dry chemical fire extinguishants, in a manner than adds negligible cost and complexity. The goal would be to improve the firefighting performance of dry chemical extinguishants, pound for pound, sufficient to increase their AB rating (the size of a liquid fuel pool fire or textile material that can be extinguished) for a given charge of dry chemical and extinguisher size. This same principle could also possibly be applied to non-solid liquid droplets, to assist them in absorbing heat and vaporizing (and thereby absorbing latent heat of vaporization better), and perform in a manner similar to smaller droplets while having the improved "throw" characteristics of larger droplets.

Several techniques have been devised and proposed [5] to effect this enhancement to either dry chemical particle or liquid droplet fire extinguishants. With one technique, the particle (liquid or solid) has its surface modified by a dye to change its color to one more conducive to absorbing thermal radiation of the wavelengths most common to the hydrocarbon-based emission spectra and temperatures encountered in fires, as opposed to the light or white colors commonly used for dry chemical particles. Many shades and colors can be used to produce this effect and improve absorption to varying degrees, although flat black or of a similar tint would be most preferable to maximize the radiative absorptive enhancement. The color or shade chosen may be influenced by economic considerations, in which some colors may be produced more economically due to the cost of the dye itself, the amount of dye that must be used, the cost or complexity of the

dyeing or color addition process, and other handling, storage, flow and extinguishing performance issues. As an example, many dyes are used in the food processing or printing industries that are very inexpensive, safe to handle and even digest, non-combustible and leave no undesired residue after treatment. Many of these dyes are normally applied to sodium bicarbonate in both industries, which is also a common dry chemical fire extinguishant. These dyes can be added by numerous techniques, such as wet treatment (by dissolving the particles with the liquid dye added) with the desired final powder particle sizes established by later grinding and treatment, or "dry" processes where the dye comes into contact with the dry chemical and is applied without dissolving the particles. These techniques can be applied in large batches, such as by use of jet mills. The treatment of only the outer particle surface has the advantage of using a minimal amount of dye. The increased heat absorbency will then apply as long as the outer dyed layer persists, until the modified surface evaporates during melting from heat, to whatever depth of penetration exists of the dye into the surface.

To achieve enhanced radiative absorption throughout the decomposition period of the particles, a particle may also have a dye applied throughout all or a substantial portion of the thickness of the particle. More limited manufacturing techniques may be used to achieve such penetration depths of the dye into the particle; liquid "wet" methods are one way of assuring such full penetration. Such techniques may prove more expensive to provide, in terms of increased dye used and more expensing processing methods, but particles so treated may perform better in use against fires. This is because the improved radiation absorbency would persist throughout the particle melting and vaporization process, until the particle completely melts and evaporates. Of course, a liquid particle would be treated using a "wet" process, which would penetrate through the depth of the liquid particle or droplet.

In another approach, a distinct outer coating is applied to the particle. This coating would be chosen for its noted ability to absorb infrared radiation, and accordingly conduct this heat into the core of the particle itself. A coating could be applied by an even more diverse array of manufacturing techniques, including soaking the particles, spray drying, electrostatic techniques and many other means. This enhancement would last until the outer coating evaporated due to heating. By this time, substantial heat will have been conducted into the core of the particle. Additionally, such coatings may have favorable features of chemical inhibition of fires in their own right when decomposed, or improved handling, toxicity, cleanup and flow characteristics.

Other alternative techniques are possible, such as the incorporation of additive particles that enhance such radiative adsorption. In this approach, an extinguishant particle (liquid or solid) has had smaller additional particles adhered to the particle's surface, which are of low cost and have increased absorptivity of thermal radiation. For example, a myriad of substances can be acquired at very low cost, having absorptivity coefficients near 1.0, and with particle sizes anywhere from sub-micron to tens of microns, many of which are much smaller an average dry chemical particle diameters of 34 microns, which would facilitate their adherence and covering of all or part of the dry chemical particle's surface, at a small fraction of the dry chemical volume and mass. These particles would absorb large quantities of thermal radiation, rather than reflect it, and conduct this heat to the dry chemical's surface.

In yet another approach, inexpensive, small particles can be mixed with dry chemical fire extinguishing particles, which have a surface conducive to the absorption of thermal radiation,

and leave residue on surrounding dry chemical particles that retain these absorptive properties which transmit heat into the dry chemical particles. Such an inexpensive additive is activated charcoal, which has very high thermal absorptivity, and leave such residue. These particles also have numerous pores that can entrap reactive species released in the fire zone to prevent their interaction in the flame. This material may also react exothermically when exposed to a sufficiently high temperature environment, generating heat which may assist in the decomposition of the surrounding dry chemical particles into beneficial chemically-reacting species such as metal ions. Other materials are available that exhibit similar properties.

One of the additive particles evaluated in previous tests has also shown additional significant benefits. Its significantly higher density compared to regular dry chemical extinguishants increase permits larger quantities by mass to be stored in smaller, lighter weight and cost extinguisher containers. Furthermore, additional enhancements have also been observed after discharge. It is thought that, in general, larger particles have an improved “throw”, or the ability to discharge through the air to the fire without being entrained into local air turbulence and redirected via eddys, since the particle mass (and hence momentum imparted to resist re-direction) increases with the cube of the radius, whereas the presented area (on which airflow forces are applied) increases as the square of the radius. However, density also has an important role; since most dry chemical extinguishants have comparable densities, this effect is not usually noted. Since the density of these additive particles is almost an order of magnitude higher than these dry chemicals, the extinguisher pressure can impart far more momentum to a particle with higher mass at a given particle size. As a result, smaller (and more heat transfer-efficient) particles can be propelled in a more effective manner to the flame. A potential additional benefit is that the significantly higher density may resist vertical entrainment away from the flame region by the hot, buoyant plume of air rising from it, and thus reside near the reaction zone and extract heat for an extended period. These additive materials can provide these benefits by simply adding them in small quantities to other dry chemical extinguishants, or they can be used by themselves as an inert thermal heat sink in their own right. Additive materials tested to date have also been shown to be relatively inert at high temperatures in the flame, which mitigates additional corrosive and toxic effects (although still being considered a “nuisance dust” as with other dry chemical extinguishants), and permits their presence in the flame for considerable periods in solid form, rather than vaporizing and being entrained away.

RECENT TEST RESULTS WITH BLACK WIDOW DERIVATIVES

Testing by Other Extinguishing Companies

A fire extinguisher company initially tested an early version of a “Black Widow” derivative, featuring sodium bicarbonate with a preliminary dye treatment, in a portable extinguisher application for Class B liquid fuel pool fires, in a UL-type setting. After failing to extinguish such a fire with a 2.5 lb. extinguisher with pure extinguisher-grade sodium bicarbonate, the Black Widow-modified material was able to quickly extinguish the pool fire, with the characteristic black plume surrounding the flame region, with significant powder to spare. Similarly, another large extinguisher company was able to show the enhanced performance using one of a series of proprietary dry Black Widow additives mixed in small quantities with Monnex in a simulated aircraft ballistic fire-type event, as opposed to commercial grade Monnex.

“Black Widow”-Filled FIRE Panels

The U.S. Army tested powder-filled FIRE Panel devices to protect vehicle fuel tanks from high-energy ballistic rounds. They reported [6] that FIRE Panels with regular Monnex were able to defeat the ballistic rounds with powder weights of 53.7 lbs., versus an effective weight of 35 lbs. with Monnex mixed with 30% by weight proprietary dry Black Widow additive. They noted that this represented an equivalent effectiveness using 58.5% of the weight required using straight Monnex dry chemical (it should be noted that continued successful tests for the limited series resulted in not determining the threshold weight performance limits of either alternative). Accordingly, the U.S. Army has requested the use of Black Widow/Monnex blend FIRE Panel variants for future testing and consideration for specific vehicle platforms. Figure 6 is a photograph of a successful ballistic test using the Black Widow/Monnex blend.



Figure 6. Successful ballistic test with Black Widow/Monnex FIRE Panel variant.

Army Test of Portable Extinguishers

The U.S. Army Aberdeen Test Center (ATC), Vulnerability/Lethality Team, conducted a Tire Flammability sub-test [7] to compare the effectiveness of four different fire extinguisher agents in extinguishing deliberately caused wheeled ground vehicle tire fires. The tires were placed in a fire pan assembly that was 8 ft by 3 ft by 3 inches deep and equally divided so that two tires could be mounted (one in each 4 ft by 3 ft area) side by side with a simulated fender assembly

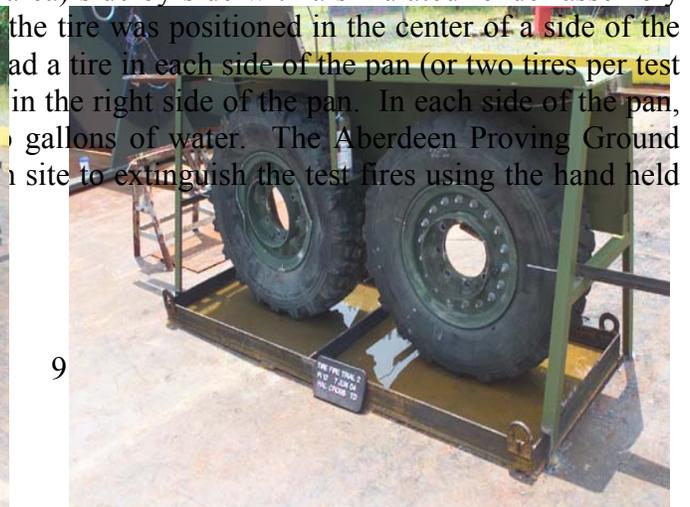


Figure 7. Photographs of tire test fixture.

The tires were remotely ignited in both sides of the pan simultaneously. When only one tire was present, the ignition source was positioned similarly so that both sides of the pan ignited simultaneously. The fire was allowed to remain burning until nearly all of the fuel was consumed, as indicated by a lack of fire on the surface area of the pan. At this point, in every test event, the fire on the tire was clearly self-sustaining by the tire material itself. The firemen were then dispatched to extinguish the fire using the prescribed agent. Following each test event the tires were inspected for damage and burn evidence. The pan and fixture were rinsed with clean water between tests and new water and fuel were added to the pan for each subsequent event. Table 1 lists the various candidate portable extinguisher alternatives tested.

Table 1. Portable Fire Extinguisher Alternatives.

4 ea Hand Held Fire Extinguishers
1 with liquid based agent ("Biosolve", 6%)
1 with liquid based agent (AFFF – Aqueous Film Forming Foam, 3%)
1 with dry powder based agent (Purple K – potassium bicarbonate, 5 lb.)
1 with dry powder based agent (2/3 Purple K + 1/3 “Black Widow” additive, 5 lb.)

Results

The temperatures and the video recordings reflected the consistent start and building of fire during each of the test events. In each test event, the fires were self sustaining on each tire and it is assumed that collateral vehicle damage would result if not extinguished by the direct application of an effective extinguisher. All of the extinguishers tested were able to extinguish the fully involved fires with a single extinguisher. After the test, the physical inspection revealed external finish damage on all of the tires as evidenced by charring, blistering, and loss of material. The conditions for each test are shown in Table 2, and the results in Table 3. It should be noted that the Black Widow/Purple K blend performed best on a weight basis, and the Purple K-only alternative was used with only a single tire mounted, versus two with Black Widow.

Table 2. Test Conditions.

TEST EVENT	TIRE: QUANTITY	TIRE LOCATION	TIRE DESCRIPTION	PAN FUEL (JP-8)	EXTINGUISHER TYPE/AGENT
1	1	Right side	Old, worn, torn side wall: NOTE: no fender assembly over tire	5 liters per side	None - Baseline fire extinguished with facility water cannons
2	2	1 each side	Old, worn, punctured treads, bent wheel	1 gallon per side	2.5 gallons at 100 psi pressurized water with 6% "Biosolve"
3	1	Right side	New tire	1 gallon	5 pounds at 195 psi

TEST EVENT	TIRE: QUANTITY	TIRE LOCATION	TIRE DESCRIPTION	PAN FUEL (JP-8)	EXTINGUISHER TYPE/AGENT
				per side	dry powder - Purple K (Potassium Bicarb)
4	2	1 each side	Tire from event #3 in right side with a new tire in left side pan	1 gallon per side	2.5 gallons at 100 psi pressurized water with 3 % AFFF
5	2	1 each side	Same tires as event # 4	1 gallon per side	5 pounds at 195 psi dry powder – Black Widow (2/3 Purple K + 1/3 proprietary additive)
6	2	1 each side	Same tires as event #4	1 gallon per side	2.5 gallons at 100 psi pressurized water with 6 % "Biosolve"

Table 3. Extinguishing Agent Performance Comparison.

AGENT	EXTINGUISHER TYPE	EXTINGUISHER CONTENTS USED
"Biosolve" (6%)	Water based 2.5 gallons	2.50 gallons
AFFF (3%)	Water based 2.5 gallons	2.50 gallons
Purple K	Dry powder 5.0 pounds	2.00 pounds
Black Widow	Dry powder 5.0 pounds	1.25 pounds

Fender-Mounted Military Vehicle Tire Protection

The U.S. Army also investigated the use of fender-mounted automatic extinguishing systems as another means of extinguishing intentionally-set military vehicle tire fires. One variant tested was a 1" diameter Pyro-flex tube, filled with a 70% Monnex/30% Black Widow dry additive blend. The Pyroflex tube is constructed so as to rupture when heated due to its proximity to a flame, forming a rupture hole to expel its pressurized internal contents of extinguishant directly to the fire. Figure 8 reveals the configurations of these Pyroflex tubes (not mounted). The tube was mounted under the fender over two tires of a vehicle, using the same test fixture shown in Figure 7, as well as the same general fire test protocol.

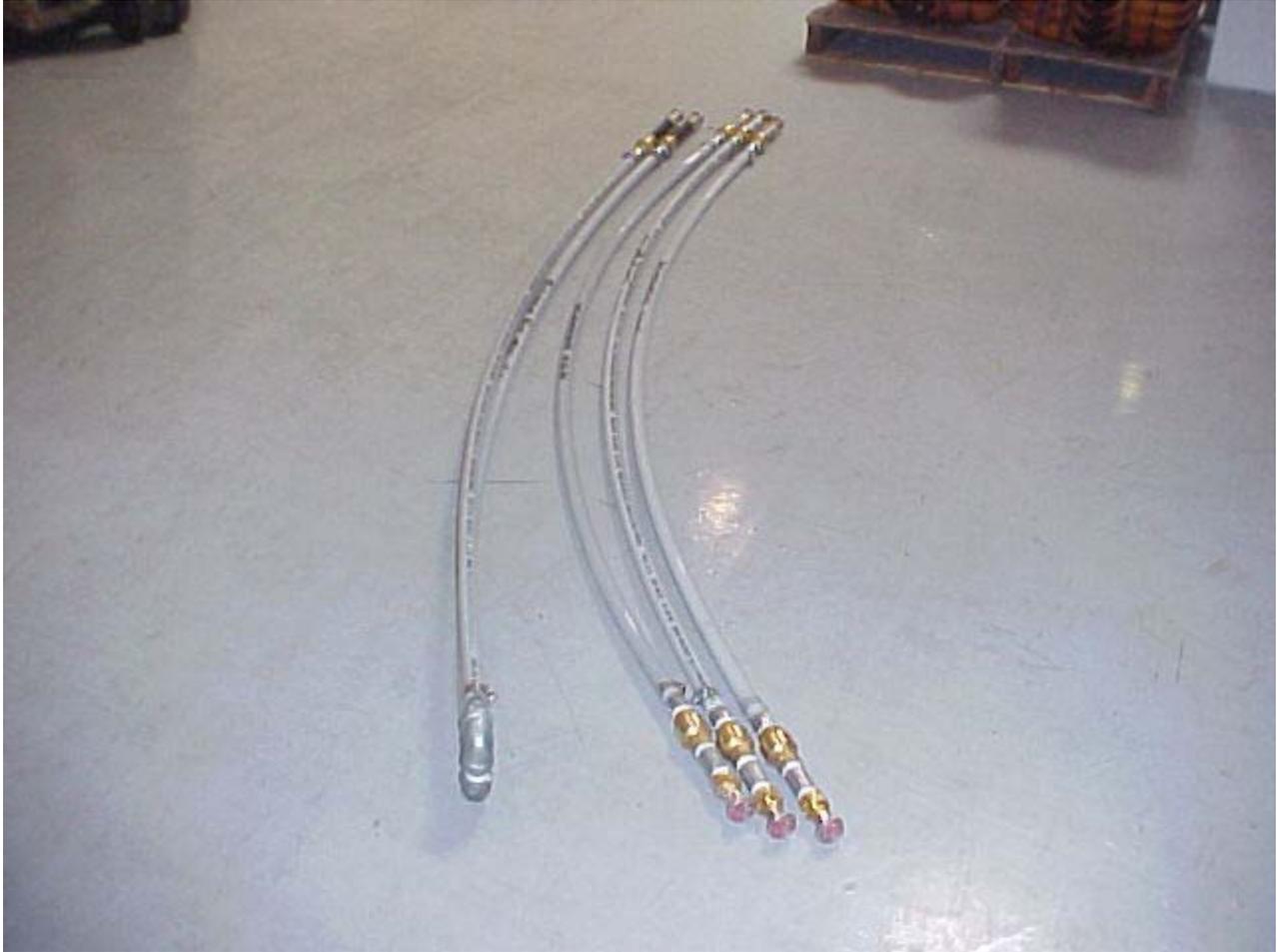


Figure 8. Pyroflex tube units for fender mount applications.

Since these units used powder internally, it was decided to use separate pressurized nitrogen cartridges with check valves, attached to both ends of the Pyroflex unit, to assure that a nitrogen pressure head would propel and push the powder out of the ruptured tube, no matter where the rupture occurs (alternatively, liquified gaseous chemicals will flash vaporize and exit the tube, without such assistance needed). A photograph of the ends of the tubes and check valves is seen in Figure 9.



Figure 9. Close-up of Pyroflex check valves and pressure gauges.

Results

The fact that the tubes were mounted approximately four feet or more from the source of the fire, and that the discharge was not contained within an enclosure to any appreciable degree, resulted in a very challenging fire scenario. As opposed to the earlier tests, the JP-8 pool fires underneath both tires were still lit and functioning, as well as the tires, when the systems fired after the extended period after the fire was able to reach the tubes and initiate them. The hidden location of some flame sites behind the tires, as well as the uncertain rupture location of the tube in each test (and varied discharge pattern and coverage area), made the fire extinguishing process even more difficult. Even with these challenges, a Pyroflex unit with 5.0 lbs. of the 30% Black Widow/ 70% Monnex mix was adequate to extinguish the combination tire and fuel pool fire.

SUMMARY

The principle of radiation absorption enhancement for condensed-phase extinguishants can be explained based upon sound fundamental principles. It can be exploited economically and practically with available materials and techniques, as demonstrated successfully in recent tests.

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