

## Effect of Polymer Coating on Ammonium Nitrate Substrate

THOMAS C. CASTORINA and ANDREW F. SMETANA, *Explosives Division, Feltman Research Laboratory, Picatinny Arsenal, Dover, New Jersey 07801*

### Synopsis

Prilled, spheroidized, and granular ammonium nitrates (AN) were coated with poly-(chloro-*p*-xylylene) (parylene C) by a vapor deposition polymerization technique. Particles of AN with a 0.2% coating remain free flowing after long exposure to ambient conditions. The effectiveness of the coating as a moisture barrier on the three forms of AN was found to be in the order spheroids > prills > granules. Water adsorption isotherms and hygroscopicity determinations indicate that a 0.7% coating hydrophobes the surface of AN by approximately one order of magnitude. The parylene C/AN interface exhibits chemical and physical stability at elevated temperatures.

### INTRODUCTION

There are numerous conventional methods reported in the literature<sup>1-6</sup> of modifying the surfaces of reactive powders using materials in concentrations of 2-5%. A thorough study of the stability of these coatings has not been reported. Any stability of coating, if attained, is by virtue of excessive thicknesses of deposition and not by an intrinsic adhesive property between adduct and substrate. The scope of the problem is to achieve, with a minimum of thickness, preferably in the range of 0.1% to 1% by weight, a continuous and stable deposition of barrier material on the surface of reactive powders. This could be accomplished by the condensation of monomer molecules on the irregular surface subsequently induced to undergo polymerization. By virtue of an intimate replication of the surface on a molecular scale, the polymeric barrier material deposited in this fashion (in contradistinction to the conventional methods) would be locked in position on the surface, and hence stabilized.

Polymer coatings by the polymerization of monomers from the vapor phase (vapor deposition polymerization) (VDP) have been under investigation only in the past decade and are still in the developmental stage. However, notable success has been achieved in the coatings of powders by this VDP technique.<sup>7-10</sup> In general, polymers have elastic properties and are thermally and chemically stable, and when deposited in this fashion, form stable protective barriers to reactive gases and vapors. This paper describes the application of the VDP technique (developed by Union Carbide

Corp.) to prilled, spheroidized, and granular ammonium nitrate (AN) to produce surface modifications that would impart desired flow properties and minimize reactivity at the substrate interface.

## EXPERIMENTAL

### Ammonium Nitrate, Uncoated (AN-u)

Baker analyzed reagent-grade AN, ground with mortar and pestle, was used for the water adsorption isotherm measurements. The surface area of this material was found, by the low temperature argon adsorption method, to be 0.76 m<sup>2</sup>/g.

Prilled, spheroidized, and granular forms were obtained from Mississippi Chemical Company, Yazoo, Miss.; Chevron Chemical Company, Richmond, Calif.; and Commercial Solvents Corporation, Sterlington, La., respectively.

### Water

The water used in the adsorption isotherm measurements and dosing experiments (see below in this section) was distilled water, redistilled from alkaline permanganate and sulfuric acid, followed by a third distillation. The water was degassed prior to use by freeze-thawing under vacuum at -78°C.

### Vapor Deposition Polymerization (VDP)

All samples of AN were coated with poly(chloro-*p*-xylene) (parylene C) in increments of 0.2% by Union Carbide Corporation, Bound Brook, N. J. under a service contract.

The procedure for the VDP technique, detailed elsewhere,<sup>9</sup> is described briefly as follows: A measured quantity of dichlorodi-*p*-xylylene supplied by Union Carbide Corp. was placed in a porcelain boat, and the boat was placed in the distillation zone of the coater apparatus. A 1-lb batch of AN-u was placed in a plastic container at the opposite end of the coater. The system was then evacuated to 10<sup>-3</sup> torr using a forepump protected with a -78°C trap. The distillation zone was heated to approximately 150°C and the dimer was distilled into the pyrolysis zone heated to 600°C. The resulting monomer gas was then led into the deposition chamber containing the AN-u. The deposition chamber was held at ambient temperature, and the coating of AN proceeded with a tumbling action by rotation of the plastic container.

### Hygroscopicity Tests

Hygroscopicity determinations were run at 76% and 100% relative humidity (R.H.) at 23°C with a saturated solution of sodium chloride and distilled water, respectively. Three-gram samples of parylene C-coated AN (AN-c) and AN-u (as controls) exposed to these R.H.'s in desiccators

kept at  $23^{\circ} \pm 1^{\circ}\text{C}$  were weighed periodically, and the rate of water uptake was reported in per cent gain in weight with time (hours).

### Water Adsorption Isotherms

The adsorption isotherms were conducted gravimetrically at  $23^{\circ}\text{C}$ , using a Cahn RG electrobalance, which has an absolute sensitivity of 1 microgram with a maximum sample load of 1 g. Pressures were measured to three significant figures with an Alpatron vacuum gauge from  $10^{-3}$  to  $10^3$  torr.

### Thermal Stability Test

One-gram samples were placed in break-seal ampoules provided with flame seals. The charged ampoules were affixed to a vacuum manifold and outgassed at ambient temperature for five to seven days to  $10^{-6}$  torr before flame-sealing. The sealed ampoules were placed in a constant-temperature bath set at  $120^{\circ} \pm 1^{\circ}\text{C}$  and heated for 40 and 80 hr as designated. The gases generated by the heating were fractionated at  $-78^{\circ}\text{C}$  and ambient temperature and analyzed mass-spectrometrically.

In the experiments where water was added to the samples, the following procedure was used: After the outgassing step (cited above), 6 torr of water vapor was dosed into the sample systems. Prior to flame-sealing, the valve, to which an ampoule was attached, was closed, and a liquid nitrogen bath was applied to freeze the water away from the flame-seal region. The section of the ampoule containing the sample/water which had been frozen brought to ambient temperature after the flame-sealed tip had cooled. The samples in the sealed ampoules then were heat-treated and analyzed as described above for the anhydrous samples.

### Explosion Temperature Test

The explosion temperature determinations were run on the modified PA Explosion Temperature Apparatus described elsewhere.<sup>11</sup>

## RESULTS AND DISCUSSION

### Hygroscopicity Determinations

The passivation of the surface of AN was studied with prilled AN (pAN), spherodized AN (sAN), and granular AN (gAN). These forms are also well suited for studying the effectiveness of the VDP technique described in the experimental section. Examination at 50-power magnification showed the prills to possess annular cavities and the smoothest surface; the spheroids to be devoid of any cavitations but with a smooth knobby topography; and the granules to have characteristic sharp edges and corners. The extent of passivation by the VDP of parylene C in various thicknesses ranging from approximately 0.2% to 3% by weight of AN was demonstrated first by hygroscopicity determinations. Since R.H.'s above

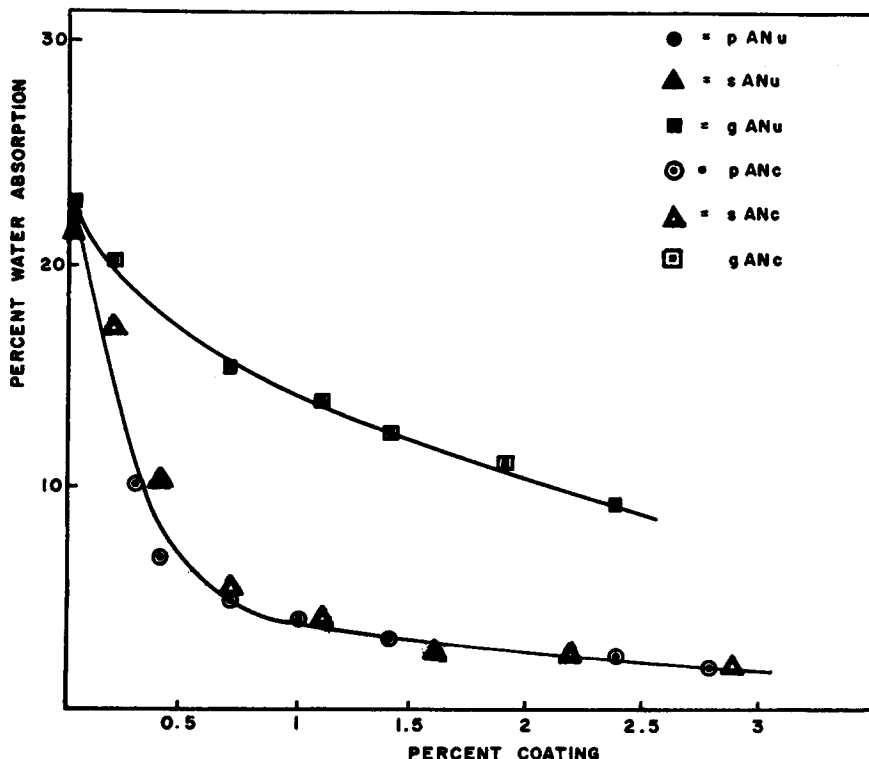


Fig. 1. Water absorption by AN exposed to 76% R.H. for 192 hr as a function of per cent parylene C coating.

52% cause caking and are more likely to be encountered in the normal handling of AN, hygroscopicity determinations were made on all three forms of AN at 76% and 100% R.H. (Figs. 1 through 5).

The magnitudes of water uptake by the coated samples (ANc) as a function of coating thickness and R.H. in comparison with the uncoated control samples (ANu) are displayed in Figures 1 and 2. The curves for pANc and sANc are superposable at 76% and 100% R.H. and are characterized by a sharp bend at the point corresponding to 0.7% coating. A slight difference in these two samples may be observed above the 1.5% coatings at 100% R.H. (Fig. 2). The sAN appears to be coated more effectively with increasing thicknesses of parylene C deposition. The difference in percent water absorption between the coated (ca. 2%) and uncoated samples of AN is approximately one order of magnitude for pAN and sAN, and only a factor of 2 for gAN. Apparently, because of the sharp edges, corners, and flat surfaces, granules do not coat completely by the tumbling action employed. The rate of water absorption is reduced significantly for the pANc and sANc with parylene C. In addition, coatings of as little as 0.2% imparted free-flowing behavior to particles of AN even after increases up to 5% of water uptake.

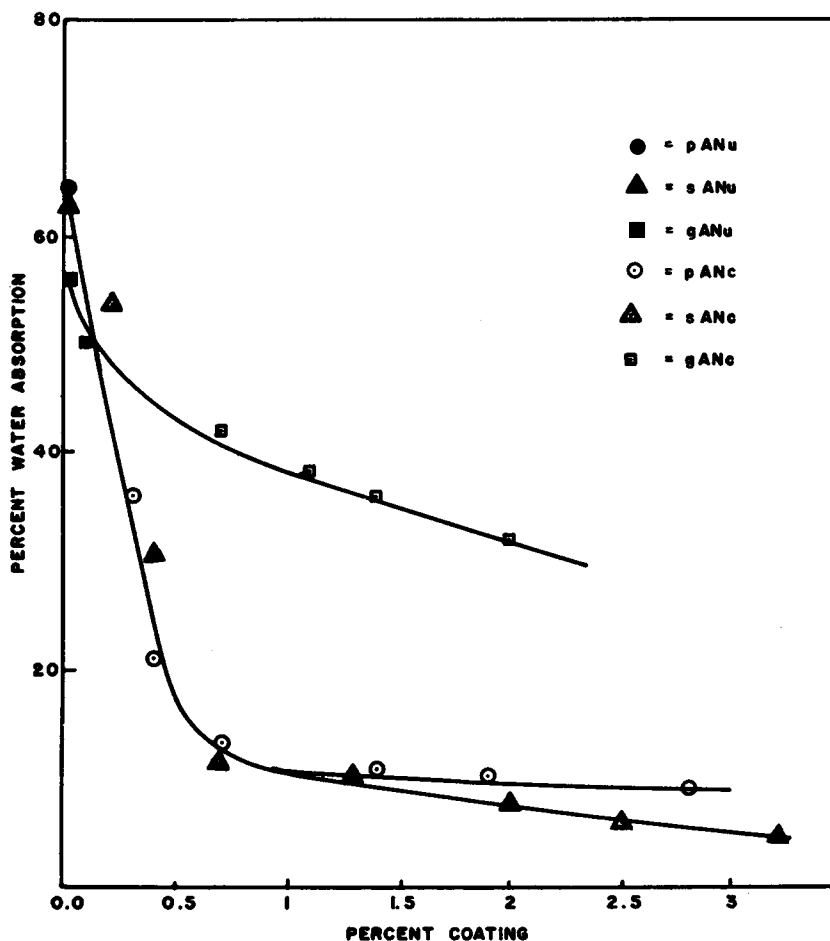


Fig. 2. Water absorption by AN exposed to 100% R.H. for 192 hr as a function of per cent parylene C coating.

In contrast to parylene C as an effective moisture barrier and noncaking agent in 0.7% and 0.2% concentrations, respectively, sAN coated with diatomaceous earth at a concentration of 2% was found to absorb as much moisture as the control, sANu.

#### Water Adsorption Isotherms

A more detailed evaluation of the water interaction with ANu and ANc was performed by adsorption isotherm determinations. The AN used for the adsorption isotherms presented in Figures 3 and 4 is ground, reagent grade, with a surface area of 0.76 m<sup>2</sup>/g. At the high coverages plotted in Figure 3, the AN surface undergoes mass water adsorption at relative pressures above 0.53. This is consistent with the hygroscopicity data which could be obtained only at R.H.'s above 52%. At the low coverages

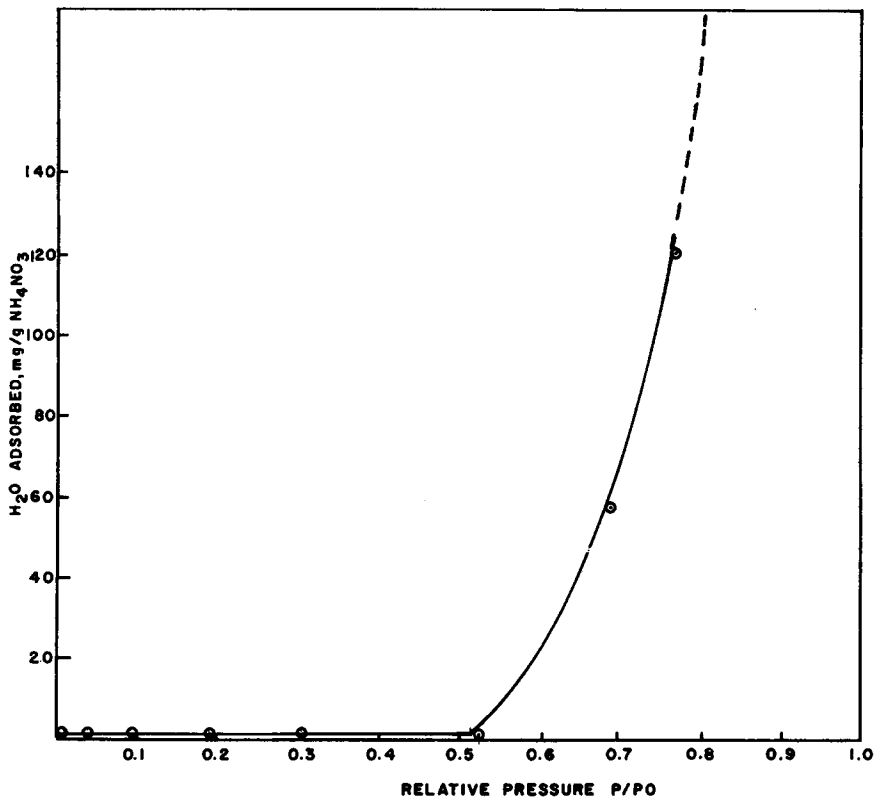


Fig. 3.  $H_2O$  adsorption isotherm at  $25^\circ C$  on AN.

plotted in Figure 4, water interaction with the surface of AN is shown, by the sharp rise and knee of the curve, to be strong. True surface absorption takes place at relative pressures below 0.5 and is found reversibly confined to the surface region. The water areas calculated from the curve is  $0.40 \text{ m}^2/\text{g}$ , and the corresponding hydrophilicity of the surface of AN is 53%.

Water adsorption isotherms are presented in Figures 5 and 6 as a function of thickness of parylene C coating of sAN at high and low water coverages, respectively. The adsorption isotherms in Figure 5 support the data in Figures 2 and 3, and illustrate the extent to which the surface of AN is hydrophobed by the polymer coating. The high-pressure points show a definite, but limited, penetration of water through the coating. At the low coverages (Fig. 6), the water interaction is shown to be progressively diminished as the thickness of coating increases. For the 3% coated sample, the water interaction is essentially with the hydrophobic parylene C substrate.

#### Thermal Stability Determinations

A minimum of five days of degassing at  $50^\circ C$  and  $11^{-6}$  torr was required to reduce the trace levels of moisture and air entrapped in the interstices of the high-density crystalline mass of pAN, sAN, and gAN. All samples

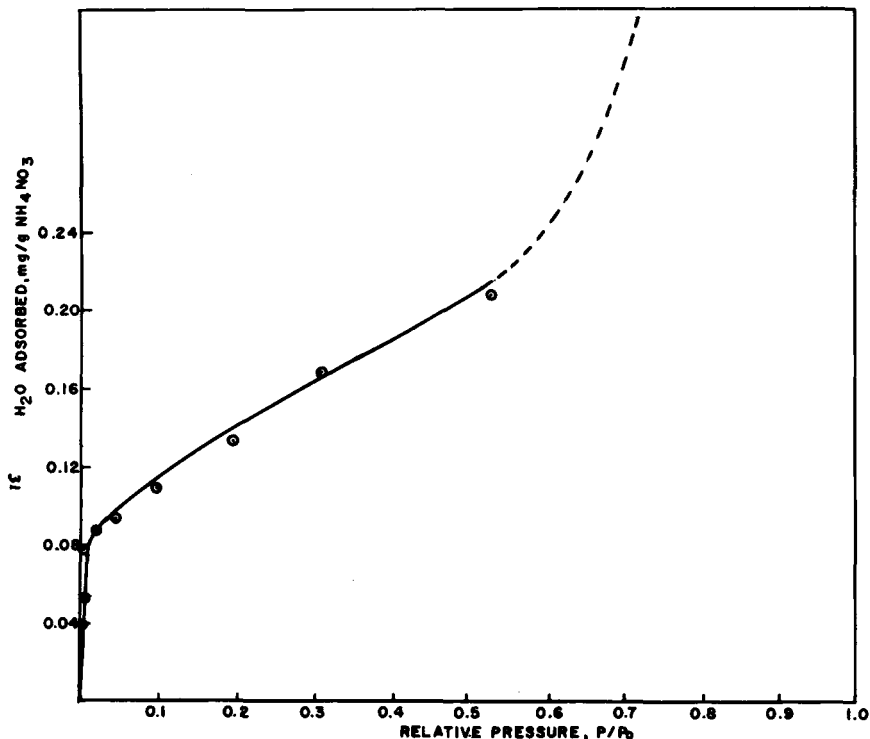


Fig. 4. H<sub>2</sub>O adsorption isotherm at 25°C on AN.

were therefore treated in this manner prior to performing the thermal stability determinations. Only the 0.7% parylene C-coated AN samples were included in the thermal stability determinations, because no differences were exhibited in comparison to the coatings cited; and the 0.7% coating represented the effective minimum barrier thickness (on pAN and sAN) that would be recommended for use in metastable formulations.

Water and hydrocarbon fractions detected mass-spectrometrically after the heat treatment at 120°C could not be determined quantitatively; and since these concentrations also represented minor contributions to the total gas volumes evolved, the reported analyses in Table I are on a water- and hydrocarbon-free basis.

The experiments described in Table I were conducted to demonstrate the effect of water on the thermal stability of parylene C as an oxidizable material in contact with AN. Water was included to approximate ambient, conditions likely to be encountered in the storage, shipment, and normal handling of AN.

AN is reported<sup>12</sup> to decompose thermally, according to the three modes described in eqs. (1) through (3):

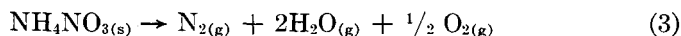
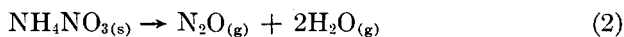


TABLE I  
Effect of Water Addition<sup>a</sup> on Stability<sup>b</sup> of Parylene C-Coated AN<sup>c</sup>

Gas	Uncoated AN						0.7% Coated AN					
	Prills		Spheroids		Granules		Prills		Spheroids		Granules	
	w/o H <sub>2</sub> O addn.	w H <sub>2</sub> O addn.	w/o H <sub>2</sub> O addn.	w H <sub>2</sub> O addn.	w/o H <sub>2</sub> O addn.	w H <sub>2</sub> O addn.	w/o H <sub>2</sub> O addn.	w H <sub>2</sub> O addn.	w/o H <sub>2</sub> O addn.	w H <sub>2</sub> O addn.	w/o H <sub>2</sub> O addn.	w H <sub>2</sub> O addn.
Nitrogen	0.005	0.006	0.018	0.019	0.028	0.038	0.006	0.006	0.015	0.018	0.016	0.026
Oxygen	0.001	0.001	0.004	0.005	trace	<0.001	0.001	0.001	0.002	0.002	trace	<0.001
Carbon dioxide	<0.001	<0.001	0.001	0.001	0.023	0.020	<0.001	<0.001	0.001	0.001	0.016	0.022
Hydrogen	<0.001	trace	trace	trace	trace	0.001	trace	trace	<0.001	<0.001	trace	trace
Nitric oxide	trace	—	0.001	trace	<0.001	0.001	trace	trace	<0.001	<0.001	trace	0.002
Total	0.006	0.007	0.024	0.025	0.051	0.060	0.008	0.007	0.018	0.021	0.032	0.051

<sup>a</sup> Water vapor at 6 torr.

<sup>b</sup> At 120°C for 40 hr.

<sup>c</sup> Figures in columns are cm<sup>3</sup> gas (STP)/g sample.



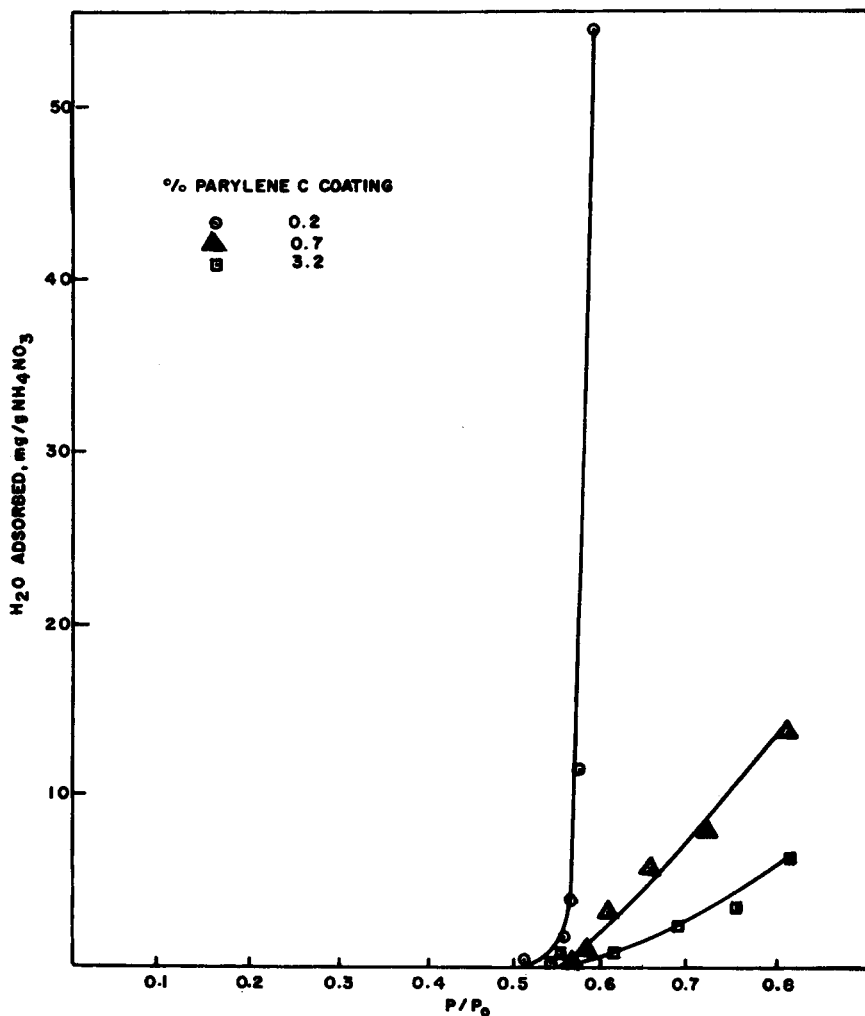


Fig. 5. H<sub>2</sub>O adsorption on parylene C-coated AN.

where the  $\Delta H$ 's are 44.2,  $-8.84$ , and  $-28.3$  kcal/mole at room, elevated, and detonation temperatures, respectively. The formation of products shown in Table I are independent of the presence of water in contact with the AN substrate, with or without the parylene C coating. The presence of H<sub>2</sub> and CO<sub>2</sub> is attributed to the neat AN and not necessarily to the parylene C/AN system. Since no detonation took place during the test period for any of the samples systems, the observed gaseous products may be due to secondary reactions of eq. (2). In addition, because the total volume of gases evolved is small, no conclusion can be drawn as to the mode of parylene C/AN interaction except that no significant difference in incipient reactivity is observed in comparison with the uncoated AN. This would indicate that there is no hazard involved with coatings of parylene C on AN.

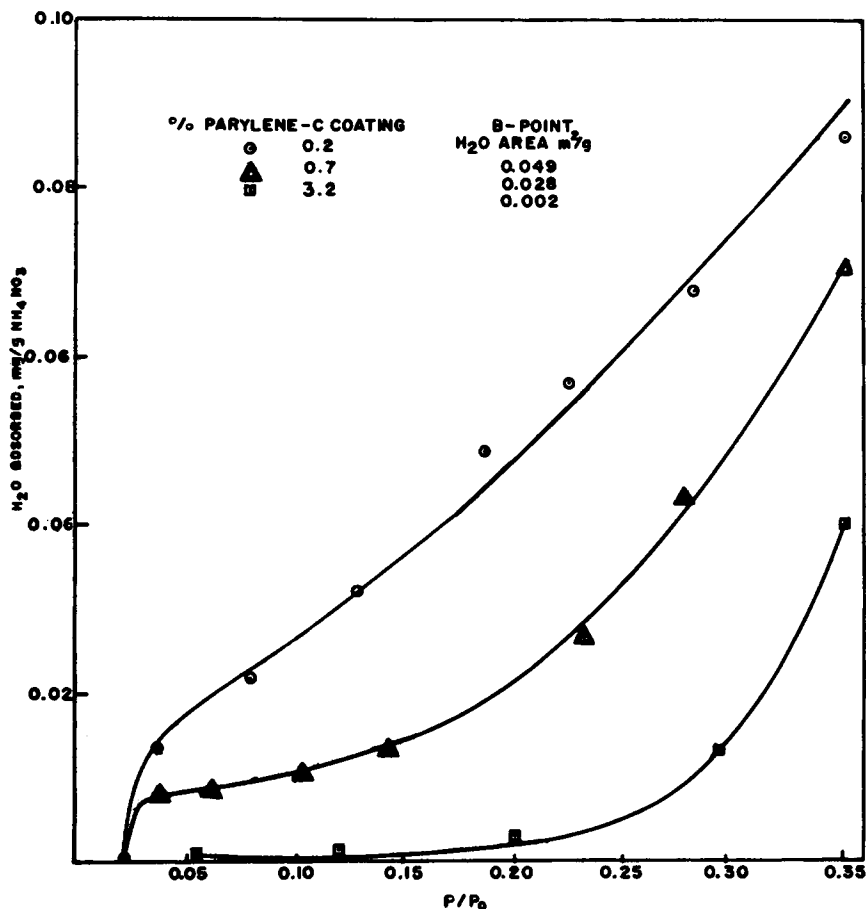


Fig. 6. H<sub>2</sub>O adsorption on parylene C-coated AN.

### Sensitivity to Thermal Initiation

The times to explosion of the neat AN in Table II shows the thermal sensitivity to be independent of the coatings on AN, the different forms of AN, and solely as a function of the intrinsic properties of AN.

### CONCLUSIONS

The VDP method of coating holds promising possibilities for the modification of the surface properties of reactive powders. The data presented in this report demonstrate the feasibility of the method for passivating AN with a polymer (parylene C) coating that is chemically and physically stable at elevated temperatures. The effectiveness of the coating as a moisture barrier on the three forms of AN studied was found to be in the order spheroids > prills > granules. Particles of AN with a 0.2% coating remain free flowing even after long exposures to ambient conditions of tem-

TABLE II  
Thermal Sensitivity<sup>a</sup> of Parylene C-Coated AN

Sample System	Time to explosion, <sup>b</sup> sec
pANu	1.9
sANu	2.0
gANu	2.3
pAN 1% c	2.1
sAN 1% c	2.4
gAN 1% c	2.6

<sup>a</sup> Determined isothermally at 425°C.

<sup>b</sup> Standard average deviation,  $\pm 0.2$ .

perature and moisture; a 0.7% coating is the minimum necessary to reduce absorption of water by one order of magnitude.

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