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DEVELOPMENT OF A COMPOSITE THERMAL BARRIER COATING

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Abstract

A comparison between commercially available and a newly developed thermal management coating applied to steel substrates is presented. A successful coating must protect a thin 76 by 152 mm steel plate during a direct flame test and withstand low temperature flexural tests without cracking or delaminating. The only coating to meet both requirements is the newly formulated composite consisting of fiberglass in a silicone matrix.

Introduction

Thermal barrier coatings (TBC) insulate and protect a substrate from a prolonged or excessive heat flux and enable the substrate material to retain its mechanical property integrity during service. Selection of the type of system and its components depends upon the application. Heat may be dissipated away from a substrate by several methods, including heat sinks [3], active cooling [3], transpiration cooling [3], radiation cooling, [3], and intumescence [2, 4].

Intumescence is defined as the swelling of certain substances when exposed to heat. Upon heating, intumescent coatings form an expanded multicellular layer, which acts as a thermal barrier that effectively protects the substrate against rapid increase of temperature so that the structural integrity of the substrate is maintained [4]. Typically, an intumescent coating increases in thickness by 50 to 200 fold under the influence of heat [1]. Intumescent coatings contain active ingredients bound together by a binder that may include an acid source, a blowing agent, and a carbon source or char former [4], and some coatings contain hydrates that release water when exposed to heat.

In radiation cooling, much of the heat flux is reflected away by a high emissivity coating on the protected substrate [3]. Radiation cooling is based on the principles of emissivity, a material's ability to absorb and radiate energy as a function of its temperature. Emissivity is defined as the ratio of the total energy radiated by a material to a black body at the same temperature. A black body absorbs all electro-magnetic radiation and is an ideal radiator with an emissivity of 1. The emissivities of all materials are less than one and are determined by the material's temperature, surface characteristics, and chemical composition. In order to absorb and dissipate heat, high emissivity values close to one are desirable.

A new TBC composite to protect steel substrates was developed for this work and is compared against seven commercial products in a direct high temperature flame test and low temperature flexural test. Both test methods were developed as simple methods for preliminary screening prior to expensive, full scale testing. The direct flame test determines the coatings ability to protect the steel substrate from a heat flux, and the low temperature flexural test indicates the toughness (or strain to failure) and adhesion capabilities of the coating under harsh, cold temperatures while subject to high mechanical stresses during bending. The coatings were applied to standard 76 by 152 by 0.735 mm steel coupons. Three specimens per sample, or coating type, were tested for both experiments to show repeatability. Results from preliminary testing using steel coupons will suggest which product will protect steel ammunition containers in military service.

Materials

The commercial coatings are tabulated in Table 1 with a description of the coating and the employed cooling mechanism. Most of the commercial fire retardant coatings selected for this work function by intumescence, in which the coating swells and forms a cellular protective layer upon application of heat. Commercial coatings were applied to the steel coupon substrate with a brush and permitted to cure according to the manufacturer's instructions.

Initially, new TBC development was based on the concept of intumescence consisting of Polyurethane as the polymer binder, magnesium hydroxide as the water releasing agent, and azodicarbonamide as the foaming agent. After subsequent flame tests and low temperature flexural tests, it was apparent that selection of a polymer binder with low temperature high strain to failure was crucial in order to pass the low temperature flexural test, and perhaps a different cooling mechanism would enhance the high temperature performance.

Silicone (polydimethylsiloxane) was selected as the binder due to its mechanical flexibility and thermal stability over a broad temperature range (-79 to 204 °C). Silicone maintains relatively high strain to failure and durability at low temperatures and is utilized in automotive applications due to its high temperature performance. Furthermore, silicone decomposes at a higher temperature than most other flexible polymers and absorbs a considerable amount of energy in the process. Silicone has high surface tension, which enables this material to wet a wide variety of substrates including steel and other metals, glass, masonry, wood, and plastics.

Radiation cooling mechanisms were investigated and fiberglass was selected as the filler due to its high emissivity (0.87 – 0.95), high geometric aspect ratio (1-20 mm in length and 6-19 microns in diameter), low thermal conductivity, and its ability to bond to silicone. High emissivity enables fiberglass to behave similarly to a black body by absorbing a significant amount of energy and dissipating heat away from the substrate through radiation. The high aspect ratio of the fibers and low thermal conductivity allow the fibers to glow red on one end and radiate heat away from the substrate, while the other end of the same fiber remains at a cooler temperature in deeper layers of the silicone coating near the substrate.

A secondary cooling mechanism occurs at high temperatures during the chemical degradation of silicone into silicon dioxide and silicon oxide, in which a large amount of heat is radiated. Furthermore, as a result of silicone degradation, large surface areas of fiberglass are exposed. This matted network of exposed fiberglass increases the degree of radiative cooling and serves as anticonvective insulation while remaining grounded in the cooler under layers of silicone near the protected surface. Thus, the substrate is subject to a much lower temperature due to the two aforementioned cooling mechanisms. The developed coating provides heat flux and fire protection to a wide range of substrates, and is composed of two inexpensive, relatively benign, and easily obtainable components, silicone and fiberglass.

The newly developed TBC composite consists of fiberglass, silicone, and trace amounts of silicone oil to increase working time and will be referred to as the fiberglass/silicone coating. In order to determine the optimum composition, blends were made of 4, 6, 8, 10, 12, and 14 % fiberglass in a silicone matrix. The components were blended in a mixer and applied to a steel coupon with a putty knife targeting a thickness of 1.6 mm or less.

Experimental Procedures

The low temperature flexural test consists of annealing coated steel plates in dry ice, approximately -79 °C, for at least 15 minutes followed by bending around a 0.64 cm mandrel to an angle of 180º. During the experiment, pictures are taken of each specimen at 30º, 90º, and 180º of bending. Results provide information about the product’s response to thermal shock when bonded to a steel substrate and indicate the type and severity of surface damage incurred due to bending at low temperatures. A successful coating should not have any surface damage after testing.

The flame test employs the flame produced by a propane torch applied normal to the coated side of the specimen and an IR sensor (Omega OS550 Series Infrared Industrial Pyrometer) aligned on the same axis as the flame measuring temperature as a function of time on the back side of the vertical steel coupon. The inner cone length of the flame is adjusted to 3.175 cm, and the tip of the inner cone, the hottest part of the flame, is positioned directly on the sample's surface 2.54 cm above the bottom edge and at the center across the sample width. This configuration delivers worst case scenario results for high temperature direct point heating. The adiabatic flame temperature of propane in air is approximately 1,927 ºC +/- 38ºC. The flame is applied for a total duration of ten minutes. A coating is considered to fail the flame test if the maximum temperature exceeds 316 °C. The maximum temperature reached for each coating is compared against the control specimen, an uncoated steel plate, as a point of reference. The flame test in this work is similar or comparable to those found in the literature [1, 2, 4, 5].

Results

During bending, the coating stretches to accommodate the substrate’s new, larger surface area. The surface of the coating is in tension and receives the highest percent strain during bending. Thus, crack formation is initiated at the coating surface. Failure of the coating is indicated by crack development and propagation in the coating and delamination. Common modes of failure included tiny crack formation parallel to the bending axis in the deformation region, large cracks that caused pieces of the coating to detach and expose the substrate, and some brittle failure. In some cases, the coating delaminated as well. These types of surface failure indicate a coating with low strain to failure at low temperatures that will detach or delaminate, expose the substrate, and create a point source of radiative heat. In Figure 1, photographs of the tested coatings are presented. Figures 1.1 – 1.4 show typical failures at various degrees of bending while Figures 1.5 – 1.8 show the successful 12 % composition of the fiberglass/silicone composite coating.

As indicated in Table 1, Products A, B, C, D, E, and G failed the low temperature flexural test due to crack formation that occurred at 30° of bending. At more severe bending angles, the initial cracks simply propagated, caused pieces of the coating to detach from the substrate, and/or the coating delaminated. In the Product C sample, 2 of 3 specimens passed, and in the Product G sample, 1 of 3 specimens passed. However, all specimens per sample must pass the test in order to be considered successful. Product H, a silicone-based coating, is the only commercial coating tested that did not suffer any surface damage and passed the low temperature flexural test. The fiberglass/silicone composite coating did not suffer any surface damage, remained adhered to the substrate during bending, and passed the low temperature bend test.

The coating thickness does not appear to significantly affect low temperature performance. For Product E and the fiberglass/silicone composite, specimens were prepared at various thicknesses. All Product E specimens failed while all fiberglass/silicone composite specimens passed.

The flame test results are presented graphically in Figures 2 and 3. The average temperature versus time data collected during the flame test for each sample is presented in Figure 2, and the average maximum temperature and standard deviation per sample in Figure 3. In Figure 2, the solid black line represents the control sample, and the remaining curves are indicated by color and/or labeled. The 12 % fiberglass/silicone coating maintains the lowest maximum temperature of all of the coatings. In Figure 3, the black horizontal line signifies the pass/fail temperature limit of 316 °C and delineates the coatings that pass the flame test from those that do not. Coatings with a maximum temperature below the line pass, while those above the line fail. Results indicate that the only coatings with a maximum temperature below the limit are Products D and E and the fiberglass/silicone composite coatings excluding the 6 % fiberglass composition (Table 1). The average maximum temperatures of Products A, B, C, F, G, and H all exceed the limit, thus failing the test.

The standard deviation reported in Figure 3 indicates that the maximum temperature varies from specimen to specimen per sample. After subsequent analysis, it was realized that the flame test procedure should be modified to include a heat shield around the specimen in order to prevent additional hot air flow from affecting the temperature reading on the back side of the steel plate. With the additional heat deflector, it is assumed that the standard deviation of the maximum temperature would decrease per sample.

Conclusion

The aim of this work was to compare seven commercial coatings and a newly developed fiberglass/silicone composite coating applied to 76 by 152 mm steel coupon plates during a ten-minute flame test and a low temperature flexural test.

The only coatings that provide adequate thermal management protection to the steel substrate during the direct flame test are Products D and E and all concentrations of the fiberglass/silicone coating excluding the 6 % composition. However, Product C and the 6 % fiberglass/silicone coating would most likely pass the flame test if a heat shield is utilized.

The only two coatings that passed the low temperature flexural test were silicone based, including Product H and all concentrations of the fiberglass/silicone coating. However, Product H failed the flame test. Furthermore, the investigation of other binders revealed that polyurethane, vinyl, latex, and acrylic all suffered damage due to low temperature bending. Successful low temperature performance seems to depend primarily upon the coatings ability to attain high strain to failure, a material property, and not coating thickness.

The fiberglass/silicone composite coating utilizes radiation cooling to protect the steel substrate from a heat flux. Results indicate that the optimal temperature performance occurs between 8 – 12 % fiberglass, and more specifically, at 12 % fiberglass in silicone. Below 8 %, the concentration of fiberglass is too low to promote effective radiation cooling. Above 14 %, the viscosity of the coating dramatically increases, the coating is extremely difficult to apply, and the high concentration of fibers promotes heat conduction through the mat of fibers that undermines radiation cooling. Moreover, tests have shown reduced performance when the composition is 16 % and 20 % fiberglass.

The fiberglass/silicone composite coating is the only one tested that passed both the flame test and the low temperature flexural test. The silicone binder provides excellent adhesion properties to steel and several other materials and high strain to failure at low temperatures, and the high emissivity of the fiberglass enables effective radiation cooling.

Ultimately, a very effective, novel composite coating was created utilizing a few relatively inexpensive and commonly available products (fiberglass, silicone, and silicone oil) to meet the demanding needs of the military.

Acknowledgements

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Table 1. Descriptions of the commercial coatings and newly developed coating.

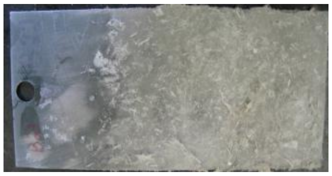
Product	Description/Components	Cooling Mechanism	Flame Test	Low T Flexural Test
A	Epoxy Resin: 4% Chlorophosphate in the (S) catalyst	Intumescent	Failed	Failed
B	Epoxy Resin: 4% Chlorophosphate in the (H) catalyst	Intumescent	Failed	Failed
C	Passive fire barrier coating, Water-based latex paint, No halogenated compounds	Intumescent	Failed	Failed
D	Water-based latex paint: Titanium Dioxide, Melamine, Vinyl Acetate/Acrylic Copolymer, Ammonium Polyphosphate, Water, No halogenated compounds	Intumescent	Passed	Failed
E	Water-based: Titanium Dioxide, Melamine, Vinyl Acetate Latex, DiPentaerythritol, Ammonium Polyphosphate, Water, Aluminum Oxide, Silicon Dioxide	Intumescent	Passed	Failed
F	Flexible, aqueous acrylic co-mixed with organic phosphinates, organo-cationic nano-dimensional clay, talc, zinc borate, and water, No halogenated compounds	Intumescent	Failed	Failed
G	Flexible aqueous acrylic and an intumescent char former composed of graphite carbon nano-fibers, No halogenated compounds	Intumescent char former	Failed	Failed
H	Silicone based coating, No halogenated compounds	Intumescent	Failed	Passed
4 %	4 % fiberglass in silicone matrix	Emissivity	Passed	Passed
6 %	6 % fiberglass in silicone matrix	Emissivity	Failed	Passed
8 %	8 % fiberglass in silicone matrix	Emissivity	Passed	Passed
10 %	10 % fiberglass in silicone matrix	Emissivity	Passed	Passed
12 %	12 % fiberglass in silicone matrix	Emissivity	Passed	Passed
14 %	14 % fiberglass in silicone matrix	Emissivity	Passed	Passed

1 – 30°

2 – 30°

3 – 90°

4 – 180°



5 – 12 % – Before

6 – 12 % – 30°

7 – 12 % – 90°

8 – 12 % – 180°

Figure 1. Low temperature flexural test specimens during testing. The first row (1 – 4) displays typical failure of the commercial coatings. The second row (5 – 8) displays the successful fiberglass/silicone coating even at 180°. The 12 % fiberglass in silicone composition is shown as representation of all of the fiberglass/silicone compositions.

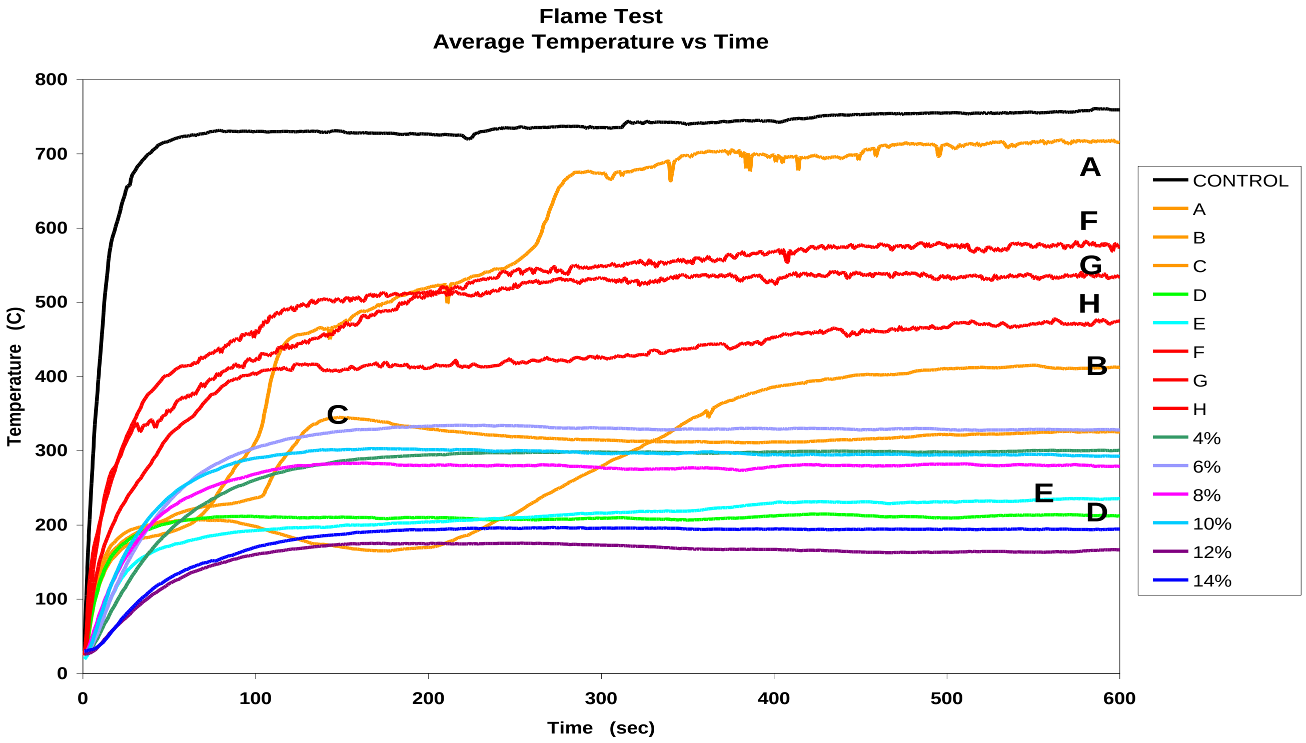


Figure 2. Average temperature versus time data collected for each product and each composition of the fiberglass/silicone coating during the flame test

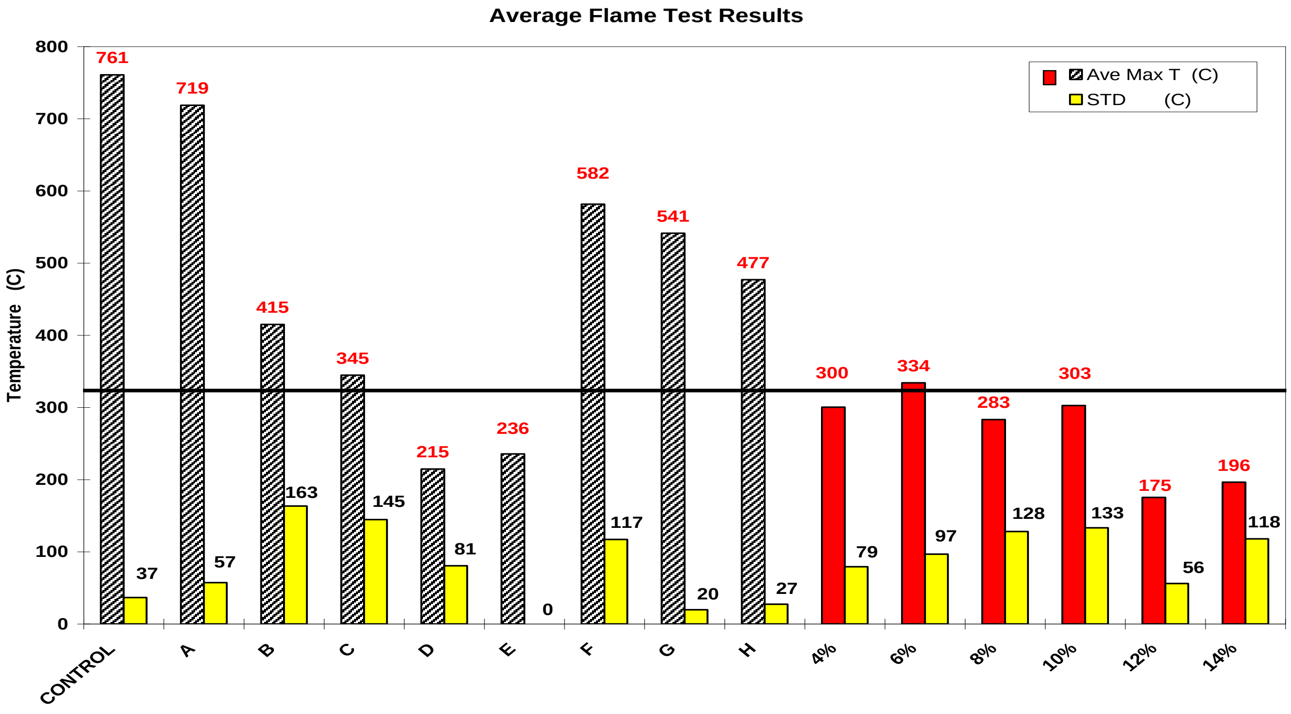


Figure 3. Average maximum temperature per sample during the flame test. The red bars correspond to the fiberglass/silicone developed coating differentiated by % fiberglass, and the black/white bars correspond to the commercial products. The yellow bars indicate standard deviation per sample.