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M E M O R A N D U M

July 17, 1968

TO: H. J. GROH

FROM: W. H. HALE *W H H*

THERMAL DEGRADATION OF NEOPRENE,
HYPALON*^{*}-COATED NEOPRENE (LEADED AND UNLEADED), AND POLYURETHANE

INTRODUCTION

A recent explosion in a containment facility at Mound Laboratory was attributed to ignition of vapors released by pyrolysis of lead-loaded, Hypalon-coated neoprene gloves rinsed in 0.35M nitric acid and placed in an oven to dry. Oven temperature at the time of the explosion was assumed to be $>250^{\circ}\text{C}$ as a result of a defective controller. At the Savannah River Laboratory, neoprene gauntlets and gloves (with and without Hypalon coating and lead-loading) are used routinely in facilities where they are heated by exposure to hot equipment. Hypalon-coated polyurethane is being considered as a material for manipulator gauntlets. The purpose of this work was to evaluate neoprene and polyurethane for potential safety hazards at temperatures up to 300°C .

SUMMARY

Neoprene, Hypalon-coated neoprene (leaded and unleaded), and polyurethane are safe for use up to $\sim 250^{\circ}\text{C}$ in air, as determined by thermogravimetric (TGA) and differential thermal (DTA) analysis. Degradation, oxidation, and loss of mechanical integrity begin around 250°C and reach a maximum rate around 300°C . Decomposition of neoprene is exothermic; of polyurethane, endothermic. Hypalon coating has little effect on the thermal behavior of neoprene. Decomposition of leaded neoprene is more exothermic than that of unleaded material, especially when the lead lining has been in contact with nitric acid, with the probable formation of lead nitrate; heating massive amounts of leaded neoprene gloves or gauntlets in a confined space should be avoided.

*Du Pont trademark.

H. J. GROH

- 2 -

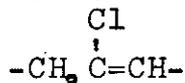
July 17, 1968

DISCUSSION

Samples were obtained by cutting small pieces from a glove or gauntlet. TGA samples were placed in a platinum cup and heated at 5°C/min in static air. DTA samples were placed in a cylindrical Pyrex container and heated at 10°C/min in static air.

Hypalon-Coated NeopreneTGA

As shown in Figure 1a, thermal decomposition of Hypalon-coated neoprene occurs in two stages - a rapid weight loss beginning at 300°C followed by a slower weight loss beginning at 400°C and lasting until the end of the run (510°C). The sample residue consisted of individual pieces although they were black and friable. The neoprene monomer unit is



The composition of vapor evolved from decomposing neoprene depends on the air supply.⁽¹⁾ In a limited supply of air, HCl, SO₂, H₂O, and hydrocarbons are evolved. In excess air, HCl, SO₂, H₂O, CO₂, and CO are the major products. HCl is the primary constituent under both conditions for both the fast and slow weight-loss periods.⁽²⁾ Decomposition of neoprene is exothermic even in a pure nitrogen atmosphere⁽³⁾, which is characteristic of polymers containing double bonds.

The thermogram of a sample soaked in 0.35M HNO₃ at 23°C for 64 hours was identical to that of an untreated sample.

DTA

Three peaks are observed in the DTA thermogram of Hypalon-coated neoprene (Figure 1b) - an endotherm at 81°C (melting of crystallites), a broader, weaker endotherm at 172°C (melting of the amorphous phase), and a sharp, strong exotherm at 310°C (decomposition). The TGA and DTA decomposition temperatures are in good agreement.

A sample preheated at 250°C for 1 hour remained flexible and elastic. DTA (Figure 1c) showed that the decomposition temperature was lowered to 297°C and the intensity of the crystallite melting peak was reduced as expected.

NeopreneTGA

Neoprene began to decompose at 320°C (Figure 2a) compared to 300°C for Hypalon-coated neoprene. Other features of the two thermograms were identical.

July 17, 1968

DTA

As shown in Figure 2b, the DTA thermogram of neoprene was very similar to that of the Hypalon-coated sample. The three peaks occur at 82°, 180° and 330°C. The TGA and DTA decomposition temperatures were in good agreement.

A sample preheated at 250°C for 1 hour showed reduced intensity of the melting peaks and a 10°C lower decomposition temperature (Figure 2c).

Leaded Hypalon-Coated NeopreneTGA

The leaded sample gave a TGA thermogram (Figure 3a) essentially the same as that of unleaded material. Decomposition began at 320°C.

DTA

The DTA thermogram (Figure 3b) of leaded material shows intense melting endotherms at 92°C and 196°C, a sharp decomposition exotherm at 326°C, and an additional weak exotherm (at 446°C) which was not observed in unleaded samples.

A sample of leaded material soaked in 0.35M HNO₃ for 24 hours gave the altered thermogram shown in Figure 3c. The first two peaks are near the melting endotherms of the untreated sample but are exothermic rather than endothermic as previously observed.

Another leaded sample was cut in several places to expose the lead layer, then it was soaked in 0.35M HNO₃ for 24 hours. As shown in Figure 3d, the first two exotherms were changed only slightly from the solid sample. However, the two degradation exotherms were much broader and stronger.

The presence of lead (in the form of Pb₃O₄) has a definite effect on the thermal decomposition of Hypalon-coated neoprene. Degradation is highly exothermic when leaded material has been soaked in nitric acid, probably due to formation of lead nitrate which decomposes at ~470°C. When massive amounts of material are heated in a confined space, heat dissipation cannot occur. Heat from exothermic degradation raises the material temperature releasing more heat until an explosively rapid decomposition can occur. In a limited air supply, hydrocarbons are evolved which might be detonated by lead nitrate at its decomposition point, by the active lead oxide decomposition product, or by Pb₃O₄ at high temperature.

In a thermal excursion such as in the decomposition of leaded material with limited heat dissipation, the hazardous temperature is the point at which degradation begins (~250°C) rather than the exothermic peak position (320-345°C).

H. J. GROH

- 4 -

July 17, 1968

Hypalon-Coated PolyurethaneTGA

As shown in Figure 4a, weight loss from a sample of Hypalon-coated polyurethane began at 310°C and steadily increased in rate. At 410°C smoking occurred and the run was terminated. The sample was recovered as a black, tar-like mass.

A sample soaked in 0.35M HNO₃ for one hour gave a TGA thermogram identical with that of the untreated sample.

The polyurethane monomer unit is



Decomposition occurs primarily by loss of CO₂⁽⁴⁾; no HCN is evolved.⁽⁵⁾

DTA

The DTA thermogram (Figure 4b) shows two strong endothermic melting peaks at 88° and 182°C, and a weak degradation endotherm at 285°C. Endothermic decomposition is not surprising since polyurethane contains no carbon-carbon double bonds and some of the carbon atoms are already bonded to two oxygen atoms.

A sample preheated at 200°C for 1 hour remained flexible and elastic. The DTA thermogram (Figure 4c) showed greatly reduced intensities of both melting peaks with the degradation peak virtually unchanged.

Danger of explosion from Hypalon-coated polyurethane is small since thermal decomposition is endothermic, the main gaseous product is CO₂, and there is no oxidizing agent incorporated in the material.

WHH:mc

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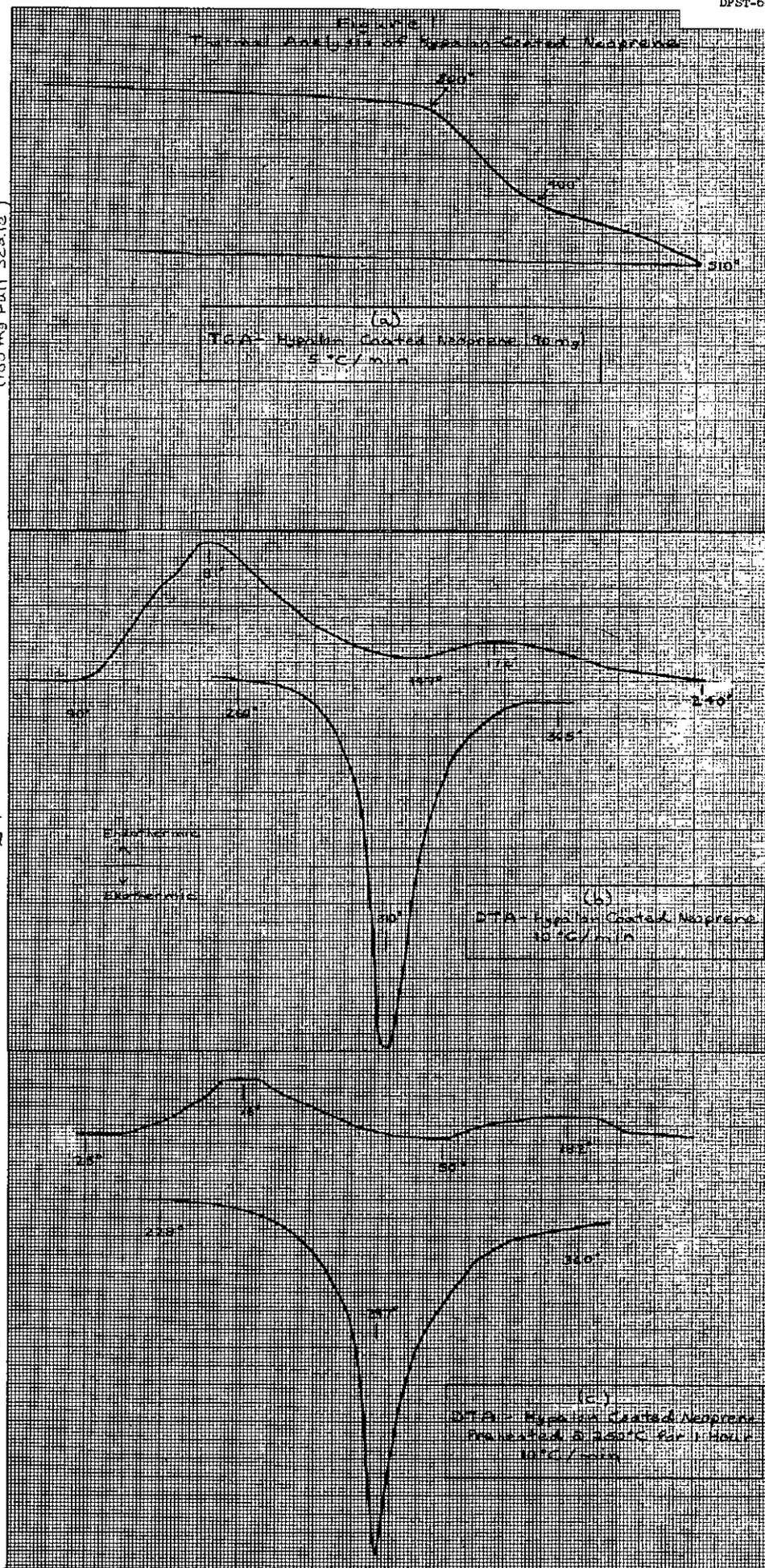
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Figure 1
Thermal Analysis of Epoxide-Coated Neoprene

Weight →
(100 mg Full Scale)

-ΔT

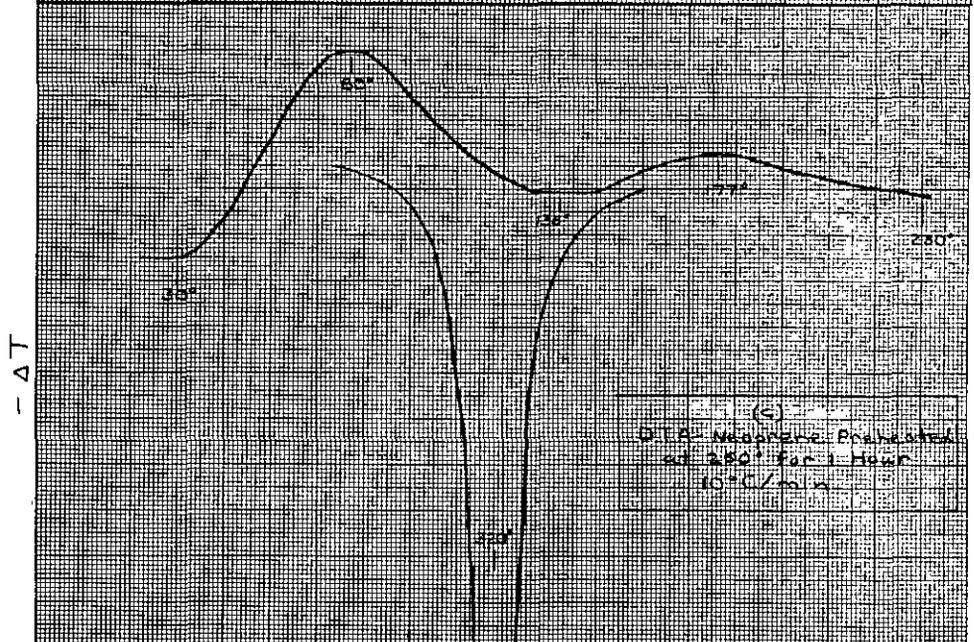
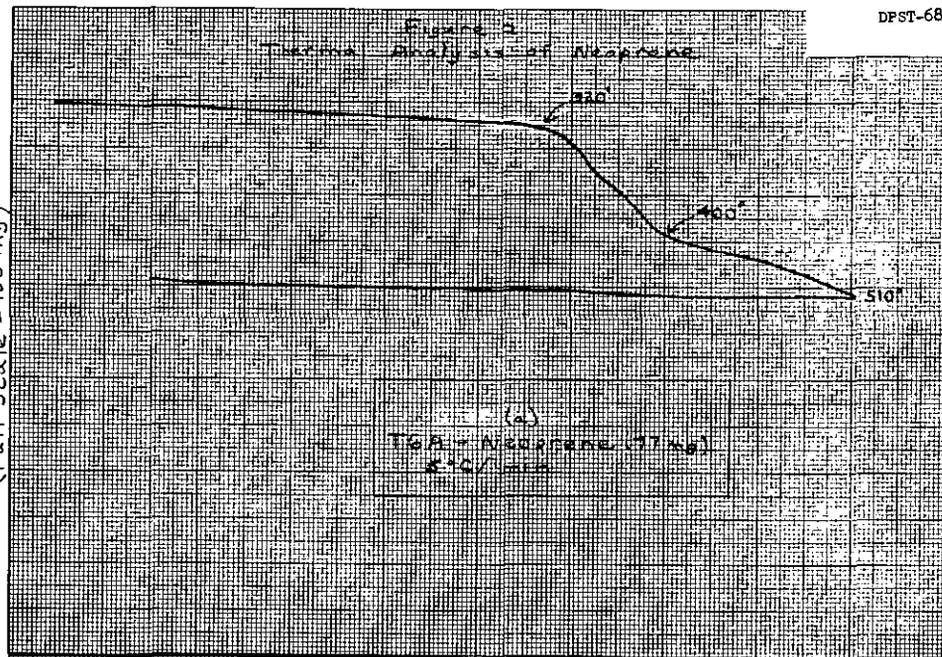
-ΔT



Reference Temperature, °C

Figure 2
Thermal Analysis of Neoprene

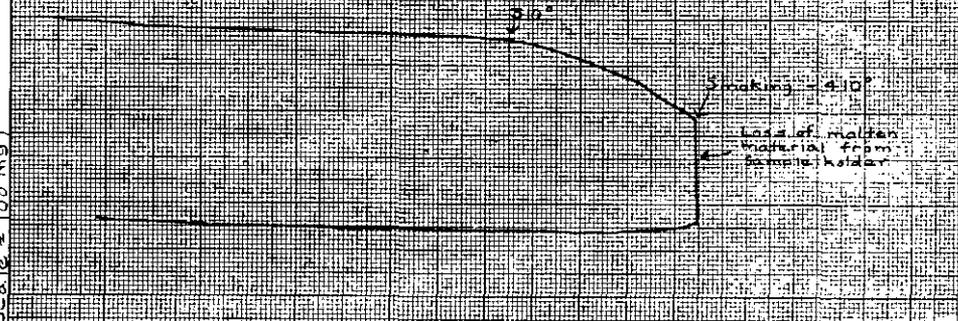
Weight
(Full Scale = 100mg)



Reference Temperature, °C

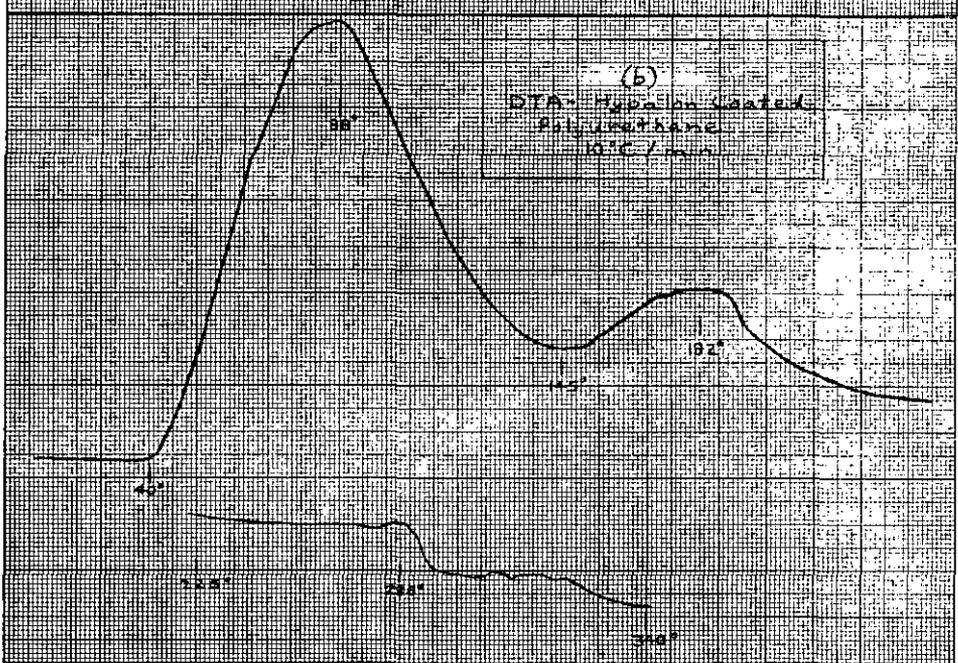
Figure 4
Thermal Analysis of Hypalon-Coated Polyurethane

Weight →
(Full Scale = 100 mg)



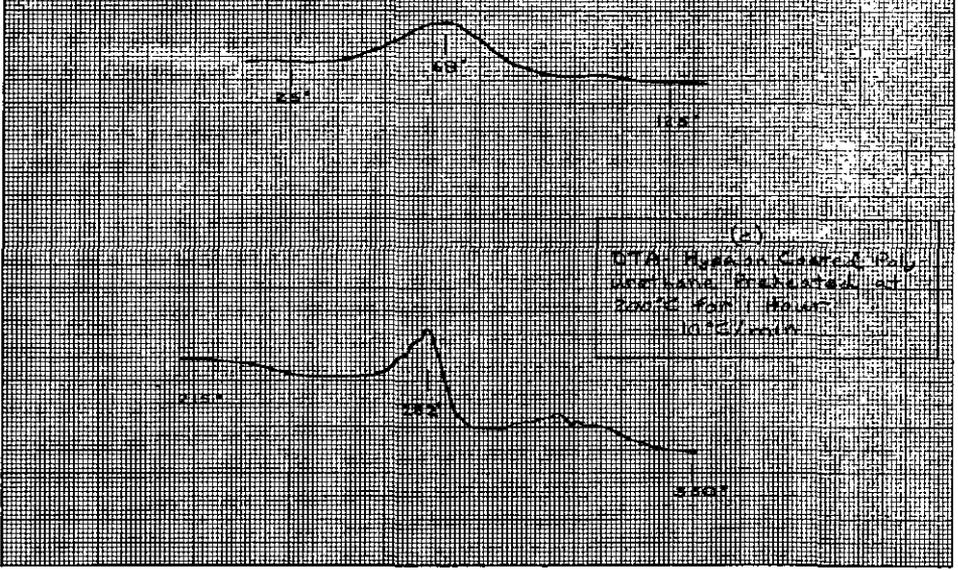
(a)
TGA - Hypalon Coated Polyurethane (100mg) 5°C/min

-ΔT



(b)
DTA - Hypalon Coated Polyurethane 10°C/min

-ΔT



(c)
DTA - Hypalon Coated Polyurethane Preheated at 200°C for 1 Hour 10°C/min

Reference Temperature, °C