

Intumescent Coatings Based on 4,4'-Dinitrosulfanilide

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Nitroaromatic amine based intumescent coatings have been developed which offer improved thermal protection to a substrate by reducing the backface temperature rise. This was accomplished by the use of an intumescent monomer agent, 4,4'-dinitrosulfanilide, which has a lower temperature of intumescence (220° C vs. 300° C) than previous nitroaromatic amine agents investigated. The sulfanilide compound offers a 12-fold reduction in water solubility which minimizes leaching in water media as well as maintaining the foaming process after exposure to a high humidity environment.

The selection of a polymer that functions as a flame quenching binder was determined from differential thermal analysis (DTA) and screening tests using a propane flame impinging on the cured binder films. A chlorinated polyolefin-epoxy-reactive butadiene acrylonitrile rubber blend met the selection criteria and was incorporated with the 4,4'-dinitrosulfanilide. This resulted in a coating which, upon exposure to fire, offered a substantial improvement in thermal protection of the substrate.

KEY WORDS: Intumescent coating; Intumescence; Fire-resistant; Thermal protection; 4,4'-dinitrosulfanilide.

INTRODUCTION

Intumescent coatings which swell or expand when exposed to fire or heat can be effective barriers in protecting heat sensitive substrates.^{1,2} Our work has been directed toward improved thermal and environmental performance of intumescent coatings. This has led to the use of acid salts of nitrosubstituted aromatic amines which have been shown to yield voluminous residues upon heating.^{3,4,5} Intumescent coatings based on the ammonium salt of 1,4-nitroaniline-2-sulfonic acid have demonstrated improved thermal protection and environmental stability for heat sensitive substrates over state-of-the-art materials.^{6,7,8}

The objective of this study was to advance the technology of nitroaromatic amine based intumescent coatings. The intumescent agent, 4,4'-dinitrosulfanilide, was found to have desired intumescent properties.⁹ It had an intumescent temperature of 220° C compared to 300° C for the ammonium salt of 1,4-nitroaniline-2-sulfonic acid. It had a comparable

residue yield of 45% but a very low solubility in water. This intumescent agent led to the development of coatings which may protect substrates to lower temperatures than attainable with the ammonium salt of 1,4-nitroaniline-2-sulfonic acid.

EXPERIMENTAL

Materials

The 4,4'-dinitrosulfanilide (*Figure 1*) was prepared according to the synthesis performed by Parnell.¹⁰ The temperature of intumescence was 220° C as determined by thermogravimetric analysis. The water solubility of this compound is 0.12 g per 100 cc of water. Infrared analysis and elemental analysis were performed on the compound to confirm chemical structure.

The resins (*Figure 2*) selected for the binder system were:

(1) A bisphenol A type epoxy resin (Epon[®] 828, Shell Chemical Co.) that has an average molecular weight of 389 and an epoxide equivalent weight of 185-192.

(2) A reactive butadiene-acrylonitrile that has terminal primary amine groups (Hycar[®] ATBN, B.F. Goodrich Co.).

(3) A chlorinated polyolefin with a chlorine content of about 60% (CP 310-6 Eastman Chemical Products, Inc.). This material is supplied as a solution at 50% resin content in xylene.

Coatings

The coatings developed in this program are composed of two parts. The Part A component was dispersed in a Kady Mill dispersion unit, Model L. The resin components of Part A are added to the mixing vessel along with the solvent blend. The sulfanilide is then added and the ingredients are dispersed for 20 min to form a homogenous mixture. Part B, the reactive ATBN and solvent are mixed with Part A prior to application. The coating is applied to a substrate using a DeVilbiss Type MBC, No. 96 aircap spray gun with a pot pressure of 2-3.5 × 10⁴ pascals (3-5 psi) and air pressure of 2.8-3.2 × 10⁵ pascals (40-45 psi). A coating thickness of 0.15 cm (60 mils) was generally utilized for all thermal and mechanical property measurements. All coatings were air dried for one week prior to testing.

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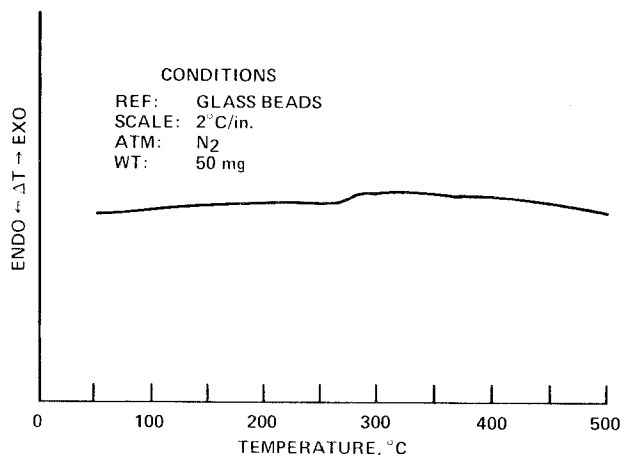


Figure 4—Differential thermal analysis (DTA) of binder system for 4,4'-dinitrosulfanilide

(2) The binder system, upon anerobic thermal decomposition, should not be exothermic in nature.

These criteria narrowed the possible binder systems to blends of chlorinated polyolefin polymers. These blends were screened by using a flame test (modified ASTM 1692) and observing whether the polymer was nonburning or self-extinguishing. The amount of smoke generated and the structure or stability of the charred residue could also be observed. In addition to this laboratory flame test, a differential thermal analysis (DTA) was run on each blend to observe the anerobic thermal decomposition and ascertain the mode of energy release, endothermic or exothermic (Figure 4). The binder selection based on the above tests and the previous criteria is shown in Figure 2.

Polymer Properties

In addition to the fire or thermal properties of the binder system, one must consider the physical/mechanical properties of the polymer to determine the quality of finished coating when the filler is added. It was observed that, with the chlorinated polyolefin selected, two inherent properties required correction. One, the flexibility of the polymer, and two, the low residue stability and adhesion during thermal decomposition. From previous data and studies, it was ob-

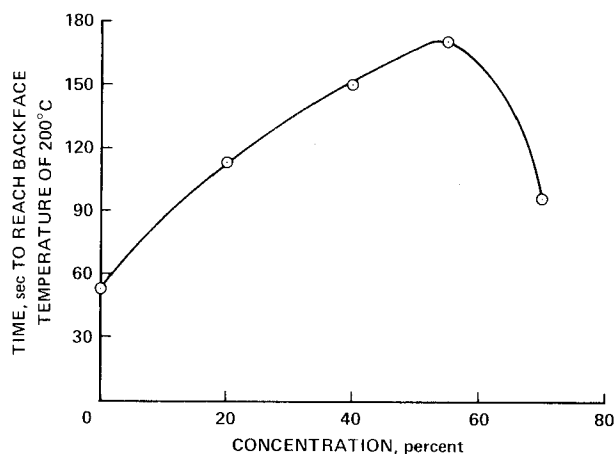


Figure 5—Effect of 4,4'-dinitrosulfanilide concentration on thermal efficiency

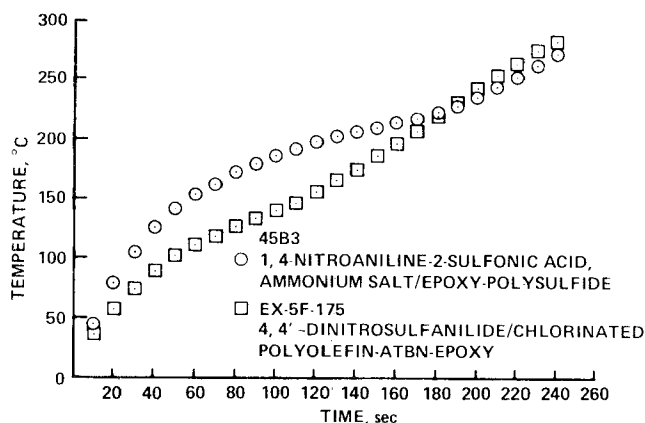


Figure 6 — Comparison of time-temperature history of nitroaromatic amine based intumescent coatings

served that, by using a flexible epoxy resin copolymer system, the chlorinated polyolefin system could be improved. To this end, an epoxy resin cured with an amine terminated butadiene-acrylonitrile rubber (ATBN) was selected for addition to the base chlorinated polyolefin. This ATBN-epoxy cured system gives two advantages over other systems in that it can act as a long polymer chain amine curing agent for the epoxy resin which produces flexibility and, secondly, it provides for the char stability in the epoxide. The addition of this copolymer to the chlorinated polyolefin did not hinder the intumescent process but in fact provided a more stable system.

Coating compositions were prepared with varying intumescent agent concentrations in the selected binder system. These coatings were prepared and applied according to the procedures described in the Experimental section. Compositions ranging from 20 to 70% sulfanilide content were evaluated for backface thermal protection and suitability as a film-former. From the results of the thermal testing shown in Figure 5, the compositions provide varying degrees of thermal protection. The sharp break in thermal protection above the 55% sulfanilide concentration was caused by the deterioration of the char during fire tests (mechanical spalling) which was due to the lack of binder residue in the formulation. This confirms the requirement for a

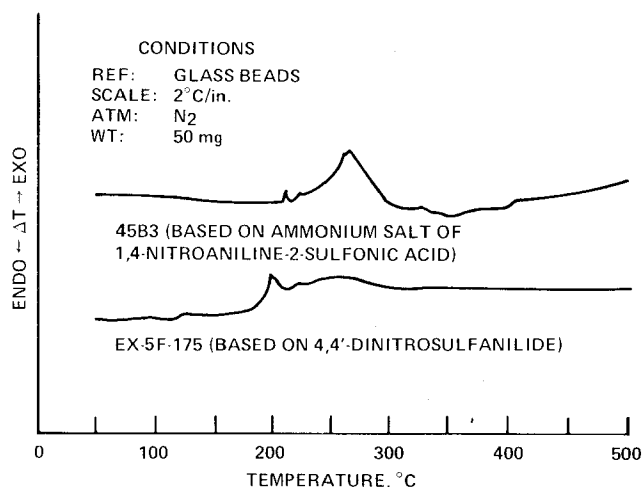


Figure 7—Differential thermal analysis (DTA) of coating systems

Table 1 — Sulfanilide Type Intumescent Coatings

Material	Parts by Weight			
	EX-6F-25	EX-6F-19A	EX-5F-175	EX-6F-19B
Part A				
4,4'-Dinitrosulfanilide	9.6	17.6	26.9	24.9
Chlorinated polyolefin	57.7	39.6	32.9	15.8
Epoxy	1.7	1.2	1.0	0.5
Toluene	22.8	30.6	28.8	43.2
Methylene chloride	8.2	11.0	10.4	15.6
	100.0	100.0	100.0	100.0
Part B				
Amine terminated butadiene acrylonitrile	6.8	4.8	4.0	2.0
Toluene	6.8	4.8	4.0	2.0
	13.6	9.6	8.0	4.0
Dry Wt. % of intumescent agent	20	40	55	70

binder system that contributes to char adhesion and char formation during intumescence.

The compositions used for Figure 5 are reported in Table 1 and were chosen as intumescent coatings for comparison with an earlier type of nitroaromatic amine intumescent coating, one using the ammonium salt of 1,4-nitroaniline-2-sulfonic acid as the self-intumescent monomer agent.^{6,7} It is evident from Figure 6 that the sulfanilide intumescent coating (EX-5F-175) reduces the backface substrate temperature in the zone from room temperature to 200° C at a thickness of 15 cm (60 mils). This reduction in backface temperature can be attributed to the lower intumescent temperature associated with the sulfanilide agent (see Figure 1) which permits the foam formation to occur more rapidly, thus insulating the substrate sooner. In addition, from DTA data shown in Figure 7, the lower energy release of the sulfanilide intumescent coating provided an overall improvement in the basic thermal protection of this coating as compared to the other nitroaromatic amine coatings reported.⁶

The effect of the intumescent agent content of the sulfanilide type intumescent coating compared to the coatings based on the ammonium salt of 1,4-nitroaniline-2-sulfonic acid over the range of 20 to 75%

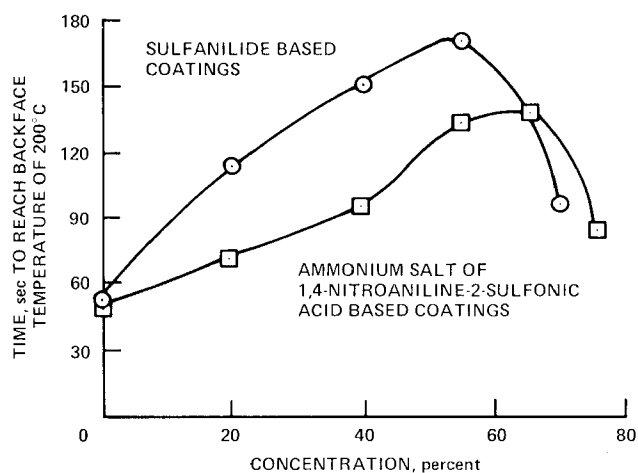


Figure 8—Effect of intumescent agent concentration on thermal efficiency

is shown in Figure 8. The purpose of this comparison was to demonstrate the influence of a lower intumescent temperature and the lower exothermic nature of 4,4'-dinitrosulfanilide type coatings in maintaining thermal protection was applicable over a broad spectrum of coating compositions. This confirms the selection criteria established for improving the thermal protection properties of nitroaromatic type intumescent coatings.

Exposure Resistance

An important consideration in the performance of any thermal protection coating is the ability to maintain physical properties during exposure to environmental attack from humidity or water. Degradation of coating properties due to the environment could cause adhesive failure or cracking which would reduce the effectiveness of these coatings by permitting the fire to penetrate the substrate being protected. Additionally, leaching or extraction of the intumescent agent by water can alter the expansion process, thereby destroying the thermal effectiveness of intumescent coatings. The sulfanilide based intumescent coating (EX-5F-175) was exposed to a 38° C and 90% relative humidity condition for 30 days in a humidity chamber prior to testing in the JP-4 fuel fire (T-3 Test). From Figure 9, it is evident that the

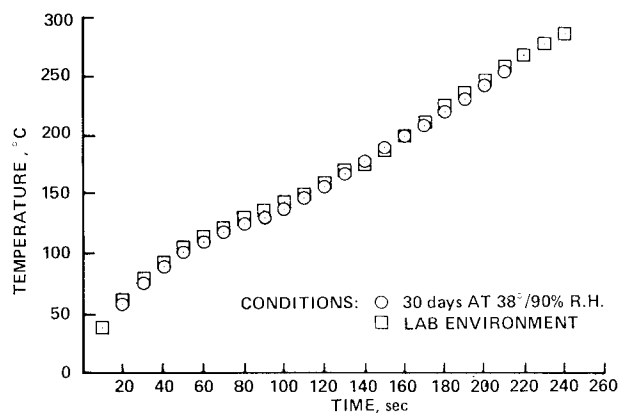


Figure 9—Time-temperature history of coating exposed to humidity environment

temperature-humidity aging had no effect on the thermal protection compared to the same coating composition conditioned at standard laboratory conditions. No change was observed in coating appearance, swelling, erosion, or brittleness after removal from the humidity chamber. Additionally, thermal test observations indicate that the coating composition using the sulfanilide salt produced a uniform, black expanded foam residue which was more resistant to thermal erosion than other coatings investigated. Fire exposure time-temperature data of coatings that have been subjected to long term, high humidity conditions supported the use of the sulfanilide compound.

SUMMARY

A sulfanilide based intumescent coating has been developed which can be an effective thermal insulator to a fire or heat source by reducing (slowing) the backface temperature rise of a substrate. This higher thermal efficiency coating was based on:

(1) Use of 4,4'-dinitrosulfanilide, which has a lower intumescent temperature permitting faster foaming response to the fire.

(2) Development of a compatible polymer blend that is not exothermic and is flame quenching.

Some advantages of lower temperature, thermally efficient intumescent coatings are in applications to areas where weight or thickness is a critical factor for thermal protection coatings. Also, the range of protection offered by varying the 4,4'-dinitrosulfanilide content should allow considerable latitude in formulating to

specific physical and thermal requirements. For example, the thermal protection of aircraft components would constitute an application where a reduction in the coating thickness could result in weight savings while still maintaining the required thermal protection. Physical properties of coatings could be adjusted without unduly sacrificing thermal insulation when compared to the higher intumescent agent content required for other nitroaromatic amine intumescent coatings. □

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