

An Intumescent Coating For Improved Fuel Fire Protection Of Heat Sensitive Articles

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Intumescent coating compositions have been prepared using the ammonium salt of 4-nitroaniline-2-sulfonic acid and a copolymer of polysulfide-epoxy resin as the binder, into which have been dispersed various fillers. The fillers used in the study were low density micro-balloons for density control and fibers for controlled intumescence on contoured substrates. The filler effect on the thermal-physical efficiency of coatings has been measured. The coating utilizing short length silica fibers has been shown to have superior mechanical, environmental, and thermal properties. The coating applied to the exterior of loaded weapons has increased the time-to-detonation from three minutes for the unprotected weapon to 10-13 minutes.

KEY WORDS: Intumescence; Intumescent coating; Nitro-aromatic amine; Fire retardant coating.

INTRODUCTION

THE use of coatings to protect sensitive substrates from heat due to fuel fires has been known for some time. One such class, the intumescent coating, swells when subjected to heat, forming a thick insulating layer.¹

The objective of this study was to provide an intumescent coating which would extend the time-to-detonation for explosives contained in steel casings without detrimental effect on stability under high humidity conditions.

Early intumescent coatings contained a carbohydrate char-forming material (starch) and dehydration agents (ammonium phosphates) dispersed in polymeric vehicles.² The more recent coatings use other carbonific substances such as pentaerythritol and dipentaerythritol, in combination with a gas producing material, dicyandiamide, and catalysts such as ammonium polyphosphate or melamine phosphate.³ Sev-

eral commercially available intumescent coatings provide thermal protection as prepared; however, they often provide only limited protection when subjected to extreme weather conditions (rain).

The intumescent coating of this study was based on a dispersion of the ammonium salt of 4-nitroaniline-2-sulfonic acid⁴ and short length silica fibers in a binder system formed from a polysulfide and an epoxy resin.

THERMAL TESTS

Thermal evaluation of the coatings was performed on 7.62 cm × 7.62 cm × 0.159 cm cold rolled steel plates, the center of which contained a 2.54 cm diameter hole into which was cemented (epoxy-novolac/polyamide adhesive: 60/40) a 2.36 cm diameter by 0.159 cm thick cold rolled steel calorimeter disc. Time-temperature histories of the calorimeter disc were determined in the NASA T-3, JP-4 fuel fire test facility at a heat flux of 11.34×10^4 watts/square meter (w/m^2).⁵

A second configuration utilized a 38 cm long steel cylinder with a 0.64 cm wall thickness which simulated an explosive casing. The cylinder was instrumented with a thermocouple to measure the backface temperature and filled with sand to simulate the mass of the explosive charge. A measure of the adhesive behavior during intumescence was obtained by visual observation when the cylinder was immersed in a relatively large scale, free-burning JP-4 fuel fire.

Finally, to test in a simulated use situation, two full-size explosive cases were coated with the prototype coating and exposed to a JP-4 fuel fire. *Figure 1* depicts a schematic of the test facility used for full-scale testing. During the test, the time-to-detonation or deflagration of the loaded cases was recorded.

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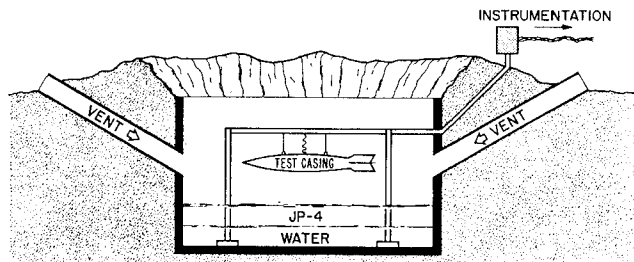


Figure 1—Scale-up test

DISCUSSION

Previous in-house studies have suggested that the following criteria are necessary in selecting a binder system for use with the nitroaromatic amine class of intumescent agents. These criteria were:

- (1) Binder polymers must soften or decompose below the activation temperature of the intumescent agent allowing the expansion process to form a stable foam
- (2) Binders must be processable with the intumescent agent to provide a coating
- (3) Binder residues should contribute to the physical stability of the intumesced foam after thermal activation.

The binder system (see Experimental) selected from investigations was a blend of polysulfidated and epoxy resins catalyzed by a tertiary amine. Thermogravimetric analysis (TGA) of polymer blends was used as a preliminary screening tool for selection of the polymer binder system. Figure 2 shows the char yield at 700 C of the binder as a function of the percent polysulfide in the resin blend. From the data, it can be seen that the higher the polysulfide resin content the lower are the char yields of the blends. Small scale dispersions of a series of mixtures with differing polysulfide to epoxy ratios with varying amounts of intumescent agent were then prepared. Coatings at or near the 100% polysulfide binder level formed soft or

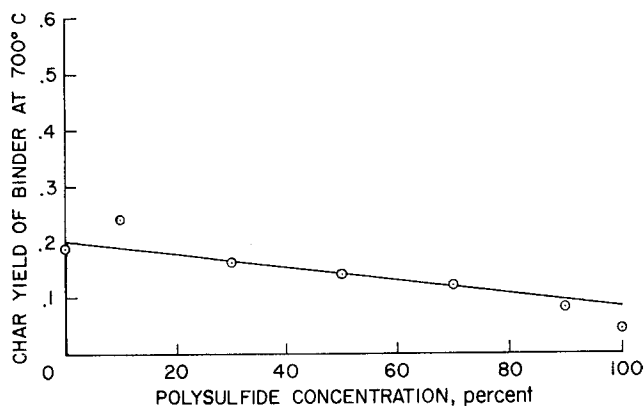


Figure 2—Effect on char yield at 700 C of polysulfide-epoxy binder as a function of polysulfide concentration (3 C/min in N₂ at 1 atm)

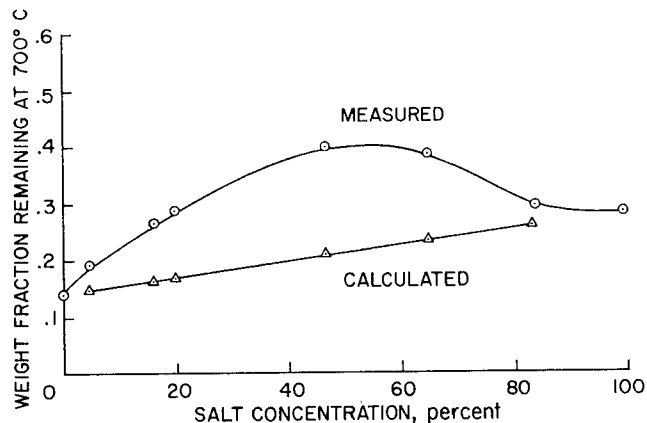


Figure 3—Effect of salt concentration on char yield at 700 C of 1:1 ratio polysulfide-epoxy, amine catalyzed intumescent, thermal protection coating. Heating rate = 3 C/min in N₂ at 1 atm. Char yield at 700 C

tacky films, and upon intumescence melted and flowed excessively. Conversely, at or near the 100% epoxy binder fraction, a hard, tough film resulted which restricted intumescence. From the polymer degradation data and the small scale rub-out experiments, a polysulfide (epoxy ratio of 1:1 by weight) was selected as providing optimum intumescence for a given concentration while still maintaining processability with the intumescent agent.

The effect of the intumescent agent (4 nitroaniline-2-sulfonic acid ammonium salt) concentration on char yield of the coatings was studied using the 1:1 polysulfide: epoxy ratio. Salt loadings were varied from 5-85% and thermogravimetric analysis conducted to ascertain the effect on the char yield at 700 C. Figure 3 shows the experimental weight fractions remaining at 700 C for various salt-resin combinations as a function of the salt concentration. These remaining weight fractions are then compared to the calculated weight fractions from the anticipated additive effects of each ingredient. From the data, it can be seen that the calculated weight fraction (char yield) increased from about 20% to a measured weight fraction of about 40% in the salt range from 50-65%. The synergistic effect of the salt and binder in this range has yet to be explained. From the char yield and the small scale dispersion data, a coating containing 65% salt was selected as the optimum for further studies in this program.

When the above composition was applied to steel cylinders simulating a casing containing explosives and exposed to JP-4 fuel fire, the material exhibited flow, causing excessive localized intumescence and did not provide the required thermal protection. Figure 4 represents the post-thermal condition of the coating evaluated on the steel cylinder. The coating indicated a flow to the hot zone, exposing the steel side walls and intumesced foam fissures to the steel surface. From this test it was obvious that the basic composition had to be modified for application to cylindrical surfaces. Thus, the following basic coating

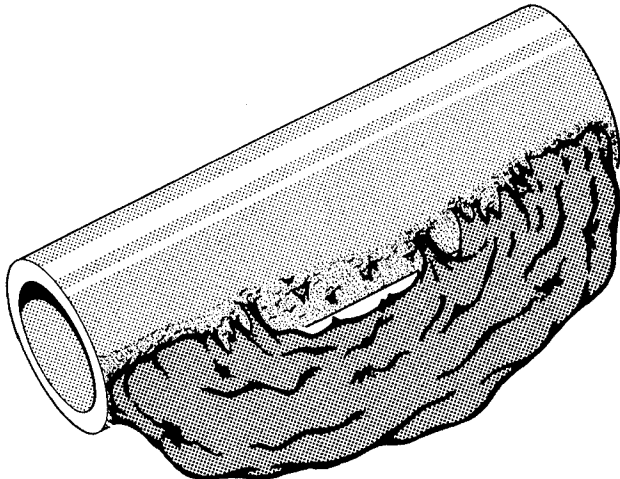


Figure 4—Effect of melt flow on intumesced foam

characteristics needed to be controlled to provide a coating for such applications:

- (1) Reduced flow prior to intumescence to prevent coating migration to the hot zone
- (2) Reduced coating density to provide a lower thermal conductivity and provide improved time-temperature performance.

With the coating requirements defined, specific material components were selected for addition to the basic composition (Table 1).

To control the melt flow prior to thermal activation, to improve the intumesced foam integrity, and at the same time enhance the physical toughness, short length silica fibers were added to the composition. Figure 5 shows that the thermal performance of the coating containing fibers was as effective as the basic composition in providing thermal protection.

To reduce the coating density, phenolic and silica microballoons were added to the composition. This

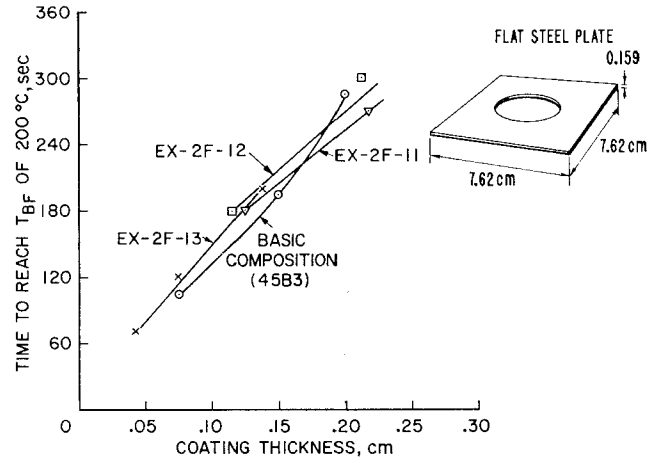


Figure 5—Effect of microballoons and fibers on time to reach T_{BF} of 200 C

addition resulted in a density reduction of the composition of 25-30% (Table 2). However, the flat plate thermal data (Figure 5) indicated that coatings with the lower density did not offer substantially improved thermal performance when compared to the basic coating. This was attributed to the fact that the back-side temperature response is controlled by both the activation temperature of the intumescent agent and the amount or degree of intumescence occurring during exposure to the thermal environment and not by the thermal conductivity of the coating. That is, the intumescent zone to substrate distance is very small and, therefore, the substrate temperature is not influenced to any great extent by small thermal conductivity changes caused by lowering the coating density. Further, the low density coating had poor physical integrity eliminating further interest in these materials.

The fiber loaded coating also provided thermal protection of the steel substrates after 30 days exposure to a 90% relative humidity, 38 C environment (Figure 6). Additional properties of the coating are listed in Table 3. From these results, the fiber-loaded coating was selected for further evaluation. Figure 7 shows the effectiveness of the coating when applied to steel cylinders. The coating, although showing a higher

Table 1—Use of Microballoon and Fibers For Thermal Protection

Material	Basic Composition (45B3)	EX-2F-11	EX-2F-12	EX-2F-13 (313)
Part A				
Polysulfide	14.1	14.1	14.1	14.1
Ammonium salt	57.0	57.0	57.0	57.0
MEK	28.9	28.9	28.9	28.9
Phenolic				
microballoons	—	7.2		
SiO ₂ microballoons	—	—	7.2	
Refrasil fibers	—	—		7.2
	100.0	107.2	107.2	107.2
Part B				
Epoxy	14.1	Same as basic composition		
Toluene	4.8			
	18.8			
Part C				
Tris-(dimethylamino-methyl) phenol	2.8	Same as basic composition		
Toluene	2.8			
	5.6			

Table 2—Effect of Microballoons and Fibers On Dry Coating Density

Coating Type	Dry Coating Density, g/cm ³
Basic composition (45B3)	1.425
45B3 + 10% phenolic microballoons	<0.973
45B3 + 10% phenolic microballoons w/45B3 + 10% fibers topcoat (EX-2F-11)	1.152
45B3 + 10% SiO ₂ microballoons w/45B3 + 10% fibers topcoat (EX-2F-12)	1.102
45B3 + 10% fibers EX-2F-13 (313)	1.549

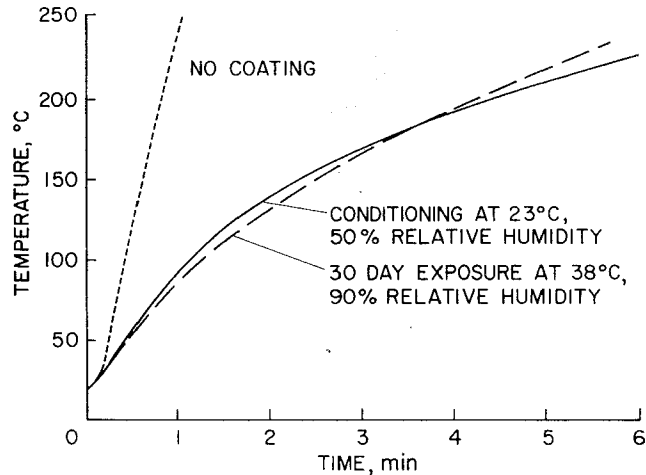


Figure 6—Fire-protective effectiveness of fiber-filled intumescent coating heating rate in JP-4 fire = 11.34×10^4 watt/m² 0.20 cm coating on 0.159 cm steel substrate

initial backside temperature, provided twice the backside thermal protection at the same thickness when compared to a commercially available coating. The coating showed no foam separations, fissures, or breaks when compared to the basic composition originally evaluated. From the flat plate and cylinder thermal test data, the fiber-loaded coating was selected as the prototype coating for full-scale testing on casings containing explosives.

Two experimental explosive casings were sprayed with 0.114 cm of the fiber-loaded coating. Full-scale testing of the two coated casings in a JP-4 fuel fire environment gave times to failure of 10 and 13 minutes. An uncoated control under similar conditions gave a time to failure of three minutes. These results confirmed our laboratory experiments in selecting the fiber-loaded intumescent coating.

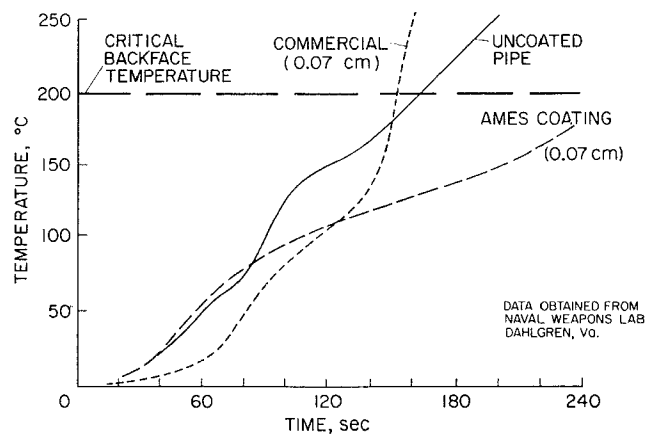


Figure 7—Comparison of time-temperature histories of Ames (313 coating) and commercial coating steel cylinder, 38 cm \times 10 cm od with sand interior heating rate in JP-4 fire = 11.34×10^4 W/m²

Table 3—Comparison of 45B3 and 313 (Fiber Filled) Coatings For Mechanical Properties

Properties	Basic Composition (45B3)	313 (fiber filled)
Tensile, newtons/m ² $\times 10^6$	110.3	97.5
Modulus, newtons/m ² $\times 10^8$	5.22	6.70
Elongation, %	2.2	1.4
Density, g/cm ³	1.425	1.549
Abrasion, mg wt. loss/1000 cycles	208	122
Flexibility, newtons	5.8	5.8

CONCLUSIONS

An intumescent coating has been successfully developed which extends the time required for detonation or deflagration of steel casings containing explosives. Also, the coating demonstrated hydrolytic stability not previously available with state-of-the-art coatings.

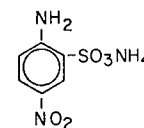
The major methods of achieving these objectives were:

- (1) Use of ammonium salt of 4-nitroaniline-2-sulfonic acid
- (2) Combination of the polysulfide and epoxy resins to provide a processable intumescent binder system for the salt
- (3) Use of short length silica fibers to control intumescence on cylindrical surfaces and improved physical properties of the coating.

EXPERIMENTAL

Ammonium Salt of 4-Nitroaniline-2-Sulfonic Acid

The 4-nitroaniline-2-sulfonic acid ammonium salt was prepared from the commercially available sodium salt. The sodium salt was dissolved in hot water and the ammonium salt precipitated by the addition of ammonium chloride to the solution. The precipitated product is filtered, washed, recrystallized, and dried. Elemental analysis: Calculated C, 30.64; H, 3.83; N,



- | | |
|--------------------------------|-------------------|
| 1. INTUMESCENT TEMPERATURE, °C | ~ 300 |
| 2. WATER SOLUBILITY, g/cc | 0.014 |
| 3. EQUIVALENT WEIGHT | 235 |
| 4. COLOR | YELLOW, |
| 5. APPEARANCE | CRYSTALLINE SOLID |

Figure 8—Ammonium salt of 4-nitroaniline-2-sulfonic acid as an intumescent agent



Paul M. Sawko is currently involved in research studies of high temperature polymers, fire retardant materials and intumescent coatings. He has co-authored several papers and has several patents pending. After receiving the B. S. Degree in Chemistry from St. Francis College, Loretto, Pa., Mr. Sawko worked for Benjamin Moore and Co. and the National Cash Register Co. with responsibilities for the development of specialty and industrial coatings. He joined NASA in 1966.

Edward J. Fontes is presently assisting in processing and application studies of fire retardant materials. He has had extensive experience with experimental and specialized coatings.



S. R. Riccitiello conducted his undergraduate studies at New York State University at Buffalo, N. Y. and graduate studies at Iowa State University. Before joining NASA-Ames, he was on the staff at Emerson Electric of St. Louis, Mo. working in the area of ablation materials. He has authored articles on ablation materials, organic synthesis and polymer synthesis.

17.87; Found: C, 30.41; H, 3.72; N, 17.68. *Figure 8* shows the thermochemical properties of the ammonium salt. The equivalent weight was 235 and the temperature of intumescence was 300 C as determined by thermogravimetric analysis.

Resin Binder System

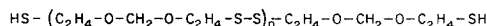
The resins for binder system shown in *Figure 9* were:

- (1) A mercaptan-terminated polysulfide resin (LP-3, Thiokol Chemical Corp.) having an average molecular weight of 1000 and a mercaptan content of 5.9-7.7%
- (2) A bisphenol A type epoxy resin (Epon® 828, Shell Chemical Co.) having an average molecular weight of 380 and an epoxide equivalent weight of 185-192.

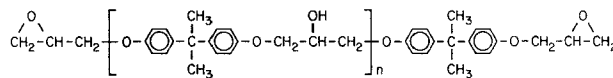
Catalyst

The catalyst used was tris-(dimethylaminomethyl) phenol available from Rohm and Haas Co. as DMP-30 (*Figure 9*).

POLYSULFIDE



BISPHENOL A EPICHLOROHYDRIN TYPE EPOXY RESIN



CATALYST: TRI-(DIMETHYLAMINOMETHYL) PHENOL

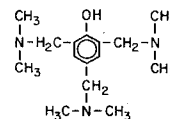


Figure 9—Polymer components for intumescent thermal protection coating

Fillers

Silica filler used was Hitco Refrasil A-100-1/32 fiber (0.03 cm length). Other fillers used were silica microspheres (Eccospheres® SI, Emerson and Cuming, Inc.) and phenolic microspheres (BJO-0930, Union Carbide Corp.).

Coatings

The coatings were prepared in a Kady Mill dispersion unit. The ammonium salt was dispersed in the polysulfide resin for 20 minutes (Part A), then, the commercial silica fiber, nominal .03 cm length, was added and dispersed for three minutes. The epoxy resin (Part B) and the catalyst (Part C) were added separately and each mixed for five minutes to a homogeneous blend. Coatings of 0.05 cm and 0.23 cm thickness were prepared on cold rolled steel substrates for thermal and physical property evaluation. The coatings were cured at room temperature for 72 hours prior to evaluation. All coatings were sprayed immediately after mixing, although up to four hours pot-life has been obtained.

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