Passive Dosimeters: (Feasibility Study 4032A-78) M. A. Centanni and M. P. Dreyfuss -- The objective of this project is to develop new and novel passive personnel monitoring badges for specific pollutants. We envisage the basis to be chemical fixation of the pollutant in combination with new rapid electronic measurement techniques. This quarter we have identified one material which shows promise as a trapping agent for acrylonitrile (AN). Tetrachloro diethylenediplatinum (II) appears to react with dilute AN vapor in air with a gain in weight and formation of a stable insoluble product from the soluble starting complex. We have shown maximum weight gains of 10-12% using the powdered complex and using thin films of the complex coated on glass. We have also shown that the complex can be coated on quartz crystals and the uptake of AN monitored by the change of the characteristic resonant frequency of the crystal. Thus the development of an AN dosimeter employing quartz crystal technology is a real possibility. The exact nature of the reaction and the product is under study. Also possible interference from other olefinic contaminants such as styrene and butadiene is being checked. In addition, we have to determine if the reaction will occur at the ppm levels that will have to be monitored. More sensitive analogs of the platinum ethylene complex may have to be synthesized. An initial screening of this complex in a VCM atmosphere suggested some interaction took place, but that an unstable product may have formed.

The use of a quartz crystal microbalance as a means of analyzing the amount of contaminant picked up by a dosimeter appears to be a viable concept. We have recently purchased fifteen quartz crystals which resonate at a frequency of ten megahertz. This frequency is twice the resonant frequency of the Sloan crystals. We will not be able to coat as much material on the surface, but we hope that the sensitivity of these crystals will be much greater than that of the Sloan. A circuit is presently being built which will drive the crystals at this frequency.

Further work with the rhodium ethylene complex and related derivatives for VCM and AN detection has not indicated any promise. Several other approaches did not yield any promising leads either. These approaches included the use of cuprous chloride or PVC for AN absorption, of picric acid or chromium chloride for benzene absorption, and of polyacrylonitrile for VCM absorption. The use of potassium permangenate as a trapping agent for VCM has been briefly studied by R. B. Whitehead and P. M. Zakriski. We are planning to do additional work along these lines.

The possibility of using a phosphazene-catechol derivative supplied by R. E. Myers for benzene detection was studied further. Some of the phosphazene derivative was vacuum deposited on a quartz crystal surface. Only a very small amount could be coated while still maintaining the ability of the crystal of resonate. Such thinly coated crystals were exposed to rather high levels of organic vapor. There was no change in the resonant frequency suggesting that the

thin phosphazene coating would not absorb the compound into a clathrate matrix with the same ease as does the bulk material in powder form. We are not planning further work on this approach at this time.

Solubility Parameters of Solvents in Polymer Films: (M. A. Centanni -- We are currently building a device to look at the solubilities various solvents in an assortment of polymer films. The technique is sensitive and requires little time. Essentially we will coat quartz crystal with the polymer to be investigated expose this crystal to a gaseous solvent at a known pressure and monitor the change in frequency. The frequency should change in direct proportion to the amount of solvent sorbed.

Preliminary investigations with Kraton and cyclo-hexane have indicated that the technique is sensitive to relaxation phenomena. was noticed that the time for the solvent to leave the Kraton was alot shorter than the time it took for the solvent to sorb into the Kraton. This difference in entry and exit times is attributed to relaxation of the polymer as it is exposed to the solvent.

This area of investigation is an off-shoot of the passive dosimeter concept in that a polymer film acts as an adsorbent for the gaseous pollutant. We also see this area as a source for highly tailored sensors which are rugged and inexpensive.

High Strength, High Modulus Carbon Fibers from PVC Precursor: (Feasibility Study 4032B-78) M. A. Centanni -- In all cases, the pyrolysis of PVC and PVC with melamine molybdate has generated carbon fibers plagued with huge volume and surface voids. The dehydrochlorination and subsequent evolution of HCl along with benzene and other aromatics are the processes which cause this bubbling and cratering.

This quarter, E. D. Dickens and I mathematically modeled these processes and performed a few rudimentary calculations on the diffusion rate of HCl in PVC as a function of temperature. We also looked at the rate of generation of HCl as the polymer degrades. Indeed, if HCl is being produced at a rate faster than it can diffuse from the sample, then pockets of the gas will form and produce bubbles in the fiber. For the particular temperature an fiber geometry used, we arrived at the conclusion that the formation of voids was inevitable.

If we alter the geometry, by decreasing the diameter for example the model breaks down. At this point we cannot mathematically predict the results. In fact, the generation rates and diffusion rates are on the same order; however, each is extremely sensitiv to variations in both geometrical parameters and thermodynamic parameters.