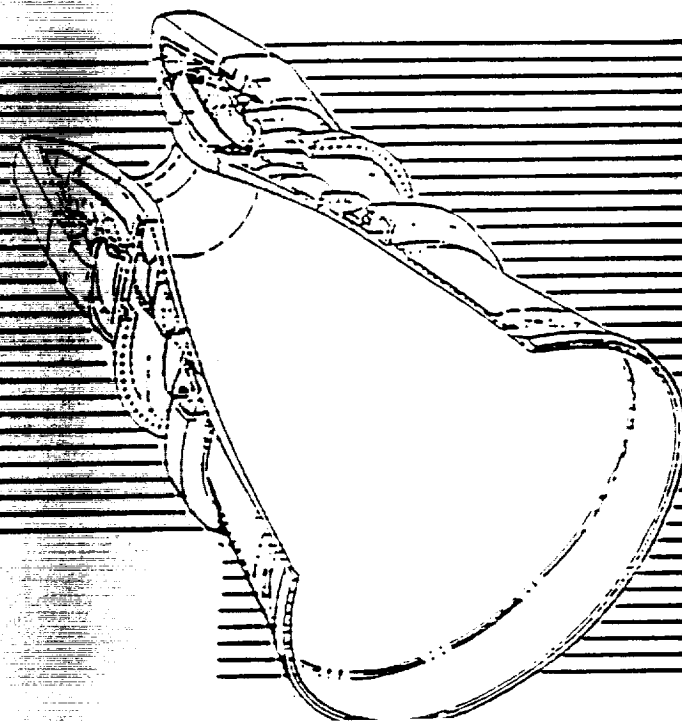


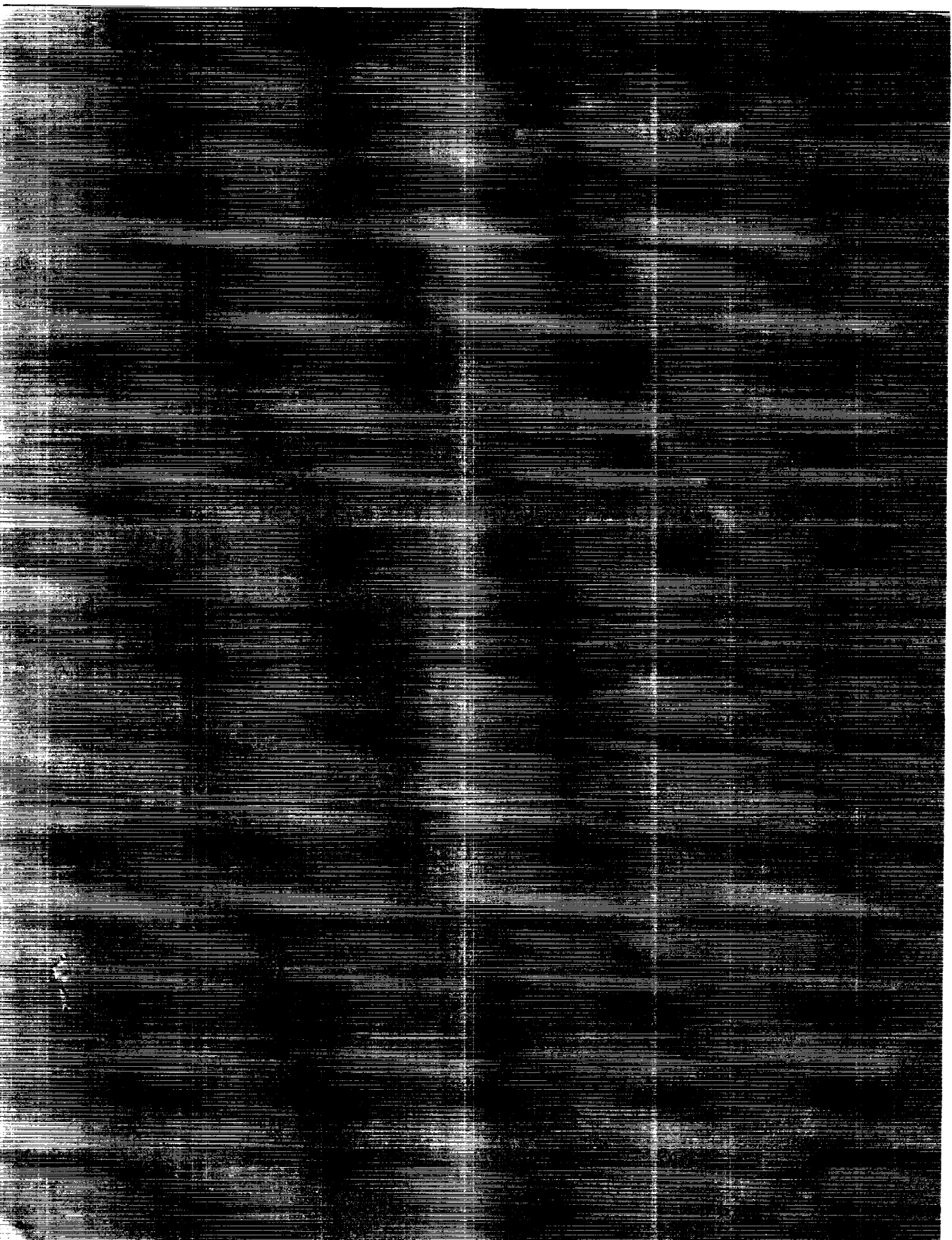
**PROCEEDINGS  
OF THE  
NINTH SEMI-ANNUAL MEETING  
OF THE  
INITIATIVE INDUSTRY ADVISORY COMMITTEE  
ON STANDARDIZATION OF  
CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS**

**ALPHARETTA, GEORGIA  
MAY 16-17, 1991**



(NACA-CO-10720) PROCEEDINGS OF THE  
NINTH SEMI-ANNUAL MEETING OF THE INITIATIVE  
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STANDARDIZATION OF CARBON-PHENOLIC TEST  
METHODS AND SPECIFICATIONS (Mississippi

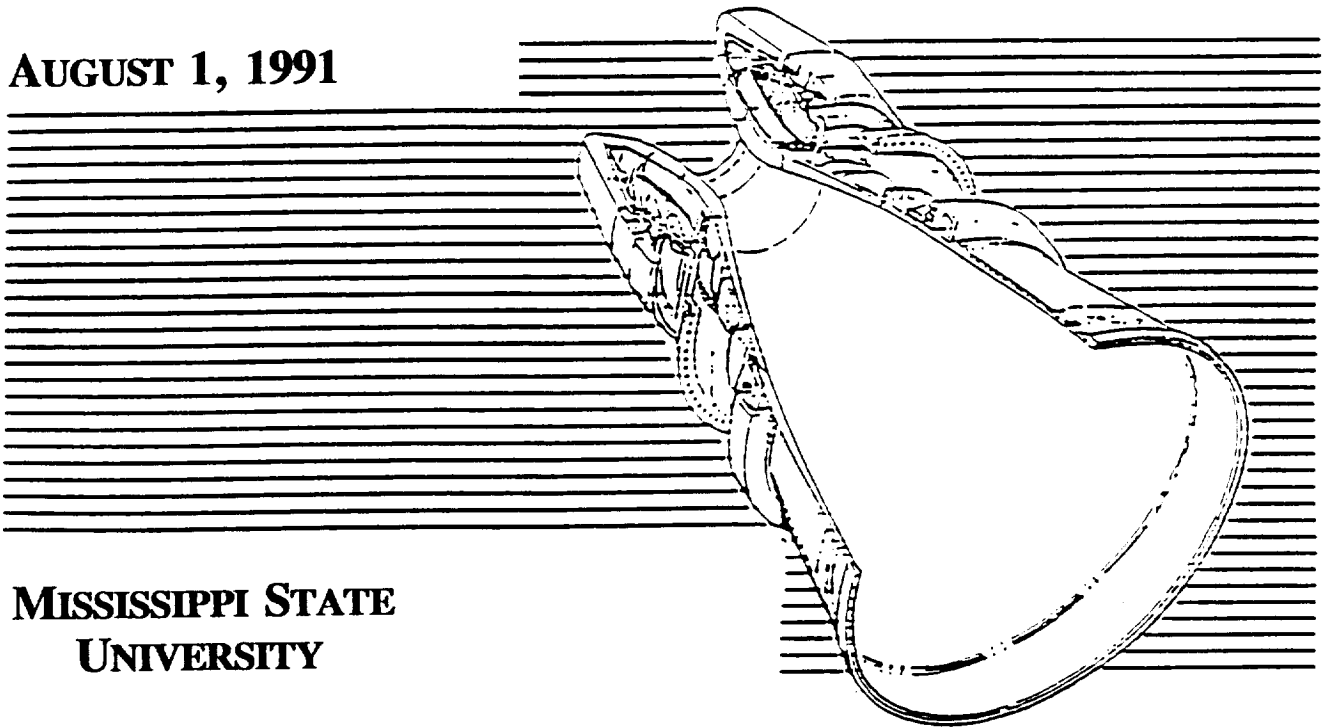
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**PROCEEDINGS  
OF THE  
SEVENTH SEMI-ANNUAL MEETING  
OF THE  
NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE  
ON STANDARDIZATION OF  
CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS**

**ALPHARETTA, GEORGIA  
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**AUGUST 1, 1991**



**MISSISSIPPI STATE  
UNIVERSITY**



**NASA GRANT NAG8-545**





**PROCEEDINGS  
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OF THE  
NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE  
ON STANDARDIZATION OF  
CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS**

**HELD AT**

**AMOCO PERFORMANCE PRODUCTS  
ALPHARETTA, GEORGIA  
MAY 16-17, 1991**

**COMPILED BY**

**EXECUTIVE COMMITTEE**

**WILLIAM B. HALL  
MISSISSIPPI STATE UNIVERSITY**

**PAT C. PINOLI  
LOCKHEED RESEARCH AND DEVELOPMENT DIVISION**

**CINDY G. UPTON  
NASA - MARSHALL SPACE FLIGHT CENTER**

**AUGUST 1, 1991**



**SEVENTH SEMI-ANNUAL MEETING  
OF THE**

**SPIP - NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE  
ON STANDARDIZATION OF  
CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS**

**AMOCO PERFORMANCE PRODUCTS, INC.  
4500 MCGINNIS FERRY ROAD  
ALPHARETTA, GEORGIA 30202**

**AGENDA  
THURSDAY, MAY 16, 1991**

- |                     |  |
|---------------------|--|
| 8:00 am - 8:30 am   | Committee Preparation  |
| 8:30 am - 8:45 am   | Welcome by D.J. Delong and Dr. Chuck Moses   |
| 8:45 am - 9:00 am   | Introduction by Committee Chairman, Bill Hall, Mississippi State University  |
| 9:00 am - 10:00 am  | Non-Isothermal Oxidation of Carbon Substrates in Air<br>• Ismail M.K. Ismail, AF. Phillips Lab   |
| 10:00 am - 10:30 am | Advisement Task 5, Rayon Specifications, Status of NARC Production, Alternate Source Activity and Lubricant/Sizing Issues<br>• Bob Looney, NARC<br>• Bill Hall, NASA/MSFC  |
| 10:30 am - 11:30 am | Advisement Task 2, Fabric Oxidation Mass Loss Test<br>• Myles Towne, Amoco<br>• Ed Hemmelman, Fiberite<br>• Pat Pinoli, LPARL  |
| 11:30 am - 12:00 n  | URA-2000 Technology for Prepreg Constituent Measurement<br>• Gloria Ma   |
| 12:00 n - 1:00 pm   | Lunch  |
| 1:00 pm - 3:00 pm   | Advisement Task 4, Carbon Assay Testing Calibration<br>• LECO Representative<br>• Cindy Upton, MASA/MSFC<br>• Pat Pinoli, LPARL<br>• Gene Rubin, PB/Hitco<br>• George Peasley, BP/Hitco<br>• Tom Paral, Polycarbon<br>• Myles Towne, Amoco |
| 3:00 pm - 3:30 pm   | Advisement Task 3, Phenolic Resin Advancement Test by NMR<br>• Cindy Upton   |
| 3:30 pm - 4:00 pm   | Carbon Fiber Electrical Resistivity Testing, Round Robin Results<br>• Jim Kirkhart, Aerojet<br>• Pat Pinoli, LPARL   |
| 4:00 pm - 4:15 pm   | Silicone Contamination Update<br>• Tom Bhe, Aerojet<br>• Don Beckley, BP/Hitco   |



**SEVENTH SEMI-ANNUAL MEETING  
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SPIP - NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE ON  
STANDARDIZATION OF CARBON-PHENOLIC  
CONSTITUENT TEST METHODOLOGY**

**AMOCO PERFORMANCE PRODUCTS, INC.  
4500 MCGINNIS FERRY ROAD  
ALPHARETTA, GEORGIA 30202**

**AGENDA  
THURSDAY, MAY 16, 1991 (CON'T)**

- |                   |   |
|-------------------|---|
| 4:15 pm - 4:45 pm | Carbon Fiber Density Test, Displacement Fluid Assessment <ul style="list-style-type: none"><li>• Pat Pinoli, LPARL</li><li>• George Peasley, BP/Hitco</li></ul> |
| 4:45 pm - 5:15 pm | SPIP Product Identification Code <ul style="list-style-type: none"><li>• Jack Williamson, Consultant</li></ul>  |

**AGENDA  
FRIDAY, MAY 17, 1991**

- |                    |  |
|--------------------|--|
| 8:30 am - 9:30 am  | Review action items from Thursday meeting; Prepare executive recommendations |
| 9:30 am - 11:00 am | Tour of Amoco Carbon Fiber R&D Facility                                      |
| 11:00 am - 12:00 n | Open Discussion of Issues Under Advisement                                   |



**SEVENTH SEMI-ANNUAL MEETING  
OF THE  
SPIP - NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE  
ON STANDARDIZATION OF  
CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS**

**AMOCO PERFORMANCE PRODUCTS, INC.  
4500 MCGINNIS FERRY ROAD  
ALPHARETTA, GEORGIA 30202  
MAY 16-17, 1991**

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Ismail Ismail	Edwards Air Force Base	Univ. of Dayton PL/RKFC Edwards AFB, CA 93523 PH (805)275-5306 (805)275-5766 FAX (805)275-5041



**THE INDUSTRY ADVISORY COMMITTEE**  
**FOR**  
**CARBON - PHENOLIC CONSTITUENT TEST METHODOLOGY**  
**IS**  
**CONSTITUTED UNDER PROJECT 3:2.1.1**  
**OF THE**  
**SOLID PROPULSION INTEGRITY PROGRAM**  
**(SPIP)**  
**SPONSORED BY**  
**MARSHALL SPACE FLIGHT CENTER**



Towne: I would like to introduce the Amoco people that are here. Starting over here on the left is D.J. Delong, Director of Marketing for carbon fibers, composites. Next is Bill Bennett and next is Chuck Moses, the Director of Carbon Technology and Neil McCarthy who is market manager for ablative material. I would like to make a couple announcements about protocol before we get started here. If any of you have duplicating requirements or transparencies, we can take care of those. The facility is a non-smoking facility. Anybody needing to smoke, the hall that goes to the left and out to the south parking lot is the area where people smoke. That is about it and I would like to introduce D. J. and Chuck will follow along it a little bit.

Delong: Thank you Myles. I would like to welcome everyone to Atlanta, to our new home since last August. Myles has asked me to talk to you for a few moments to explain to you what is Amoco Performance Products. I want to start out by giving you an overview of our company. Our parent company is the Amoco Corporation, the old Standard Oil of Indiana, and we are part of the Amoco Chemical Company. The other two arms of Amoco Corporation are the folks who drill holes in the ground and pump oil out of it, and the oil company is the refining and marketing organization that you see along the highway. Amoco Chemical of which we are a part produces a wide range of organic chemicals and Amoco Performance Products is a wholly owned subsidiary. We were acquired by Amoco from Union Carbide and most of our employees are long term with Carbide that were here when we were acquired back in 1986. If you look at our head count today, we are really only slightly above 50% Carbide. Amoco has helped us grow and prosper as a company. Amoco Performance Products is really looked at as an extension of Amoco Chemical and giving them an important addition of performance materials. There is a lot of industrial products that they have dealt with historically. We are made up of two businesses. One is the engineering polymers business under Russ deLucca, really high temperature thermoplastics for consumer products like coffee makers to automobile parts and that kind of thing. The other half is the one that we are talking about here today, which is the carbon fibers advanced composites business. Back in March Lynn changed the organization to have two business managers, myself for carbon fibers and Dave Nethero for the composites emphasis. Mike Michno, who is the R & D manager for both fibers and composites has two R & D directors, one is Chuck Moses. Chuck is a member of my business team is not only responsible carbon fiber service but product development and process quality of work carried out here on site. The rayon fiber business, while it is not as large as PAN and pitch, is one that we have been involved with since the early 1970's, but although, it is not as large as PAN and pitch, it is certainly important an important business for us and one that we have invested significant resources in over the last several years. We are certainly happy to be a part of this committee and the SPIP program and are very happy to put our resources and time and effort into this program. With that, I will turn it over to Chuck, who will tell you a little bit about the site and our R & D work. I will be available at the break if you have any specific questions.

Moses: Thank you, D.J. Welcome to Alpharetta. Let me take a minute to talk about the site, particularly, you will see more of this when you go on the tour tomorrow. The property you saw as you drove in is a site of about 62 acres that we actually own and in addition there are 44 acres that are what are called deed-restricted buffer around it. Originally that was supposed to be a golf course. We were all very excited about that and thought that would be wonderful. Apparently it is wetlands and you can't do anything on wetlands. It is going to be nice, nice wild area giving us a nice rural setting. We are all happy about that. As I show you this building, you will see that we designed this building with Amoco Performance Products in mind, the kinds of things we do, the carbon fibers, etc. were all taken into consideration in the design. Here is what the building basically looks like from a plan view. The laboratories are located on wings in the east area and the north area. In addition, then, there is the fabrication area where the pilot equipment, the process equipment is located. As you go on the tour, you will see that these laboratories are laid out in very much standard R & D laboratory fashion, in modules. If you have seen one

module, you have seen them all. Our architecture is a very pleasing building. We think they did a very nice job to make it a good work environment. The actual processing work, much of it goes on in these areas that you will recognize as carbon fibers areas by the long runs. We do a lot of what you call thread-line operations, long straight lines. The composites area is here where a lot of prepregging and autoclaving work goes on. This is the engineering polymers area. This block down here is our support area, maintenance, warehousing, and that sort of stuff goes on down here. Then we have a separate chemical pilot plant where we actually do polymerization, resin formulation. That is sort of an overview of the laboratories. Again we will come back to that tomorrow on your tour and give you some details on it. The building is approximately 300,000 square feet. This building was designed and built for future expansion. Hopefully as we grow and are more successful, we will be able to add a second wing here and here of additional laboratories and we will be able to grow with this fabrication area also. The other couple of key points, design and construction maintain flexibility and the building design promotes multi-disciplinary interaction. We do have a broad range of skills going on here. We have chemists, materials scientists, process engineers and the way that the building is laid out is to focus the effort so that you don't have isolated groups of people working, but instead you have a good work environment.

Just briefly, I want to touch on the comments D.J. made about organization. He said that this is the R & D for Amoco Performance Products as a total, but there are really two major businesses here. The one you are most familiar with is the carbon fibers and advanced composites is managed by a Manager of R & D and as D.J. says there are two managers who report to him, carbon fibers, my position, and advanced composites. The other half is the engineering plastics business and he also has two directors reporting to him, marketing technology group and operations support group and he handles the analytical part.

Finally, just to give you a flavor of the kind of things that go on here, I know you are very familiar with all of our carbon fibers, pitch family, the T300 PAN family. These are the composites that we also market pitch and our proprietary epoxy composites. Just to give you some typical properties, this is one of our brochures. If you don't have one, just ask Myles. This is what our side of the business makes. I know you are fairly familiar with that and I don't want to spend a lot of time on it. The other half is in the engineering polymers. These came about as a result of Amoco Performance Products buying out Dart Industries, a plant down in Augusta, Georgia, in 1988. That is a real quick overview of the kinds of things that go on here and the product lines to give you a sense of what Performance Products is all about. When you come back on the tour tomorrow, we will have more to show you and talk about it. Once again, welcome to Alpharetta and if there is anything we can do to make your stay more comfortable, just let us know.

Hall

On behalf of the committee, I would like to thank Myles Towne for several things. The hotel that we are staying in is excellent and he did a good job in preplanning and the facilities are just wonderful, so we are very pleased to be here and we thank Amoco. Everything is great and we appreciate it. This committee is part of the Solid Propulsion Integrity Program (SPIP) program which is administered at Marshall Space Flight Center. The overall charter for the SPIP is to improve our baseline information and to improve the whole solid rocket motor industry. This program was originally funded for a three year period. That time is up and SPIP is undergoing a second three year evaluation right now and we will talk to you a little more about that later. This, on the chart, is why we are here. We appreciate the companies that are represented here because they have to sponsor you for you to be here. We appreciate you being here and your companies sponsoring you.



Originally we were concerned with the RSRM, and it is a fairly simple materials flow diagram. We are interested in the materials that go in the nozzle and this is the diagram for the nozzle material. The rayon precursor is supplied by North American Rayon. We have two weavers, Highland and Milliken. All three of these are undergoing qualification at the present time. Highland was our weaver, and they were qualified under a certain loom. Milliken and Highland, both are qualifying under a different loom, a more efficient, faster loom, and, of course, North American is qualifying as a source of the rayon. The rest of the chart are all old-timers in this. Carbonizers--Polycarbon, Amoco, and Hitco. The resin is supplied by Borden and Ironsides and both prepreggers have their own proprietary filler. The prepreggers are BP and the other one is Fiberite. The finished prepreg is the MX4926 and FM5055B and these prepreps are shipped to Thiokol and Thiokol processes them into the final nozzle components. This committee covers materials and specifications up through the prepregging step. There is another committee just like this that has to do with the cured or processed prepreg. Is there anybody new here who might have some questions?

This committee considers test methods and specifications, basically on two premises. First, does the test method that we utilize accurately measure the property that you are trying to measure. Today we will cover several areas where there is some question as to whether this is true or not. If this does accurately measure the property you are trying to measure, does this yield useful information for evaluation of the product. This is the purpose of this committee. To accomplish this, we have biannual meetings and we try to cover the subjects that are important at that time. All of you have an agenda and first up is Ismail. Ismail are you ready?

Ismail

I want to thank Dr. Hall and Pat Pinoli for inviting me to this meeting and to all of you attending and listening to me.

Carbon fibers and fabrics (CF) are essential materials for fabricating the carbon composites used in aerospace applications. When exposed to high temperatures in air, the CF gasify and the mechanical properties of composites degrade. To understand the oxidation kinetics and mechanism, the reaction may be performed under isothermal or non-isothermal conditions (referred to here as IC or NIC). The first objective of this work is to address how some experimental parameters can affect the results obtained under NIC. Then a comparison between the oxidation kinetics under IC and NIC is made. Finally, a summary is given on the advantages and drawbacks of isothermal and non-isothermal oxidation (IO and NIO) of carbons.

Several CF, chars and carbon blacks were examined, including Saran (a microporous char), WCA (a graphitized rayon fabric) and several carbonized rayon fabrics. The physical/chemical properties of the two carbons and their kinetics of IO are outlined elsewhere [1,2]

Using a thermogravimetric analyzer (TGA), CAHN system 113, the as received carbon (8-10 mg) was placed in a quartz pan suspended on the balance beam. While flowing air at ambient pressure over the sample at 50 cc/min, the TGA reactor temperature was increased at a heating rate (HR) maintained linear above 300°C; 1, 2, 5, 10 and 20°C/min. The decrease in sample weight due to gasification was recorded as a function of time and temperature until the entire sample gasified.

The oxidation under NIC is sensitive to the experimental parameters including heating rate, sample size and flow rate. The latter is not critical in affecting the kinetics, as shown in Figure 1 for the highly microporous Saran char. Increasing the flow rate by a factor of 4 slightly affects the rates and raises the apparent activation energy ( $E_a$ ) from 46.1 to 51.8 Kcal/mole. The rates under IC, reported earlier, are at least one order of magnitude higher than those computed under NIC. Further, the values of  $E_a$  for IO (42.6 Kcal/mole) and NIO are close, indicating that the oxidation mechanism is essentially the same for IO and NIO. Thus, for highly microporous reactive chars

oxidized under either condition, the reaction takes place exclusively in Zone I. That is, the oxidation kinetics are controlled by surface reactivity; chemisorption of  $O_2$  on active/reactive sites, located inside the micropores, and desorption of  $CO_2$  and  $CO$  to yield gasification products. With the present setup, air flow rate has little effect on Saran oxidation.

The NIO data of the WCA fabric can be presented in several ways. Figure 2 illustrates the burn-off (BO) curves which relate the percent of ungasified carbon to oxidation time. Increasing HR shortens the time required to gasify the entire carbon or 50% of it;  $t_{0.5}$ . When the HR rises from 1 to  $20^\circ C/min$ ,  $t_{0.5}$  decreases from 140 to 13.5 min. The empirical relation between the two is  $(HR)^{0.78} \times t_{0.5} = 135 \pm 5$ . Figure 3 shows the dependence of BO on temperature, increasing HR displaces the thermograms to higher temperatures. A second empirical relation was developed:  $T_{0.5} = 750 + 115 \times \text{Log}(HR)$ , where  $T_{0.5}$  is the temperature at 50% BO. Combining the two equations gives:  $T_{0.5} = 1064 - 147 \text{ Log } t_{0.5}$ . The relation between time and temperature required to gasify 50% of the CF is independent of HR.

Figure 4 illustrates the oxidation rate profile (ORP) taken from Figure 3. The ORP is a relation between the differential rates of oxidation (based here on the starting CF weight), and sample temperature. Increasing the HR not only shifts the ORP to higher temperatures but also raises the rates. This trend was verified for all the carbons studied (CF, Saran and blacks). With a lower HR, the carbon "sits" with  $O_2$  for longer periods of time, and the carbon gasifies slower at lower temperatures. The product of "lower" gasification rate times "longer" interaction time yields a "large" amount of carbon gasified. This is not the only legitimate interpretation for the data. Heating under NIC is also associated with a lag between the sample and furnace temperatures. As the HR increases, the lag becomes larger. Using calcium oxalate as a standard with the present TGA, the largest lag for oxalate decomposition temperatures between HR of 1 and  $20^\circ C/min$ , was less than  $35^\circ C$ . Therefore, the results in Figures 3 and 4 are not only dependent on the carbon/oxygen system but also on the temperature lag imposed by the TGA setup.

A comparison between the Arrhenius plots of IO and NIO is shown in Figure 5. While the IO yields on line with an  $E_a$  of 40.9 Kcal/mole, the NIO plots are not linear. They show a continuous curvature; the slope starts high at the lower temperature then declines with increasing temperature. That is, there is a slight continuous drop in  $E_a$  as the oxidation progresses. Yet, for practical purposes, at least two linear regions could arbitrarily be defined on each line. The first is computed at BO below 5% and the second is between 5 and 55% BO. The corresponding  $E_a$  values are 108-112 and 32-44 Kcal/mole, respectively. The first linearity can be attributed to sample activation and opening its micropore system. This step enhances the WCA surface area by as much as two orders of magnitude. Once the structure is opened, the oxidation continues inside the micropores (second region) in a manner similar to that of the IO. The overall kinetics for NIO continues mainly in Zone I with minor contribution of Zone II which becomes increasingly significant at higher temperatures.

In Figure 1 and 5, the rates of IO are higher than those of NIO; the trend has been confirmed with many other samples. There are three possible explanations for this discrepancy. First, the pretreatment procedures used in each case are different. With IO, the samples were degassed at  $1000^\circ C$  and cooled to the projected isothermal temperature in  $N_2$ . Air was then introduced to the clean carbon surface which had fresh active sites. For NIO, the samples were heated in air without treatment. The active sites were occupied and the surface was preserving the original impurities. Second, the rates of oxidation are calculated in different ways. The IO rates are computed on a global bases when the BO/time plot showed a constant rate of gasification. The oxidation rates below this linear region (beginning of oxidation) and above it (when the micropore structure collapses) are lower than the maximum rate of the linear region. With NIO, the rates are instantaneously computed at small temperature segments; they represent the rates encompassed

by all different events occurring at a given time and temperature. Third, the structure of the carbon during IO is not the same as NIO. With the IO, the micropore system of WCA is opened at one temperature, it is opened gradually at multi-temperatures during NIO. As illustrated earlier, there is a large effect of activation temperature on developing porosity of this fabric. The higher the temperature, the lower the extent of developing porosity.

Next we address here the critical issues that affect the results, and apply the NIO method to compare the relative reactivity of several types of carbon fibers/fabrics CF obtained from different companies. Figure 6 displays the Arrhenius plots of five carbon samples which have been well characterized by several authors over the past three decades. The NIO was executed with  $W=40$  mg,  $HR=10^{\circ}\text{C}/\text{min}$ , and air flow rate (AFR)=100 cc/min. The values of active surface area (ASA) of SP-1, V3G, Graphon, V3 and Saran, as determined by oxygen chemisorption. Looking at Figure 6, we note that for the five carbons, the sequence of reactivity is the same as their corresponding order of ASA. At one extreme, the highly reactive disordered Saran char, occupies the right side of the graph and is displaced upwards. The char gasifies with high rates at lower temperatures. At the other extreme, the least reactive well-ordered SP-1 graphite is at the far left side of the graph and slightly displaced downwards. SP-1 is one of the hardest graphitic materials to gasify. The V3G was prepared from its precursor V3 by graphitization at  $2800^{\circ}\text{C}$ . As expected, V3G is less reactive to oxidation than V3, this is also evident in Figure 6. Therefore, by applying this concept to several CF, we can predict their relative oxidation reactivity, as it will be discussed shortly.

The data displayed in Figure 6 show two distinct regions with the graphitic materials, and a curvature with V3 and Saran plots. At the beginning of oxidation, the rates increase sharply with temperature then decline to almost constant values independent of temperature. With graphitic carbons, the oxidation kinetics starts in Zone I then "jumps" to Zone III until the carbon is completely gasified. Zone II is either absent or only present for a short time during the transition from Zone I to Zone III. At the beginning of oxidation, carbon gasification rates are solely controlled by the chemical reactivity of the surface (Zone I). Then suddenly, the rates attain a constant value independent of sample nature. The rate limiting step becomes the diffusion of air to the external surface of the carbon (Zone III).

With the TGA, the apparent oxidation mechanism is very dependent on the experimental conditions selected for the run. Figure 7 illustrates this point. By changing the experimental variables from  $W=40$  to 10 or 5 mg, and from  $HR=10$  to  $5^{\circ}\text{C}/\text{min}$ , the shape of the plots and their locations change. Reducing the starting weight of the carbon (lower bed height) and reducing the heating rate, not only yield a more linear plot but also gasify the carbon at lower temperatures. Using a small value of  $W$  and a high AFR with moderate  $HR$  is probably the best combination to perform the NIO test. Yet, if  $W$  is too small and AFR is too high, the error in measuring oxidation rate is significant due to particle entrainment and the noise in balance signal. For these reasons, most of the study on CF reported was executed with  $W\sim 10$  mg,  $HR=5^{\circ}\text{C}/\text{min}$ , and  $AFR=50$  cc/min.

Figure 8 illustrates the ORP for three graphitized CF namely, T-300 polyacrylonitrile (PAN) fiber, VSB-32 pitch fiber, and WCA rayon fabric. The relative reactivity, based on  $T_{\text{max}}$ , is  $T-300 > VSB-32 > WCA$ . Values of  $T_{\text{max}}$  for T-300, VSB-32, and WCA are 764, 824, and  $864^{\circ}\text{C}$ , respectively. The corresponding ASA are  $0.067\text{ m}_2/\text{g}$  for graphitized T-300,  $0.029\text{ m}_2/\text{g}$  for the VSB-32 and  $0.068\text{ m}_2/\text{g}$  for WCA. These values do not completely support the ORP of Figure 8, as it was the case in Figure 6. For example, the ASA of T-300 and WCA are the same but the T-300 gasifies faster than the WCA. This indicates that the ASA is not always a good parameter for indexing the reactivity of CF. Perhaps the values of  $T_{\text{max}}$ , taken under well defined TGA experimental conditions, are more appropriate for this purpose.

There are two remaining features in Figure 8 that need further clarification, the height of the peak and its width. From the limited data, it appears that there is a correlation between the width and height. While with WCA, the peak is broad and short, it is narrow and high with the VSB-32. The WCA gasifies over a wider (and higher) temperature range than the VSB-32. It is possible that the physical geometry of CF has a large effect on ORP. With the weaved WCA fabric, the accessibility of Air to the internal surfaces is somewhat restricted. As a result, the rate at  $T_{max}$  is suppressed. The VSB-32 fiber has a larger filament diameter (11 micron) than the graphitized T-300 (5.8 micron). Therefore, with the VSB-32 fiber, the volume of voids/gaps between the filaments is larger, and the accessibility of air to the internal surface is high. Possibly this is the reason for obtaining the sharpest peak in Figure 8. At the present time, these speculations are offered until verified experimentally.

Now we consider the NIO data on carbonized and graphitized rayon fabrics. For the sake of clarity, only typical examples, representing the limits of each group of fabrics, are shown in Figure 9. At the left side of the graph, the two (graphitized) WCA samples represent the limits of 15 other tested WCA fabrics. They are the least reactive CF in the graph. In the middle of the plot are curves for three carbonized rayon fabrics; CCA-3, CSA and VCL. The activation energy of the carbonized fabrics is 35-43 Kcal/mole which is close to that of Saran. The oxidation is taking place in Zone I where the surface reactivity controls the kinetics. Even though these fabrics are highly microporous materials, there is no diffusion limitations on the oxidation reaction, that is Zone II is absent. There are two reasons to explain this; either, the oxidation temperature is low for imposing a diffusion barrier, or the micropores are converted to larger meso- and macro-pores during gasification.

The last class of rayon carbon fabrics is shown in Figure 9 by the data of CSA-4671. The behavior of this fabric in air is unique. To my knowledge, this is the first time to report this peculiar Arrhenius plot for a typical C/O<sub>2</sub> reaction. It has been reported on coals but was attributed to loss of volatiles. In the present work, the oxidation rates of the fabric increase, then level-off, and finally increase, once again, with temperature. This behavior will be discussed later in this presentation. Since the oxidation characteristics of this class of fabrics is not fully understood, and because of their high reactivity in air, the utilization of this class of fabrics is not recommended for manufacturing carbon composites.

The Arrhenius plot of CSA-4671 fabric is illustrated with other samples in Figure 10-plot A. The NIO rates, based on starting sample weight, first increased with temperature (or BO up to 12 %). The Arrhenius plot in this (first) region was slightly curved, showing a continuous decrease in activation energy. Then the rates leveled-off during the next 50°C temperature increment, yielding the second region. Finally, the rates increased with temperature until the complete BO of the fabric was achieved (third region).

It may be added that while sample A (CSA-4671) has the highest Na level (3153 ppm), sample B (CCA-3 1641 B) has the lowest (13 ppm). Samples C (Csa-96813) and D (CCA-3 K15 D) have the nominal level of Na noted for other carbonized rayon fabrics (100-500 ppm). Prior to oxidation, most of the samples reported in the following section were evacuated to 10<sup>-5</sup> Torr at room temperature (RT), flushed with ultra high purity Ar to ambient, heated under AR flow (50 cc/min) to 1000°C, held at this limit for 30 min, and finally cooled to RT. This treatment is designated here as (O) for outgassed. Air was then injected at 50 cc/min to replace Ar, and the furnace temperature was raised at a designated heating rate, kept constant above 300°C, until the complete carbon BO was achieved. Additional experimental details on HR and sample weight are given on the graphs. In a few cases, the NIO was carried out in "one shot". That is, starting from RT, the CF was just oxidized in air (50 cc/min) at a constant HR without prior evacuation or heat up to 1000°C in Ar. The experiments performed in this manner are designated as (AR)

for as-received fabric. Figure 10 displays, we note that the peculiar Arrhenius plots, with their pertinent three oxidation regions, were only obtained for the samples with the highest and lowest Na levels; CSA-4671 and CCA-3 1641 B. Yet, all other rayon CF examined, with nominal Na levels, yielded a reasonable Arrhenius line with  $E_a$  close to 40 Kcal/mole. Typical examples in Figure 10 are samples C and D. The values of  $E_a$  are in line with the published values for C/O<sub>2</sub> reaction.

Let us focus the attention first on sample A. The peculiar behavior can be attributed to two possible explanations. First, the catalytic effect of Na may be more pronounced at the beginning of oxidation (first region) and diminishes at higher temperatures due to particle agglomeration (second region). This region could be representing the beginning of the uncatalyzed reaction which continues through the third region to a complete BO. Since in the first region,  $E_a$  decreases with increasing temperature, this explanation is ruled out.

Second, the peculiarity may be somewhat related to the effect of pretreatment (O vs AR) on fabric surface prior to NIO. From Figure 11, the ORP plots after the outgassing treatment are shifted to higher temperatures. Using the as-received samples without pretreatment not only lowered  $T_{max}$  but also yielded a different ORP especially in the first and second regions. Thus, the presences of functional groups and/or other surface impurities enhanced oxidation rates. To separate the effect of functional groups from that of impurities, the CSA-4671 fabric was first cleaned (O treatment). Then it was exposed to an air flow (50 cc/min) for 24 hours at 50, 75, 100, 125, 150, 175 and 200°C. This procedure removed the impurities but "loaded" the surface back with functional groups to different extents, depending on chemisorption temperature. Figure 12 shows that as chemisorption temperature increases up to 150°C, there is an increasing weight gain because more functional groups are added to the surface. The maximum uptake was 0.28% O<sub>2</sub> (at 150°C) which corresponds to an active area of 8.75m<sup>2</sup>/g. This computation was based on the value of 0.083 nm<sup>2</sup>/active carbon atom as proposed by Laine, et al. At 200°C, the rate of gasification, occurring concurrently with chemisorption, was significant. After 10 min of exposure to air, the net effect was a weight decrease. That is, the sample was activated during chemisorption.

Figure 13 displays the ORP of the CSA-4671 fabric before and after chemisorption to different levels.. The introduction of C-O functional groups displaces the plot and  $T_{max}$  to the left, this trend is qualitatively similar to that of Figure 11 with one exception. The shape of all plots in Figure 13 is not similar to plot I in Figure 11, which was taken on the AR fiber. This suggests that the external surface of the fabric is contaminated with some impurities that are removed by heating to 1000°C. For chemisorption at 200°C, however, there is a distinct dip (Figure 13) in oxidation rates at 430-440°C. As shown in Figure 12, this sample has been activated during the chemisorption reaction. The activation process, together with the high population of functional groups, are clearly responsible, in part, for exaggerating the peculiar behavior. It may also explain why the CCA-3 1641 B fabric, with the exceptionally low Na content, showed the same peculiar behavior (Figure 10). Apparently sample B went through some purification process that removed the Na to a level well below the nominal. With it, the fabric was activated and its active area became higher. It is also possible that the external surface of the fabric has acquired additional super active sites. Thus, the "penalty" for removing Na which catalyzed the C/O<sub>2</sub> reaction was to end up with a fabric that was very reactive to O<sub>2</sub> due to enhancement of active area.

The reason for the peculiarity of the CSA-4671 fabric is different, it is the presence of high levels of Na. Figure 14 compares the ORP of the CSA-4671 fabric before and after washing with double distilled water. Both oxidation profiles were executed after the normal outgassing procedure. Washing with double distilled water was carried out overnight and reduced the Na

level from 3153 to 1773 ppm, the process removed essentially the Na present at the external surface. Removal of Na displaced the ORP to the right (less reactive fabric), and it considerably suppressed the first and second region. The shape of the ORP for the washed sample is now less peculiar and similar to those obtained with other fibers.

## CONCLUSIONS

1. Both IO and NIO techniques are valuable tools to study the kinetics of carbon oxidation. The IO is more traditional and perhaps more fundamental than NIO. However, IO relies on computing a single oxidation rate that is normally computed either at a given BO (usually 50%), or at the linear portion of the BO/time plot. Generating the Arrhenius plot for one sample requires several days or weeks.
2. By contrast, NIO is a faster way for observing continuous trend, it is more realistic than IO. When a carbon composite, for instance, is exposed to high temperatures in aerospace applications, its temperature gradually increases and the recession likely occurs under NIC.
3. For carbonized rayon fabrics, neither the very high nor the very low level of Na is desirable. At one extreme, the C/O<sub>2</sub> reaction is catalyzed by Na. At the other extreme, the surface is activated and the rate of uncatalyzed reaction is high. A compromise has to be made between the two effects to obtain the least reactive fabric.

Thomas Even if you went to a larger crucible and went up in your sample size, do you think you would get the same results? The volume that you are trying to fill, the volume of the crucible,

Ismail You are talking about the cross-sectional area where the flow goes through. This could be one of the important parameters in addition to air and the height of the bed where you are oxidizing.

Thomas I guess what I would be concerned about is the difference in the equipment that each lab is using. If you use a larger crucible and a given sample size, are you going to get a different rate?

Ismail Yes sir. In fact, as you can see here, even by just keeping everything the same, except sample size, we get different rate. But again you could still standardize the procedure in each lab. In other words, let's say you are sitting in your lab and you say, "This is my standard fiber or fabric". Then use it as a standard and see how the rest of the materials behave with respect to the standard material.

Hall This problem comes up again today when we talk about LECO, standardization of carbon assay. This is a very definite problem that we are having right now.

Thomas Is the bundle separated?

Ismail If you start taking it apart, how are you going to guarantee that the way you take it apart is the same way I take it apart? You have to remember that I am evaluating a product. A company gave me a product. We are dealing with this product. Now the question is, do we want to do it in a very fundamental way, or would we like to evaluate the product as we receive it from the manufacturer and we use it to make our composites?

Armour You could unravel it.

Ismail            You could, but I was hoping to get a nice sample from a manufacturer before and after weaving. I have this.

Beckley           It is about 2 inches of WCA yarn.

Drake            Two inches long? How about the diameter?

Beckley           Take two inches and decide that if you want it a count of 20 per inch. He would have just a little tiny...

Williamson       Any way, you buy the fabric, you want to the test fabric, you want to see if it is the same as the last lot. You aren't going to do that by taking it apart.

Ismail            That is one way of seeing it. I agree with you that one way of evaluating the material is don't change it, don't play with it. Just take it from the manufacturer and use it as supplied.

Pinoli            Keep in mind that the T300 has about 6% by weight of nitrogen in it, so to assume that this TGA plot, or weight loss plot, is truly representative of carbon-oxygen reaction kinetics of, isn't true, because of the nitrogen coming off. There is also hydrogen and chemisorbed oxygen coming off in an weight loss. I think it is strongly influencing the initial shape of the curve. If you want to truly compare carbon-oxygen kinetics, we have to increase fiber carbon assay number closer to 99%. That should shift the curve closer to the VSB 32 plot.

Ismail            I agree with that to a point. Now back to your first point about oxidation of nitrogen and the oxidation of hydrogen. This is yes and no again, Pat. Yes, fundamentally, you do have rates of the three reactions going parallel: carbon/oxygen, hydrogen/oxygen and nitrogen/oxygen, but who gives a damn, if you are evaluating the entire material in one shot?

Pinoli            No, I agree, you are getting a pure carbon-oxygen reaction behavior for that fiber. But trying to interpret weight loss fo carbon-oxygen reaction may not be accurate.

Ismail            Most of that reaction doesn't occur at such low temperature. Most of the nitrogen-oxygen, hydrogen-oxygen reactions (desorption), as I noted from other experiments occurred above 700. In other words, when you heat this material, you don't see much hydrogen. In fact, I published this in one of the JANNAF meeting papers about five years ago (1985). You don't see much of the hydrogen or nitrogen coming off below 800.

Pinoli            That is hard for me to imagine. You are telling me that the hydrogen that is still functionally bound to the carbon structure is not going to oxidize until it goes up to 800°C. Hydrogen and oxygen are just to reactive to not react prior to reaching 800°C.

Ismail            Well, yes and no. Hydrogen does not come off that easily. We are talking about two things, when it comes off and when it is oxidizing. These are two separate items. The hydrogen does not come off, nitrogen does not come off. They are oxidized.

Pinoli            I agree, hydrogen would not come off in an inert atmosphere up to 800°C.

Ismail            Yes. Whether it oxidizes before the carbon or after the carbon, that was not answered in the present work.

Pinoli            Myles, have you ever looked into the reactivity of residual fiber hydrogen?

Towne Well, I just want to make the comment, Pat, that the T300 has been heated so much higher than the temperature that Ismail is looking at here now, it is only something related to oxidation that is taking place here. It wouldn't be any other component coming off. It would all be oxidation reaction.

Pinoli I agree that whatever hydrogen and nitrogen remains is stable. I just cannot imagine that any hydrogen, functionally bound, however, is going to resist oxidation. When we saw some early weight loss on low-fired PAN, I suspected that it might be hydrogen reaction.

Ismail Carbon-hydrogen bonds are very stable.

Pinoli I think your mid-range rayon fabric represents material of about 1000 ppm Na.

Ismail Yes, you are right.

Thomas Is that CSA 4671 material, that 300 pounds you were testing? Is that STS-8, STS-8A? That is STS-8A. Is it of the same time period. Is the 4671 the 300 pounds tested?

Hall This was earlier material.

Pinoli What you are doing now is providing some time for chemisorption of oxygen. The reason you don't see early weight loss is oxygen chemisorption is occurring.

Ismail Yes, yes.

Thomas What is the sodium level in the 4671?

Ismail 3000 ppm.

Thomas You said that you did not think it was all associated with the sodium level.

Ismail We are coming to that. I have a slide for that.

DeVane What is outgassing?

Ismail Outgassing means that you take the sample and heat it to 1000°C under a vacuum for several hours and we are talking about  $10^{-5}$  Torr.

DeVane Was carbon assay done on all the other materials?

Ismail Carbon assay was done on 4671. Pat, how much was it?

Pinoli CSA-4671 should be in the neighborhood around 94% carbon assay.

DeVane Versus 97.8%.

Ismail 97 to 98. This material is a good one, CSA, the one on the right hand side. It has high carbon assay.

Pinoli Do you know what I get out of that, Ismail. The carbon assay data may be telling us that product is different and is not the same product that we tested 5 years ago. This particular product with



the very sharp peaks has a lot more chemisorbed oxygen on the surface and can be increasing by sitting out in the atmosphere.

Johnson Was the carbon assay the same on both of those?

Ismail Pat?

Pinoli Probably within about 1%. The first one is standard CCA3. That was about 97 or 98%. CCA3-1641-B is about 97%. Carbon assay numbers, as you will see later today, are only reproducible to about 1-2%. What you should really look at is the firing temperature and a higher firing temperature should increase carbon assay. The indication that it is lower there is very surprising. For those that haven't been exposed to this particular product, CCA3-1641B, I have seen this effect that Ismail is talking about and I agree with him wholeheartedly. In the process of removing Na, the fiber is further activated. The thing that is very informative to me where the hump occurs cannot be related to Na. It has to be associated with the active sites.

Williamson Sodium content is an indication of the condition of the fiber, is it not? The sodium isn't really the determining factor, is it? 3000 ppm, 100 ppm, is indicative of the condition of the fiber.

Ismail What do you mean by the condition of the fiber.

Williamson Well, the physical structure, the chemical structure, the number of sites that are available. Wouldn't it be more proper to label the condition rather than say it is sodium.

Ismail Yes, but you expect to know more about a product and how they made it.

Williamson Are you saying we need a less simplistic definition of the condition of that fiber with regard to sodium.

Ismail I think that sodium is not the only concern that we need to be looking at, but I would say that sodium is one of the important factors. You have to remember, Jack, that when I get some fabric, I have the slightest idea about what they have done to it. Pat just sends me a plastic bag containing the fiber.

Williamson I want to compliment you. Excellent.

Beckley I think this work shows a very interesting ability to bring out some characteristics and I have no doubt that the work he has done says that sodium between 100 and 500 in air flowing at that rate is a critical factor and a suitable gauge for it. A rocket nozzles says one thing, a re-entry heat shield says another, and they are not the same experimental conditions that you are simulating. I don't want somebody to decide that what works in air, or a set of limiting numbers in air, is appropriate for their particular activity. I think that this is work that shows characteristics of that situation, but we have to look at a particular application and say what works here. You really wouldn't predict from your work that 1641 makes a very good heat shield. You would say that it is probably going to oxidize at a very high rate. But it turns out that the rate at which it does oxidize is perfectly suited for the end application. It was very important in that application to get that sodium level down to where it is for other reasons. The reasons being signature and characteristics that had to be there. They sacrificed, it was a balancing act and it is a sacrifice to stop the signature and other factors from happening while still preserving an adequate amount of oxidation resistance for then end application.

Ismail What do you mean by signature?

Beckley           Essentially the ability to read in coming the characteristics of the vehicle and what it is that shows up to due to ionization of sodium. In other words, they read the sodium signature coming in. The only way to avoid leaving a signature that is known is to get the sodium out. That is the reason for the extreme cleanliness.

Ismail            I am surprised that you are saying that in re-entry. The rate of fiber oxidation is not that critical.

Beckley           I know you are. That is why I wanted to make the point for the group. The erosion rate, instead of being prohibitively high, is relatively low. They have a very thin cross-section of the heat shield and yet it survives a flux that is higher than a rocket nozzle and it survives an oxidation potential that is higher than a rocket nozzle. I think the mechanism that is operative in that field is that you just cannot get enough oxygen to it to do any more than a certain amount of diffusion to the surface and oxidation.

Ismail            So what you are really saying in a different way is that it doesn't really matter how much sodium you have there in terms of erosion.

Beckley           In terms of erosion, probably up to the level where we hit that 1000 ppm and up into 3000. That has turned out to be an area that is sensitive. The signature is another, and I only want to go back to rocket nozzles and say that even the sensitivity you are showing to oxidation of that 1641, if you put it in a rocket nozzle, it may turn out to be no different than the standard material because that environment is really deficient in oxygen and that is why these materials work anyhow. You really have to look at the application to find out what works. You have a new environment inside your experimental device and all the work that is there is accurate for that environment.

Hall              Thank you very much, Ismail. We appreciate it. Next on the program to bring us up-to-date on the status of our qualifying of our rayon source is Bob Looney of North American Rayon. Would you say a few words on that?

Looney            Since most of you were in Tennessee last November for the last meeting, we have had the first full-scale solid rocket booster firing at Utah. Some of you were there, but for those of you who weren't, we wanted to share a little story with you.

The human side of things is very important and the last few months, different civic clubs and also rayon-acetate council meetings with student groups that are studying fiber and fabric technologies have been interested in what is going on with this particular product. It has caught the imagination of a lot people, many of whom had no idea that rayon fiber and fabric is used in such an exotic fashion. It has been our pleasure to be able to share with them what we are contributing to that and in that regard they have been just as interested in the human side of things as in the technical side of things.

When North American Rayon first was approached about making this product, of course the average person at the plant had no idea of what this meant. But those of us that been familiar with it before had a good idea that this would be a very attractive thing for us to get involved with. The 1500 employees at North American Rayon generally have not a whole lot of connection with the final products that are made. We make a lot of good high-fashion dress wear, some fine denier, silk-like fiber that go into some very expensive ladies fashions, some very attractive velvets and so forth. The truth of the matter is that once a product is made, it goes to the shipping department and disappears as far as the average worker is concerned. He can't go to the local J.C. Penny or any other store around the area and see a label that says North American Rayon.

Now with this product, he suddenly has a link to outer space exploration and a link to the nation's most visible program, the space shuttle. Let me tell you, those people are suddenly proud of where they work. It used to be that they would go downtown and want to cash a check, and of course with 1500 people in that area, we are the largest employer in Elizabethton and Carter county. It is the usual mill town type of environment, and it's , "Oh, you work for North American" and then just a shrug of the shoulders. They would go to cash a check and they would say, "Where do you work, boy? North American Rayon". They weren't all that proud of it, because again they couldn't see those beautiful fashions that are made with the product that they produce. The same is true if they went somewhere and wanted a loan. "Where do you work? North American Rayon (hushed)" But now that there is this link to outer space contributing to the nation's defense and shipping to the NASA program for the shuttle, it's now "North American Rayon (proudly)".

We had some T-shirts, sweatshirts, and caps made up that has the NAR Space Operations on it and a picture of the shuttle on the back and have started a NASA store. The excitement of the people and the enthusiasm has really generated benefits in the quality and the overall excitement about working in that plant. That is what it is all about in order to be able to produce high quality goods. You have get the attention of the people, so that they pay attention to detail.

There is an added story. When we knew that the test firing was going to be in December out in Utah at the Thiokol operation, we asked the Owners Advisory Council to select the people from that group to go on the trip to see this. The Owners Advisory Council is a and advisory group to management, composed of a cross-section of the production workers. They come from all departments, from the beginning end of things where they are dealing with the pulp all the way through the shipping. They selected, by lot, 8 people to go out and witness the test firing and they were excited about going. Of course, most had no idea what this entailed, but they were excited none the less. We got out there and we were treated like royalty by Thiokol. We were just very well-treated. We understand that this was the first time that a plant had brought out production workers to witness one of these test firings. You know that's kind of a shame, because usually it's those of us in the coats and ties and not production workers. We had our production workers there that represented a cross-section of the plant. After the test firing, we had a very good idea that we were going to be successful, so we had given, we had some of these things (jelly bean packets) made up, and given these to our employees and they had stuck them in their pockets. After the test firing, while we were waiting for the initial evaluation, they gave us a tour around the plant. Our employees passed these out to all the Thiokol people. This was their way of saying "thank you" for having us out and that we are glad to be here and we knew that this was going to be successful all along. They got a kick out of passing those things out and we introduced everybody to the Thiokol people and the other witnesses that were there.

When we came back, this group was asked at the next Owners Advisory Council if they would share with their peers what they had seen and what they felt about it. Wayne, I know that you know Roger Mohler, one of the guys that went out, and he showed up out in Utah representing the company with jeans on and motorcycle boots and one of these little short leather jackets, a baseball cap, and his wallet was attached to his belt by a chain. Roger is a good fellow. I don't mean to make sport of him, but he recognizes this, too. Everybody got up and said what they thought about the trip and Roger was the last one. He had written his out so that he wouldn't leave anything of what he wanted to say for his co-workers. He got up and said, "I was watching through the binoculars and a lump came in my throat", and about that time a lump came up in his throat and his voice got quavery and his chin started quivering and he said, "I realized at that time that what I do is important." Now Roger works in the spinning department. He was the only that directly handled the carbonizable fibers and he said the most eloquent words I have ever heard in my life. " I realized that what I do is important." A real deathly quiet was over the room, and

everyone started applauding and it was just marvelous. I still get emotional when I think about it.

That has really gotten a lot of mileage around that plant because the people went out and told everyone else. Now Roger is a hero around the plant. Whenever any of the people related to this business come through, Roger is always there to say hello. He has done a 180° turn-around since that experience. He is terribly excited about all this as are the rest of us at North American.

As far as the business is concerned. We have completed the first 1.95 million pounds for NASA. We just did that in the last shipment, last week. We have, of course, the capability of producing up to 3 million pounds per year. As it is now, we could produce much more than that with some capital expenditure that would allow us to increase that. We do have the, Bill, do you want me to go ahead with the specification thing, too?

Hall Go ahead and mention it. We plan to have it finished by the first of June.

Looney We hope to. The new specification has some changes in it that will shift some of the specifications a little better to meet the statistical spread. We also have some additional things that have been imposed on us to monitor the quality and the character of the fiber. We are in agreement to do those things. Again we are not changing the process. We are not changing the process control. We are not changing the manufacturing conditions at all. What this amounts to is just recognizing the statistical distribution and shipping to that so that nobody has any difficulties with NASA about the numbers that go out, thinking that a certain percentage was going to fall out of bounds.

Pinoli I would like to clarify your changes to the specs. Primarily, they are associated with the production data. You are indicating that NAR material is a little bit stronger and has more elongation. The other question that everybody is interested in - did you, in terms of re-establishing these new limits, take into consideration that material which was taken out of the system? In other words, did you reformulate the limits based on statistical analysis of only the material that was shipped?

Looney It was taken out of, it was a complete manufacture.

Pinoli All yarn that was made for one year?

Looney They did both, actually, Pat. They monitored the statistical analysis of only those pounds that were shipped, the methods and specifications and they also looked at all of our manufacturing.

Pinoli The total. Okay. What do these spec limits allow you to do? Do they allow you to achieve 98% efficiency with your process? Or, will you reject a large quantity of yarn?

Looney We will still have some rejectable material, but that is mostly for broken filaments. We have talked before about how it's not textile, it is not industrial, and as such it tends to be on the brittle side. It has low elongation and low strength, but broken filaments is probably the most common cause of our off-quality...

Pinoli I know that statistically they would like to take a  $3\sigma$  or a  $4\sigma$  limit. Do the limits really reflect a  $3\sigma$  limit?

Looney Essentially, yes. It makes it more comfortable for us, but it also very clear.

Pinoli Are you going to be under the same guidelines previously with Avtex, no change in process allowed?

Looney Absolutely.

Larson Bob, along with the strength changes, will there be any change in modulus?

Beckley It is not monitored as a number.

Beckley Effectively, each number would be shifting as a result of those two numbers.

Looney Normally in rayon technology, we monitor a wet modulus, depending on whether or not it is going into a fabric. We don't put much into that.

Larson But in the carbonized form, does it show up there?

Beckley If you are saying its the composite modulus shifting, it is not recognized as such. The evidence is that the NARC material is structurally stronger, with a higher carbon compatible breaking strengths.

Looney One item, Bill, that was on there had to do with the finish.

Williamson Don, about this elongation...

Beckley I haven't seen any data that really says the modulus or the elongation is different. The key numbers that we have looked at for a long time are fill tensile and that number is only stabilizing in the upper end of the normal range rather than going anywhere, so the composite hasn't seemed to change, so I don't think the modulus is really affected, or the strength.

Thomas It's better.

Hall It's higher, whether it's better or not...

Williamson A narrower range.

Thomas What was your question, Jack?

Williamson Did it affect the elongation of the composite and the answer was no. Second one, the general properties tend to cluster closer to the upper range, but the spread is narrower, which makes it more .....

Beckley We had an average fill tensile, this is a CCA3 Avtex years back, that was around 13 and the current number out of SORI is more like 18 now and the upper on both numbers was around 21 to 23, I think. So the upper hasn't really gone up any, but the average is definitely moved towards that upper side. That is more or less the number that RSRM looks at as a pocket tendency.

Hall If you really want to see the limits, Bob has them. The thing is, they have not been officially approved yet. The last time I talked to NASA, they were trying to get this through by the first of June. They were still arguing about when and where to take samples rather than the spec limits. The spec limits have already been approved. It was sampling that was holding up the final

agreement and I think that has finally been settled. Hopefully by the first of June this will all be over with and we will publish these specs as far as the rayon is concerned.

Drake Will this spec be a Thiokol spec?

Thomas It will be in the Thiokol document for space shuttle-aerospace grade rayon yarn.

Hall Which Fiberite and BP will use to pass on down?

Drake What happens to the material doesn't pass the spec, do you throw it away or do you have a market for it?

Looney There is a market for it.

Johnson If you are changing the spec, how is this going to be relayed to the DOD side of the house?

Drake That is a good question.

Hall We can only speak from the NASA point of view.

Looney I think what North American intends to do is to leave it Lockheed, and other people like that, to announce that an agreement has been reached, and we can approach it from two different directions. One would be that our intention is to ship to that specification which does not involve any manufacturing change. The other would be to ask them what they think.

Hall We need to move on. Were you going to say a few words about the sizing?

Looney Only that we produced back in the winter, we produced some sample quantities that went to Polycarbon for their evaluation. Two approaches were made. One was to try and wash it out and that was thought not to be a good idea because rayon might not be the same after it is washed in water. Of course, the whole idea was to reduce hydrocarbon emission and some of the solvents used to eliminate the finish from the fabric are more ozone depletive than others. Maybe those that are less ozone depleters than others could be used, but the ones that the less ozone depletive are the less effective as a solvent. Our attempt is to help find something that will be carbonizable without being removed. The initial look, and Tom Paral is not here, from what I have heard is promising, but we didn't produce it at various levels of finish, so we are in the process of producing it in varying levels of finish so that we can evaluate the performance at carbonization but also in friction resistance characteristics.

Drake I think you have been working with the 1650. Do you care to give us an upgrade on the 1100?

Looney Well, we haven't been making any for a number of months. The 1100 denier as we make it, fits the original specifications better than the 1650. I don't anticipate any kind of a spec change on the 1100. We haven't been asked for any production of 1100 denier for several months.

DeLong Is it your intent to supply this new sized fabric to all the carbonizers?

Looney If that is the wish, yes.

DeLong How are you going about assuring that the de-sizing operation is compatible with the other two carbonizers?

Looney Well, we.....

Pinoli That is the function of SPIP. That is where we step into the breach. We need a sponsor to make a change of this magnitude. Bob, in his capacity at NAR, is not in a position to say this is a better way to go. What you need is somebody to sponsor the effort, work with all three of the carbonizers and report the results out to the end users. We need your opinion, along with the other carbonizers, then try to proceed along those lines. We cannot wait for DOD to make a decision; they just don't like changes and they generally don't care about your problems. Environmentally, I think they will pass the buck. Somebody has to stand up and we just have to get the ball rolling recognizing that environmentally, we have to do something. If we don't do something, we could end up out of production.

Hall Thank you, Bob.

Pinoli Have we written into the new specifications, the wet properties: wet elongation and tensile strength?

Looney Yes.

Hall There is one last subject that we wanted to cover in this area. This is the alternate source. SPIP is carrying forth the second or alternate source. We have two possibilities, one is a Mexican source and one is a German source. We have obtained material from both. SORI will do their characterization of the carbon fabric woven from this rayon source. They will be fired in two forty pound charge motors from Thiokol and in a M NASA motor at Huntsville. It is going to stop right there. All we are going to do is the preliminary look-see. We have a little problem with the German source. They make two different aerospace grades and they furnished us with one grade which is not the grade we really wanted to test. We will be looking at an alternate source, just as a backup, in case it is ever needed. Any questions?

Hall Next up is Pat.

Pinoli I would like to make a few comments on Advisement Task 2, Fabric Oxidation Mass Loss. We began this task at our first meeting. We wanted to develop a test which would screen out carbon fabric that was very susceptible to oxidation weight loss. As a result of that activity, we did come up with a TGA test procedure, SPIP-3, for measuring mass loss of carbon fiber. We submitted that test procedure to the committee and the committee essentially rejected it on the basis that it required too-sophisticated a piece of equipment, it was too involved and would be too difficult to run a routine test. We went back and rethought the situation. Myles Towne has pretty much taken the bull by the horns on this issue and developed a test procedure which is very simple and looks like it would be amenable as an acceptance test procedure. It is a go or no-go test. It is on the basis of that assessment that Myles and I conducted round robin tests.

In the handout, we have identified the test procedure as SPIP-4. We are using a Kimax 151464080 weighing bottle. Just to give you some idea of what it looks like. This bottle has a ground glass top that allows us to pre-weigh the sample in the bottle and after the test is completed. We remove the bottle from the oven, place the cap in place and during cool-down you are not required to put the bottle into a desiccator. You can leave it out at room temperature because you have a confined atmosphere. As it cools down, it develops a slight amount of vacuum.

The procedure that is defined will require a 3" x 4" piece of fabric, a 2" x 5" piece of fabric is a little bit better and will fit neatly into the bottle. Three inches high is a little tight. cYarn is

coiled to fit inside the bottle. Pre-dry the sample under vacuum overnight or comparable time and simply introduce it into an air circulating oven as 375°. At the end of four hours, you take the sample back out, put the lid on the sample, cool it down to room temperature and take the weight. One observation that our technician came up with is the weight of the fabric sample is small in relation to the bottle weight. This particular bottle weighs about 75 mg.

Towne Excuse me, Pat, this size sample could be 1.5 grams.

Pinoli But the weight loss associated with it would be around 100 mg. The point is with a vessel that weighs so much will influence test results sensitivity since the fabric weight change is so small with respect to the weight of the bottle. It turns out, we are looking at changes at 5 or 6 significant. Most balances, however, are very good to a tenth of a milligram. I would also say we had no difficulty getting very reproducible and accurate numbers, using the recommended bottle size.

Towne Pat, I might make one additional comment - when the samples in the those bottles start cooling down, it is important that it not be a tight seal at the top so that it does allow the air to go back in. This will make a significant difference. It has to be, you don't want to grease it up so that it can't suck it in. It has to equilibrate, pressure-wise.

Pinoli Do you think, then that there is a need to put it in the desiccator?

Towne I calculated out that the air that goes back in makes a very significant difference. The moisture that accompanies that air, 60 RH atmosphere, is not significant. I don't use a desiccator.

Ismail That would depend on which fabric you are talking about. In other words if your fabric can absorb 20% moisture, then there would be error there.

Towne You are only going to suck in enough air till it equilibrates the pressure. It doesn't diffuse back and forth.

Ismail I can see that, but all I am saying is, let's say one of those fabrics picks up 20% moisture, then just by cooling it without the desiccator, you will have a lot more weight of moisture in your fabric. Wouldn't you?

Pinoli If it is available from the atmosphere. But typically, you have a small confined atmosphere in the bottle and residual moisture in that atmosphere will be depleted.

Towne It will be depleted very fast and then you have a dry atmosphere in the bottle.

Beckley Let me share with you one that we have just experienced that is a little analogous to this. We run extraction with samples that are about this size, 1 - 2 grams of finished fabric. If you let the sample go to a desiccator and effectively then after and coming out of the desiccator and go to weigh it, you will find enough weight gain, that it will affect your answer by 1 - 2%. I believe this is what Ismail was saying. You can't have fabric samples that even in a desiccator will find moisture. I think your point is, if you can just limit the amount to the air that is already heated plus a small amount that will come in, is probably as good as can be done.

Towne I did a sensitivity study on going into a desiccator and the procedure of putting them and taking them out varied significantly and affected the results

Beckley We are agreed that you can't desiccate.



Towne It just isn't going to work.

Pinoli If you open the desiccator to introduce the sample, you kill the atmosphere. That was one of the reasons we like the ground stoppers and bottle techniques.

Beckley Myles, did you every try it without bottles at all.

Towne Yes, we used that procedure. However, you just cannot weigh it fast enough without affecting the results.

Beckley Okay.

Pinoli I have tested fabrics that way in the past but the data is too subjective. It would not be appropriate for an acceptance test.

Beckley Are we going to get a bottle one of these days that doesn't seal. That is what I am concerned about. You might wind up equilibrating with the carbon fiber fully whatever amount of moisture ....

Towne You know some people do put on stopcock grease wherever they see a ground joint. That could be a problem.

Ismail How do you expect these to give you the same numbers each time?

Pinoli I don't think that at 375°, the moisture in the atmosphere has much affect on the carbon-oxygen reaction.

Towne Even at 100% RH, it may be a few milligrams, maybe 80 mg, but that is insignificant in view of the changes that take place in oxidation.

Beckley We were seeing 10 milligrams in the desiccator. That was the problem.

Pinoli I want to go over some of the preliminary studies that we made to give you a feel for what kind of data you can expect. In order to do that, I chose the Polycarbon Parametric Fabric, which was run about 3 or 4 years ago. This is a study where we ran material at various firing temperatures. We dropped the temperature down to -100 and -200, and we produced a very activated 10B material, and increased temperatures higher than normal. The  $\bar{x}$  values represent three test specimens that were run at the same time. The standard deviation is indicated and so is the coefficients of variation. What one would hope for is steady progression to higher mass loss factors as you reduce the firing temperature. In reality we see is a slight increase initially 0.4, 0.5%, a little scatter, but there is a definite trend and obviously with the 10B we have got the big effect we want to see. One has to keep in mind that we are not talking about a clean, super-sophisticated analytical technique. What we are trying to get to is test that would be go or no-go. We set a limit of say 5 weight %. Will this test discriminate this kind of a product? I'll go through the numbers and you make your own judgement.

Beckley Pat, your  $s$  is  $1\sigma$ ?

Pinoli Yes.

Beckley So on that first sample, 3A, you are ranging from just a little below 1 percent to above 3 on a  $6\sigma$ ?

Pinoli A  $3\sigma$  limit would reflect 96% confidence. Coefficient of variation is probably the best way to look at data variance. These are fairly high numbers and they don't give me a warm feeling. Here again, one has to take that into the context of what we are driving for. We want a simple test, straightforward, and we should expect a certain amount of variation.

After looking at these numbers, the first thing that came to my mind, was what was the role of sodium. I think there are two factors that are influencing the oxidation behavior. One being the fabric firing temperature and the other being sodium. The next chart adds the fabric sodium levels. When we went from 320 to 950, we see a very sharp rise in mass loss. Is that due to the firing temperature, or is the big shift due to sodium? I am more inclined to think that sodium is a strong driver.

Towne Pat, while you are on it, I have been over that parametric study and frankly, I strongly vote for coincidences.

Pinoli In what respect?

Towne On the high numbers being associated with the ones that had high oxidation loss. We are not in a temperature range where the processing temperature is affecting the sodium content itself. My vote at this point would be that the difference in oxidation rates is much more affected by the processing temperature.

Pinoli I see a divergence of thought.

Ismail I agree with Myles on this point. Definitely sodium is acting as a catalyst, but I think this fabric, the 10B, is oxidizing at a higher rate because of the structure. At low temperature it retains a part of the sodium and I bet you, that if you take this sample and just wash it and come back and do an oxidation rate, it is going to be higher than the other four.

Pinoli Every time we have taken this 10B type product and washed out the Na, a lower oxidation rate is measured. For those that are not familiar with the parametric study, you just might want to glance at some of these numbers. These are the fabric characteristics related to firing temperature. Most pronounced is the moisture adsorption behavior of the products. On the 10B, we are up around 24% decreasing as firing temperature goes up. What we saw in the initial analysis was a general trend toward higher carbon assays, but an awful lot of overlap. You really couldn't see the strong trends that you would expect from carbon assay numbers. The recent work that we have been doing with carbon assay testing indicates this particular test couldn't discriminate the firing temperature differences. I honestly believe there is a strong trend, but we couldn't measure it with the current LECO technique.

Electrical resistivity was very good, very reproducible, but these numbers may have a tendency to change with time as the fabric ages. I think we are seeing these numbers shifting to higher numbers, primarily due to the activated carbon structure.

Another sample included for testing was a five ply yarn and some associated experimental data that was presented before. This material was introduced into the program for comparison purposes. This is very low fired, second low, medium firing. The medium fired yarn is pretty much the target for the ASRM program. You can see that the adsorption behavior is very high for low fired as opposed to the higher fired yarn with low adsorption behavior.

This may be mixing some apples and oranges. However, I would like to utilize materials that are relevant and to ongoing efforts. The ASRM-Task I material is under an awful lot of study. These

are heat treatment samples that are being prepared both by Hitco and Polycarbon to evaluate the effect of firing temperature on downstream properties. Samples of these materials were subjected to the mass loss test for cross-reference. The first ones I have listed are the high temperature products, C-5 yarn, the next being standard temperature and a low fired version. For Hitco, we have two samples of high temperature, two samples of standard and 2 samples of fabric with low temperature.

First off, I would like to comment on the very high fired material. In both instances, the products responded by chemisorbing oxygen and we measured a weight gain. That pretty much confirms work that Myles has done. He has seen weight gain associated with exposure to 375°C. In general the data was reproducible. The standard deviations look reasonable with one exception. A very large standard deviation develops when one of them flips from negative to positive weight change. I don't put any credence in the coefficient of variation because the numbers here are so small. We did measure primarily chemisorption on the high fired products. On the standard fired material, we have seen a slight mass loss weight developing on the fabric. In the case of standard yarn, the high standard coefficient of variation was due to one sample that measured primarily chemisorbed oxygen. Here again I wouldn't put any credence in that number. The low fired versions reflect more variation. In this case we have about a five to six percent weight loss and in this case, only about 1.25. In this case I think I can account for it by the fact that there is a significant amount of sodium in the yarn. It is much higher than we would like to see. I was hoping that Tom Paral would bring the specific Na numbers with him. I strongly believe that the difference is a sodium-related effect and not firing temperature. If we had clean products, BP/Hitco and Polycarbon products would probably respond the same. Ken, do you have any sodium numbers that you can release for these products?

- DeVane            There is quite a jump at the high fired. It is in the 50-80 range. The standard, the center one has about 400, and the bottom has about 80.
- Pinoli             80?
- DeVane            Yes. 80-100. So there's an interesting quirk in there.
- Pinoli             I feel one has to be extremely careful in regards to sodium issues because each lot of fabric that is produced is influenced by the precursor. You have to analyze both firing temperature and the sodium level in the precursor. If the sodium level in the precursor was lower in this product, even though it fires at lower temperature, it will come out lower. Do you agree with that observation, Don?
- Beckley           I think we have got a overlay of factors, temperature being a primary driver, but you can definitely the resistivity and you can affect the moisture susceptibility and now a mass loss number by additional control factors in the material.
- DeVane            There may be factors in addition to the sodium. Now I am not convinced yet that the sodium is the cause. I can't go into much detail on that.
- Towne             That is the kind of difference is what I would expect from 400 ppm sodium. That doesn't surprise me at all.
- Beckley           In fact it is comforting to see the fact that the lower sodium number and the lower mass loss are there.
- Pinoli             Otherwise, I couldn't account for Na levels reported.

Johnson Pat, are you saying there is a question of how much sodium you are talking about at low temperature? Are you suggesting that that comes out of the rayon itself?

Pinoli Yes.

Johnson But you don't know that.

Beckley All the sodium was in the rayon to begin with.

Johnson I realize that, but do you have any base data that says that that is a given known fact.

Pinoli Are you saying we can't trace the sodium level of the precursor back to these specific lots of fabric that were produced?

Beckley The higher temperature material is cleaning because it has been in a high temperature and it basically boils off. That is the standard VCK type of cleanliness.

Johnson But the low one is low for unknown reasons.

Beckley Low for reasons.

Johnson I don't understand that.

Beckley It is within the carbonizers control.

Johnson Now I understand.

Pinoli Let me follow up on that.

Beckley Yes, it is going to be interesting to see how the materials perform in use.

Pinoli Do you feel that you could routinely produce this low fired material with that low a sodium content?

Beckley Might be able to. In fact, I think we are pretty confident that we can.

DeVane For the way we process that, I would expect somewhere between 50 and 300 with an average of around 200. That would probably be the normal range for the whole population.

Pinoli It was my intention when we got into the ASRM Task I that other processing parameters would be held constant. The only thing we would vary is temperature. Are you telling me that you changed another parameter? We just wanted to see what the effect of one parameter change. I am beginning to read into what you are saying that some other stuff was done. The intent was also to use the same precursor lot for all Task I material.

Beckley They are. They are the same line.

Pinoli So, what is your answer? Yes or no? Are we mixing apples and oranges?

Beckley The change is in the temperature.

Pinoli We were agreed that the only change we would make in those products were the firing temperature. We would set up the furnace runs; the feed-through rate would be the identically the same; all the other parameters in the process would be identical. If you introduce another variable, obviously, you will never know what caused that effect. The only reason that I could associate then with the lower sodium that you are reporting out is the precursor had that much variability in it. But you are inferring now that you have done something else. Is another parameter influencing the Na level

DeVane The one thing that I am saying, Pat, is the normal range of material processed the same way, is going to be somewhere from about 50 up to about 350, with occasionally it being slightly higher. The material produced over and over, the same way - that is the type of variation that I see. There is a fairly wide band. I don't think that 50 or 80 us going to be consistently the vehicle. There is a range there. I think we are looking at the low end of the range.

Pinoli What you are saying is that a roll of fabric will reflect a large variaion in Na level associated with where you have tested.

DeVane Yes.

Pinoli The sodium level is going to vary from one location to another.

DeVane It falls in bands. At this point, that is all I can say.

Beckley You have a band of material that is typical shuttle, 500 and 900, and we made for this particular study the standard material to be a tad better than that as a band. That is the basic material. The standard number.

Ismail I don't think, Pat, you really have a case here to talk about because if you tell me the difference between one sample and another is 1.5 or 1.4, 1.25, I wouldn't really bet my life on this kind of temperature. I think what you want to do, I don't know why you selected 375. I think you ought to go to a temperature depending on which fabric you have in your hands. Definitely here, you are dealing with a fabric where 375 is probably too low for this kind of fabric. You probably want to go to something like 450 to 500 and then get your  $\bar{X}$  values in the range of 10 - 20. I really don't feel comfortable with the difference of 1.5 to 1.25.

Towne If you go that high, materials like 10B will disappear.

Ismail What I think is, select two temperatures to work with and run it here and there and pick up the best temperature that is suitable for this fabric to have. If you have fabric with high sodium, then you go to the low temperature. If you have fabric like this is, I really don't believe that this is more reactive than the low temperature.

Towne I designed, I am guilty of selecting the temperature and we intentionally did that in order to get a differentiation between good products which are going to be in the 5% and 10B which is going to quite high.

Ismail Pat cannot use this to differentiate between two good products and say this is better than that. I guess what you want to come up with is what is the minimum  $\bar{X}$  value that you would trust and below that, you just throw it away and say I really cannot use it.

Pinoli Yes, I think that you are probably right. This test was never designed to tell you the difference between these two products which are so close.

Ismail I agree with Myles that it is very good test to differentiate between the good and the bad.

Pinoli The slope change at the low temperature is the critical factor

On the ASRM program, I am using 400°C and getting good discrimination. At 375° I would have to establish a new data base.

Remember what we are driving for is to eliminate the possibility of 10B material getting into our system. If we were to set a limit of 10% or 8% weight loss, I am sure the Amoco test is good enough to discriminate.

DeVane Pat, the 10B, is that the same roll that Ismail talked about earlier?

Pinoli Yes.

Myles and I have initiated round robin testing with the Amoco technique. At Lockheed we got 1.55, 1.62, 18.2 comparing with 2.71, 2.43, and 24.4 for Amoco. This indicates consistent higher values at Amoco. I ran the WCA for informational data only. data out somewhere. Standard deviations, Myles looks a little bit tighter than Lockheed data. I can only comment that our circulating oven is a very large one, with a 24 x 24-inch hot zone. It has a very high air flow. The reference thermocouple was positioned right in the same proximity of the samples and we only ran about 9 samples at one time. We made 4 runs as opposed to putting all the samples into one oven at one time.

Rubin Did you say you desiccated the samples, Pat?

Pinoli We had a desiccator by the oven and when we removed samples from the oven, we put them directly into the desiccator.

Beckley The bottles went into the desiccator.

Pinoli Right, the bottles went into the desiccator and lids place on prior to closing the desiccator.

Ismail Were you both using the same sample size?

Pinoli Yes. We followed the guidelines of the test procedure in terms of weight, but there was a little bit of deviation in the procedure on samples size. We used 2" x 5".

Towne I had indicated earlier that the samples I used were somewhat less than 3 inches. I have not been too careful in determining between 2½ and 3 when I cut. There may be a little bit of a difference there. My samples that were closer to 3 will be closer to the top of the bottle, but I think that may be something that has to be standardized a little more carefully.

Ismail I think what you need to standardize here is how high is the relation between how many samples were in your oven and the size of the space inside of your oven. When I did that work and he used the same oven and same everything, 2 sample or 1 sample, you get a tremendous difference in oxidation rate and properties of the oxidized material. It is very important to take the ratio between the surface area of how much material you have there with the volume of the oven you have there. Although it doesn't make sense, But if you try it, you will get a big difference.

Towne We also have a large amount of circulating air. You will see the oven tomorrow that we use in this and I guess I have trouble thinking that there is any insufficient amount of air contacting the samples at any time.

Beckley Just the fact that they sit in that glass bottle restricts the amount of real air that gets to that sample. That becomes its own little environment right in there and you don't get good mixing and good diffusion down inside a bottle.

Towne Yes, I understand that, Don. I guess I am assuming that at the top of the bottle, it's the same in any case. Within the bottle, it is going to different from at the top. That is why I standardized on this size bottle, rather than the larger one, because there is more opportunity for the operator to put the sample in the bottle in a different configuration. In this size bottle, he has to coil it, and it stays in the same position throughout the oxidation.

Beckley Wouldn't you expect a 5-inch strip with more overlap, that is 2 layers, is going to give you a different diffusion situation than maybe a non-overlap.

Williamson One observation on oxidation measurement. The jet engine people have gone over this thing and they have had the problem of making out enough oxygen there all the time, so they have gone to 80 psi and they are getting much more consistent results with using 80 psi air rather than the ambient pressure.

Beckley You are probably correct, but let's keep it simple. I would rather not have that accuracy for this purpose. We will be blowing samples around the laboratory.

Pinoli Ismail, you made a comment earlier in your presentation, that you haven't found that air flow has much to do with the oxidation rate. As long as the sample size is quite small with respect to the volume of air flow?

Ismail When I was talking about that, I was talking about 5 - 10 mg samples and air flowing 15 cc per minute.

Pinoli What is the difference between that ratio and this ratio within a 24 x 24-inch air circulating oven?

Ismail There is a difference, Pat, between air circulating and air going through and you are using fresh air all the time.

Pinoli You don't have a hole in the bottom of your sample pan when you test at Edwards; and the Amoco procedure does not have a hole in their bottle.

Ismail Yes, but the sample is like half of it is in and half of it is out and the height of the bucket is like 5 ml. Try one with one sample and one dish, and try the other case with a larger sample and one dish and you will get tremendous difference in oxidation rates and your properties. I did have air circulating in it. It is a huge furnace and you get this one, because this one is not really how much air gets to your sample. As Myles says that is pretty much standard. So you don't have

any problem with air until it gets to the sample. The problem you have is air deficiency between the fiber. That could change the whole weight loss.

Pinoli            You are right. This tightness of the weave could be very important.

Ismail           You remember when I talked about the way you weave it is very important. That is one parameter you ought to consider in applying your test.

Stokes          Ismail, what temperatures did you use for this study?

Ismail           450 to 550.

Towne           This is the other kind of a bottle that I had looked at and in this I was not able to place the cloth in a consistent way. Those that oxidize more get sloppy and fall over and now you have a different circumstance than you do in the taller bottle.

The stuff that I am going to present here is, if you will recall from a couple of the meetings, one of my intents is to try and get rid of the damn sodium test. I think we have seen a lot of evidence here today that is very confusing. What does it mean? We don't want a whole lot in there, but I am firmly convinced that all the carbonizers can wash it enough so that it is down below the level of concern. The statistics on it are going to be such that you can never treat it statistically and have a reasonable level to put in a specification. Fiberite is our customer and Fiberite has a specification of sodium on the prepreg. They look at their statistics and they tell us that they have had very little correlation between the numbers that they get from the supplier on the roll and what they see in the prepreg. We are both doing a lot of testing and not sure where we are going. We talked to Fiberite about checking it out to see what kind of correlations there are just to show that there is a problem. There is another way of approaching this problem; we think that this proposed oxidation test tests for the effect that we are looking at from sodium. It is not the sodium, itself, that is the concern, but the effect of the sodium. That is, what it does to oxidation.

We think the oxidation test is the inexpensive test and all the testing that we are doing for sodium is for academic reasons and according the charter of this group, is it data that is meaningful and is it worthwhile? I think from those aspects that I would like to get rid of it. The spec that Fiberite places on us is 600 ppm, just so that they will be low enough, they think, to meet their prepreg spec. If we test the fabric at one end of the roll and the other end of the roll, we can have two numbers that may not be representative of what is in the middle.

What we agreed to do with Fiberite was to cut up a roll and go through and check the uniformity. Now, I have got the results. Unfortunately, with ASRM problems, Ed Hemmelman is not able to get his prepreg data yet. We have the rest of it and I will show you what I can.

This particular test showed a little less variability than we usually see. We have a roll here and about 45 yard intervals we cut and took samples. Fiberite has taken samples from each of these areas and is prepping it. They will do the testing on the prepreg. What I have here is on the cloth, our sodium, across the width. This roll was picked as high sodium because it is around the 600 level. We go 530, 570, 550. That is pretty good. I have also included ash and have placed on each of those the oxidation weight loss and these are some of the same numbers that Pat had. This would be Sample 2 and it is A and Pat showed it 2A, so there would be three numbers-I think your number was Number 271. Right, Pat? This is the variation. I put on ash, that comes closest to telling you anything that sodium tells you. We do that in the routine also.

Let me now put this in a little perspective here. These are all the numbers from that roll and I think, you know, you are putting an awful lot of weight on this number way out here. Maybe



there is a tilt to this line, but it is sure not much of a tilt. This covers the range from a little below 400 to a little above 700 ppm sodium.

DeVane This is your 375°C weight loss?

Towne Yes. This is where I have indicated the STS-8A type material at 24.4, so we are an order of magnitude different. I think this is an excellent discriminator of the kind of material we want and don't want.

Thomas That x to your left, would you not put that in the outlier category?

Towne No. I am surprised that we only saw one of those, Jim. In a roll like this, I would have expected to see several of those and maybe even a 900.

Thomas This is a standard roll width here?

Towne Yes. We routinely do our sodium test. We cut it and have 3 samples. That is 45 tests in there.

Beckley Myles, the ash on the 390 sodium, is that a 0.17?

Towne Yes, 0.17.

Beckley Did you plot ash versus.....

Towne No, I didn't, Don.

I think this sodium test is an imposition and a cost to the supplier to be kicking out all this money for sodium testing. We are in a range that we really aren't concerned about as long as we kick out the real high number.

Peasley Myles, did you say that the test needs to be run in triplicate?

Towne Sure, yes.

I don't understand the deviation numbers. The standard deviation is not very high.

This is going to jump a little bit ahead and complement what Pat presented on the relation of some of these properties to firing temperature. We did a series of runs on the same roll of material and we did six different temperatures. For proprietary reasons, I haven't put the identifying temperature on the bottom. WCA is way up here and if you look at some of these properties, you can see the VCX 13 is out here and our standard VCL product is out here. The other one was our standard VCL and you saw what the weight losses were. This range here is not out of what has been produced for shuttle and it's perhaps okay. I put some additional things on this. I put the sodium on this at these individual points, 380, 403, 320, and now we are getting to the point where temperature itself has an effect on sodium content. I don't think it does down here, but at this point it does start to have an effect beyond the 232, now down to 140 and 37. I think you are seeing the two different effects. The other thing that is interesting and this is, I haven't had a chance to do 100% RH moisture adsorption. I did have the material at room equilibrium before I did the test, so I have these numbers for the same points are 60% RH at 73°F. This is the level of moisture that they held before I dried them. These two, the lowest ones, were both 10.2%. At this point we dropped down to 3.9. We got out to here, 0.77, 0.45, 0.06.

The other thing that I thought was interesting, when we looked at the low fired PAN program, we were looking at things in this range to duplicate what rayon was. These are the figures for those same temperatures for electrical resistivity. Just as a boost for that test, these were run in duplicate and in no case was the highs and lows outside the circle I have plotted. That is the degree of reproducibility I think you can get in a resistivity test. I have plotted on the oxidation loss the highs and lows. This one is the same; you can see where there is a little variability. I think that this one, at least it tells me that firing temperature has a dramatic effect on weight loss, oxidation weight loss in this temperature range and that is the range that we are interested in. Sodium from that tilt on the other one, I think has a minimum effect, some effect, but not great. Maybe when you get up high, I think it then it becomes very significant, but in the range that we are talking about the temperature is a much greater driver than the sodium content.

- Pinoli Myles, is there a possibility that the sodium on these products with low firing temperature, is predominantly inside the fiber itself? You wouldn't see a strong influence initially if that were the case.
- Towne It is possible, Pat. I think when we wash the fabrics, we remove it from the surface. It is internal. These fabrics, although they have been processed at a higher temperature, I don't think the way they're processed should drive sodium just to the surface. This is weight change here and this is zero, so this the point where chemisorption proceeds the oxidation.
- Beckley That one sample, right in on the zero, with the 10% weight at 60% relative humidity, that just seems high.
- Towne The relative humidity or the amount of moisture?
- Beckley The amount of moisture.
- Towne I was surprised at that, too, Don.
- Beckley The upper one makes sense, that one just looks a little out of line.
- Towne I know. You know that curve that I showed before with the water density versus firing temperature and it does this. These points would both be on the upper part of that curve. When I saw that I said, "Well, you know those two points are up there." These would give you the 1.85 type water density. Whereas if you go to this one, you would probably down below that.
- Pinoli Keep in mind that he did that at 60% RH.
- Towne I guess I should reiterate something that I have talked about in the past. On sodium analysis, we were not able to feel confident with our sodium analyses until we got a standard that was chopped and macerated until it was all mixed up and homogeneous and in the size that we were running. Until we did that, we could not have a standard for sodium. Standards, when we would run them, would jump all over the place just as much as the rest of the production.
- Beckley On the front page, your A, B, C samples, were they homogenized?
- Towne No. They were run in triplicate but in the presence of the standard that was homogenized. I am surprised that we got the uniformity that we did on that one. Usually we don't.
- Pinoli You are not questioning the measurement accuracy of sodium in the ash?

Towne No, not at all.

Pinoli What you are questioning is the uniformity of Na distribution on or in the fabric?

Towne Yes.

DeVane That is what Ken was saying.

Towne That is why I feel we are just spinning out wheels and spending money on the sodium test.

Pinoli We are talking about a very small area of carbon fabric, therefore Na level could vary widely.

Hall Thank you, Myles. Could we break for lunch now and meet back at about a quarter to one and start with Gloria?

Hall The committee has a request to make of you. This is, as I mentioned before, the first three year funding on this project, ends and we need input from everybody. Jay Larson or Cindy Upton, either one, need input from you before you leave. We need input on how you think you benefit or how your company benefits from this committee. We would appreciate your response to that if you feel like doing so.

The last item on the morning agenda is Gloria Ma from test. She will give us some information on the URA 2000 which does the chemical analysis of the composite in a non-destructive manner.

Ma Good afternoon, ladies and gentlemen. Before I start I would like to thank the committee for inviting me to give an update on the URA 2000 technology and also give some of the preliminary studies we have done on ablative material. I have quite a lot to go through, so I will go through it as fast as I can.

Just to recap the URA 200 technology, for those of you who were not present last time, basically we measure the velocity through the sample by taking very accurate mechanical thickness and ultrasonic time of flight measurements. The system is currently set up to measure properties of a two phase for heterogeneous system. With prepreg material, there is a special process that we have to go through before you can compare the samples, because prepreg materials deform as you contact them to make these measurements. This is the process whereby you extract the optimum consolidation point which is the transition point between the air collapses and the matrix extrusion, and at that point, we have a reproducible physical state of the prepreg so that you could come to this point, measure material property at this state and compare the samples. Once you have this done, and actually there is more information after the optimum consolidation that could measure flow, but I don't want to confuse the issue right now.

What I will be talking about, primarily, in the next 20 minutes or so, is an update of where we are today. We have just completed the ASTM round robin with five round robin sites and I will present the ASTM data to look at the reproducibility of the test method. There is currently a ASTM draft document being written and that document is at the subcommittee ballot level. If any of you want a copy of the draft document, please let me know that you would like to have it.

After my talk about the ASTM round robin data, I will be talking a little bit about the preliminary work with the high temperature version of this instrument which allows us to look at the ablative prepreg material.

The URA technology is basically a semi-theoretical, semi-empirical approach to acquiring a data base. We establish a set of samples with varying concentrations of the material properties, or varying degrees of the properties that we want to be looking at and we actually extract the non-destructive measurement and then look for relationship, the empirical relationship, based on the theoretical model. The curve fit is based on a theoretical fit the simplest curve fitting is a linear fit, based on the rule of mixtures. If one is not sure how this material is going to behave, then you could say within a small region, one could approximate a linear fit and you could plot that to fit the data. With most of the materials that we have looked at with fiber-resin ratio of prepreg material, this relationship has been non-linear.

We have concentrated on the 2-phase materials, but the 3-phase materials are more challenging because it depends on the variation of the material that you looking.

Williamson Will this technology be able to determine variations in filler content or the given formulation on a piece of prepreg?

Ma Yes, we think that it is technically very feasible. The answer is yes. Right now we have two parameters and two unknowns. We measure two measurements, the thickness and the time of flight and we set up our relationship that way. If you have a third unknown added into the equation, being filler, then you need to add at least one additional measurement parameter and that is precisely what I hope to do for our study. You could do longitudinal wave and shear wave or two different kinds of waves.

Larson We are talking about prepreg and yet are you saying that when you put multiple layers of prepreg together that they are not molded?

Ma These are laminated prepreg materials.

Larson They are not cured?

Ma No, not cured.

Beckley Just densified to get the air out.

Ma Yes. I am going to just go through very quickly, there's a lot of data on the ASTM round robin. The setup of the experiment, there were 5 sites involved, Fiberite, Hexcel, TRW, Boeing, and NBS. There are five instruments in this round robin and 4 materials being evaluated. They were all epoxy based, 2 graphite materials, a woven material, and a uni-directional tape and those were supplied by Fiberite, donated to the round robin. The Kevlar and glass epoxy was made by Hexcel and donated to the round robin. We have decided that with composite materials there are a couple of problems with material properties. In reality it is very difficult to get identical specimens, so we have designed the round robin experiment in two parts.

The first part is the instrumental characteristics. How do we make sure that the five instruments are measuring the same, and how repeatable are their measurements? So, we set up reference specimens. One is an ultrasonic aluminum reference block. This block was a block that was used to check ultrasonic angles and this block was sent to the five sites. We marked off the area that was to be measured and each site took 35 measurements on the same spot by taking out the block and repositioning. We wanted to see the mechanicals as well as electronic errors involved. That is the first set of experiments.

The second set of experiments is the theory part of it that we assume that there is a relationship between velocity changes and fiber/resin ratio changes. With composite materials you have material properties that are different so you don't have identical samples and these samples are altered in state during measurements because with prepreg samples, once you start pushing or squeezing the material by consolidating it, you effectively change the physical state of the sample. With that scenario, we constructed a synthetic composite and this synthetic composite is made by mixing a sandwich structure of acrylic and steel. We don't have to destroy the sample in order to get volume fractions for reference standards. You can get the volume fraction simply by taking the area times the thickness and summing. That removes the variability due to destructive results. What you get, when you are trying to establish a correlation coefficient between two sets of measurements and one set of measurements is a destructive measurement that has a high degree of variability than when you don't have good correlation, you don't know whether it's due to destructive variability or material property variability.

Williamson      Suppose you took those materials and chopped them up finely, could you still determine the measurements?

Ma                We can't because the velocity through the material ...

Williamson      Suppose you molded it and then take the finished part to establish the relationship?

Ma                If you have the data base. As long as your ingredients...

Williamson      A non-destructive method of determining resin content varies on each material.

Ma                Yes, because each material has a material specific data base that is based on the ultrasonic propagation difference between the constituent parts. You have to establish the data base for it. The technique is very applicable to any two phase heterogeneous mixtures. As long as your ingredients are sufficiently different so that you can differentiate them.

Williamson      You have intruded into what they call the "black area"?

Ma                The black area?

Pinoli            Radar absorption?

Ma                Yes. We have looked at that with GD. Let me continue with the ASTM results. So this is the second set of reference standards that we looked at. For the evaluation of composites we generate calibration characteristics at different sites and compare them. So, we had a range of resin contents because destructives variances are between 1 - 3 %, so if you have a very narrow range of resin content and you will be burying a lot of your correlations. We selected a wide range of resin contents and each site did their own ultrasonic measurements on their instrument and then they destroyed it. So, each site did their own destructive analysis. We then looked at the calibration characteristics and that was the criteria for repeatability and reproducibility of the test method, how reproducible it is and the site to site variability. Within each site we looked at the variability as well and that is how we determine the repeatability, reproducibility and bias part of the test method for the round robin.

Let me go into the results. This is the ultrasonic reference block. This is the time of flight measurement. You can see the five different labs. There are instrument differences in the measurements, and this range here is in nanoseconds. The whole range is about 17 nanoseconds. I am sorry the range is 13 nanoseconds. The mean of the measurement is this. You have a  $\pm 7$

nanoseconds difference between the measurements of different labs without correcting for machine to machine differences at sites. Even without calibration, 7 nanoseconds translates to about ½ % in resin content because typical slope is about 15 nanosecond per percentage point. In terms of thickness, I didn't bring the thickness, the thickness is much, much tighter. 4 microns seems to be the site to site difference and 4 microns translates to 0.1 % resin content. The slope is such that 55 microns per percentage point, so it is very, very small error in the instrumental characteristics.

In the steel and acrylic mixture, here is the five sites measured. We blocked out the name of the different sites but you can differentiate them apart. This is the velocity measurement. This is the percent acrylic by volume. The correlation is extremely high so we verified that the instrument performed the way it should be and the site to site difference is very, very small.

Now, when it comes to composites, it is a different story. Let me first show you the outlier rationale and analysis of calibration. The rationale for outliers is if they are 3 standard deviations from the calibration line, they are considered an outlier and would be removed from the calibration. This is the glass epoxy material. That is the time of flight and thickness calibration. This is the sites at which they are generated. This tells you the outliers that are removed. This is a sample and this will give you the type of error, whether it is destructive error, machine error or unknown. Each calibration consists of 36 points. We have four specimens at 9 different resin contents. Just enough, statistically, to give you a calibration characteristic.

I'll show you the worst data first. This is the worst set of data from a graphite epoxy. You can see this is  $\pm 3\%$ , the error and range. This is at one round robin site, we removed the names. This is the same material done at a different site. You can see that by whoever did the destructives, this is  $\pm 1\%$ . You must make sure you do the destructives right.

This is the least square error measurement. Most of the time, with the exception of this particular graphite epoxy material. This is HMF13334. It is a 5 harness satin which has directionality in the fiber.

Bhe How did they do the destructive test?

Ma Solvent wash. There are two sets of destructive techniques. For the glass epoxy, it is burnoff. You see the glass epoxy data is much nicer. There is hardly any variability.

Most of the time these measurements, if you do it well, will give good correlations. We initially didn't realize that this material has directionality of fibers and one of the problems is laying it up when you randomize it so that there were instances when the amount of fibers differed.

Williamson Take a harness satin and you have 4 potential ways that it can lay up unless you have a data base on each one of those, you have a problem.

Ma We didn't specify or identify a lay-up sequence and that is one of the problems that we see. When they give you directional tape, we say 0-90, but even on that you have to specify warp or fill side up. That is one of the reasons why we see such variability in this material.

Let me now go through the best material. Each calibration within each site right now. I haven't touched on these site to site differences. This is about ½ % which is about the limits of the what the instrument should be. All of the sites are pretty much within this 0.5 % range. The glass epoxy is the best material for this perhaps because the destructive results were more accurate than the other materials. I won't show all the sites, but I just want to show you some representatives.

This one is a Kevlar epoxy material. This is the uni-directional graphite epoxy,  $\pm 1\%$ . Typically we would say that  $\frac{1}{2}\%$  to  $1\%$  would be good results.

We started looking at the site to site differences in the destructives and here is a summary of the site to site differences. What we did here is to take, this is after the outliers are removed, we take a look at the highest, for each four specimens, we look at the highest and the lowest, and then group that as amongst the four sites that are doing it. Even there were five sites, there was only four sites analyzing each of the materials. Fiberite didn't analyze Hexcel's materials.

We generated a range and  $R_{BAR}$  is the average of the range which is taking the high and low set of samples and that is summing that. From this you generate your standard deviation and by taking  $3\sigma$  which is 99% confidence interval, this tells you, what the site to site destructive variability is. We also looked at the distribution of these differences and the bias of the destructives and there doesn't seem to be any except for one set of data where Hexcel is showing a slight bias. That is looking at the destructive differences, and keeping that in mind, we plotted the calibration curve comparing the different sites and just how equivalent are these calibrations. This is the best case, the glass epoxy material. Here you have the four sites overlapping very closely and you get a slight offset in this case. I wanted to emphasize that time of flight is much more sensitive to material property variations. If there is any error or differences in fibers and resin samples, they will be magnified in time of flight measurements. Thickness is a much more consistent measurement for fiber/resin ratio. If you have a non-wetout in your prepreg, the time of flight measurement will be affected.

The worst material, well, let me finish this first. You can see that each square is  $1\%$ , so all the sites are within  $2-3\%$ . Three of the last are right on top of one another. This one shows a little bigger variation in time of flight measurement, but still it is within  $0.5 - 0.7\%$

This is the worst material. The thickness measurement shows, we had a problem with this one site. We don't quite understand it. It is about  $2\%$  off. The weight was about  $0.3$  grams higher than the rest of the sites. You can see that these 3 labs are within  $1\%$ . The time of flight here is within  $1\%$ . That is the best case and the worst case material in terms of calibration characteristics. This is Kevlar epoxy and this is somewhere in between. Seeing that these are within the destructive error bounds, we combined the data bases into generally one data base and see if one can use that data base and then take everybody's measurements and predict the resin content numbers, how does that look and how does that correlate with the actual destructive. That is the idea of the combined calibration.

Here again, the worst case. We plotted all the data. The outliers are shown as well. This is the worst case material, graphite epoxy cloth without the bad data coming out and everything is within the  $3\%$ . If you throw out the bad set of data, which has that strange set of data, then you see that it is  $\pm 2\%$ . All the data points fall within that area. That is the worst case.

The best case material is the glass epoxy. Here everything falls within  $\pm 1\%$  and actually agreement is quite good. The URA predicted number and the destructive number are very, very tight. There is a tight correlation.

This is Kevlar epoxy. Again it is  $\pm 2\%$ .

Bhe Gloria, can you give us the resin content?

Ma For the glass epoxy, it ranges from  $32$  to  $41\%$ . So the mean would be about  $37\%$ , so if you want to look at the coefficient of variation, it is actually small, about  $0.2$ .

We have demonstrated that the repeatability in the measurement technique is quite good and your reproducibility is also quite good, because you, since you are comparing it back to destructives. It shows we are well within the acceptable standards. We have a pretty accurate way of doing these measurements.

That summarized the round robin. This will be written up and published in the ASTM literature, the round robin results, plus the draft document. There is a draft document out there that is going to the subcommittee ballot. I wanted to touch on some of the things that we are doing that I mentioned before. We have developed the high temperature version of this instrument, because of the ablative materials. We started out, oh, 18 months to 2 years ago, looking into ablative materials and we couldn't get good correlations. We looked at velocity at that time. However, with the prepreg samples, there were differing amounts of air, so we started looking at developing a high temperature version of this instrument. We have a high temperature version that operates up to 400°F and what we did was look at several things.

I have some preliminary consolidation characteristics on the Fiberite ablative prepreg. We also started looking at other measurements that could be coupled with fiber/resin ratio. We could look at the how characteristics of these materials in addition to doing the fiber/resin ratio at elevated temperature. Here is a profile of the prepreg that we have and this shows that within the first 40 seconds, you have gone down to what we call the fiber compression. This is at the cure temperature and 150 psi. We cannot compress this anymore because of the load bearing resistance of the fiber. Here you have the rate of change of the thickness which you can see. What we propose, or what we are currently looking at the rate change is after the optimum consolidation as flow characteristics. We are currently developing a standard test method which will undergo a round robin to look at this technique. This is a summary of the measurement at 3 different pressures, 100, 125 and 150 psi and these are the three sets of characteristics. On the thickness measurement, they look different as the function of time, but if you look at the rate of change at the three different pressures, they are on top of one another, and there is a linear portion which means optimum consolidation occurs somewhere around here. The final thickness here, the ratio, this is taking the thickness at the optimum consolidation point, and if you take this and the final thickness of the prepreg at the end of three minutes, which is thickness of the fibers you will see they are quite consistent.

Beckley Gloria, is heat involved in this here?

Ma Heat? Yes. These are done at cure temperature.

Beckley So they are done at 250 and you are going, effectively, to a cure state.

Ma No, this is going very quick. You put it in and the samples are very thin so within the first minute or so, the sample is at that temperature, so you are not going to cure for this short period of time. If it was there for half an hour, then it would begin to cure. I have some actual samples that I will pass around.

Beckley The thickness is in centimeters. I just don't recognize 0.15 centimeters as the thickness of 7781 prepreg.

Ma This is the multi-ply material.

Beckley Then you have divided it out, then, the thickness of ply?

Ma No. This is total thickness, I believe.



Beckley One cured ply should be about .009 and I have this at about 6.2, so I don't understand what that number is yet.

Ma This number here is thickness in centimeters. I think this is the total thickness of the sample, rather than, here's the material that we measured. You can see how the resin has flowed out and this is left on the transducer for about ½ hour. I could find out for you, Don.

Thomas Gloria, does this represent five or six plies of resin?

Ma Yes.

Thomas Is that what this represents?

Ma Five or six plies, yes. We do it anywhere between 6 to 8 plies. That is what we are able to do with the prepreg.

Thomas You only measure thickness or do you look at density, or just pure thickness.

Ma This particular method, we don't look at densities. We have the capability to do ultrasonic which would cover density. If we measure the thickness and density at the same time on the same sample, we would get a lot of information. That is precisely the kind of technique that we want to propose to you use on the ablative material, to take these simultaneous measurements and add ultrasonic information. You could use more than one ultrasonic probe. You can use longitudinal waves and shear waves. I have a Ph.D. in wave propagation that is an expert in this field.

Thomas Back to the temperature. Were the measurements taken at 250.

Ma The sample was kept at 250° at the time, all that time, for the whole duration of the measurement. These measurements were taken every second simultaneously, so you have a lot of data points.

Kirkhart Maybe I am missing something here, but supposing I had a URA 2000 how does it interpret my manufacturing data?

Ma Well, you have to establish a data base first to interpret what it means. For example, I could give you some examples, TRW is taking that information and they have generated the data base on their material, resins content, and thickness per ply, so when they have laid up the part, before they cure it, before they put it in the autoclave, they cut off a piece and measure thickness and they also want to measure resin content. This will tell them that if they don't get the right thickness per ply and the resin content, they need to do something about the bleed schedule. They need to make a change. This will help them reduce scrap in a manufacturing environment. You will want to scan the whole part.

Larson Looking at a real part where we know that the variations in bulk density range from 75- 85 %, how does this affect results?

Ma Are you talking about fiber/resin ratio?

Larson That's right.

Ma The density fluctuation will come into play, but it is a matter of the difference between the density of the resin and the fiber. Some of these differences you see here in a typical calibration curve, where the perfect fit line is here and you have measurements that are fluctuating here are due to these differences in density and fiber area weight. What you are doing is a statistical fit with your

averages and generating this based on the mean number. When you are actually measuring it, it depends on, you know most of the time, this difference would be normal. You could derive theoretical relationships on the density and how it transfers out.

Larson You could actually determine then what the density range contributing factors are to the fiber/resin ratio.

Ma Especially if you come into using more than one probe. For example, if you use shear wave propagation, the shear wave goes in this direction and the longitudinal goes in this direction. This is very sensitive to density. The amount of fiber as well as the resin/filler ratio, that is what we have proposed to do with the ablative material. We have made a proposal to the committee and NASA to really look at this. Currently we only use one mode of propagation, but if you do simultaneous propagation at high temperature, you can probably look at that. You could monitor this and take it through a cure cycle using this high temperature version. One of the ideas in presenting some of these preliminary results to you is get some feedback as to what the committee feels are the directions that they would like for us to concentrate on.

The other thing that I haven't discussed is fiber wetout. We talked about the air entrapped. After you consolidate the sample, after optimum consolidation, if you cannot get the air out at that point, that is what we define as fiber wetout. This is an experiment that we did with Fiberite where they actually changed the process variables. This is the graphite epoxy. I don't remember the exact material. They changed the process variables to give different degrees of fiber wetout. The degree of fiber wetout was measured and they gave us all the sample numbers and you can see just looking at velocity, the fastest has the least amount of air and the slowest has the most amount of air. If you have more wetout, that would mean less air. We are in the process of fine tuning this technique and we need to work with suppliers. This is something that we have a technician working on.

DeVane Just to clarify what you are saying. The ultrasonic data there, the curves, are on some uncured prepreg. For symmetry data from the cured....

Ma These are not done, these are on the same roll, and I don't know how they generate the data. Fiberite generated it. I can find out for sure from Fiberite.

Ismail Gloria, all of your plots look the same to me, except they are just displaced by y values at the beginning. In other words, you can have all these superimposed on each other and with a certain y value in the beginning. Am I right on this? These would all fit on top of each other just by playing with the y value.

Ma No. These are velocity measurements as a function of time of consolidation at the same conditions. This ultrasonic velocity is two measurements. It is a thickness and time of flight measurement. This is an absolute measurement on this sample. I don't really understand what you mean by playing with the y value.

Ismail The only difference between this plot and the others is at the beginning of the plot. Take the top one. Let's say we displace the whole curve down to 2.4 and the whole thing, you drop it down to the bottom. Make it start at 2.45. Now wouldn't you expect it to end up with number 8. Just superimpose it on 7, it looks like....

Ma I haven't done that. Let me tell you how these were made. These prepreps were all consolidated and then we looked at the time of flight and ultrasonic characteristics at that point and generate

this. These samples were continuously sampled at various times. You are actually measuring a set of parameters. If you don't consistently have a way of reproducing a reproducible state, you could be comparing different things, you are constantly changing, the prepreg is being changed, so the velocity will change. You need the optimum consolidation point so that all the air has been removed.

Hall                   Gentlemen, we are losing time for the rest of our afternoon. It is very interesting and I see sparks of interest. I suggest that you get with Gloria this afternoon or tonight. We have to move on because we have others on the agenda.

Pinoli               Our next topic is to look at the test accuracy and precision of carbon assay data that has been generated in industry. Our major concerns are concerning certain vagueness that we have picked up on with regards to the CR-12 and CHN-600 operations. Many of the specifications in use are geared for the old train method of CO and CO<sub>2</sub> for adsorption for measuring carbon content. There is very little guidance for LECO operational standardization. Are all of the LECO models acceptable? How about specimen preparation? Factors like that aren't very well defined. It turns out that two of our major suppliers of carbon fabric in the industry use LECO equipment. Myles, at Amoco, has chosen not to use the LECO, but two-thirds of the data available has been generated with the LECO apparatus. I am concerned we have not reviewed these issues ourselves, nor with LECO, as to what is the best procedure. Dennis Lawrenz is here from LECO and he talk a little bit about the apparatus function and procedures for both the CR-12 and the CHN-600. In addition he may discuss some new equipment LECO has under study. We have just concluded something like 72 carbon assay tests back at their facility at Michigan and I'll present some of that data after Dennis has concluded. Hopefully when we are done, I would like some recommendations on operational procedures for the equipment.

Lawrenz            Good afternoon, everyone. I am grateful for the invitation on the behalf of LECO Corporation. I did bring a side kick with me today, Mr. Larry O'Brien. Larry is the Instrument Development Director for LECO Corporation. Both Larry and I have been there for several years and the reason behind having Larry join me is he is directly involved with the development of the instrumentation, not only past instrumentation but also future instruments.

The two instruments that we have in question are the CR-12 and the CHN-600. What I wanted to do is just give you a quick background of the two instruments, a little bit on the original reason behind the development of these instruments was.

First, the CHN-600 was designed primarily for the coal analysis and also for oil. In other words, our designer was to come up with a system that would use a macro sample to do not only carbon, but hydrogen and nitrogen simultaneously. Therefore, we came up with a unique system whereby we could combust up to 200 mg of sample in pure oxygen and measure carbon, hydrogen and nitrogen simultaneously in less than four minutes.

The CR-12 came about sort of as a sideline to our sulphur determinator. We had a great need for macro sulphur analyzer for the coal industry. We developed the infrared SC-132 series which measured sulphur in things like coal, oil and coke. The CR-12 basically uses that same concept and we measure carbon only, although the market there at that time was really for soils and primarily inorganic geological samples and that sort of thing. It wasn't designed originally for to do pure carbon.

This little handout I have given you here is just some information compiled that I took out of some of the stuff from years back. By the way this technology was developed around the late 70s, early

80s and since then we have come up with some new and what we feel is quite varied equipment, but we won't get into that right away.

If you will turn the first page, you will notice a little flow diagram. It is kind of a simplistic flow. What we have is a pure oxygen source. We have a U-tube, a U-tube combustion system whereby an encapsulated sample is automatically dropped into a combustion temperature zone of 950°C. The sample is normally encapsulated in either a tin capsule or tin foil. When the tin ignites, the sample burns in pure oxygen and the products of combustion would be primarily CO<sub>2</sub> and we have sulphur, obviously, sulphur oxide. Hydrogen would form water vapor and nitrogen would come off as elemental nitrogen or NOX. These gases are taken to the secondary combustion side which is again held at 950 and what we have in there in the CHN-600 is a ----- which is basically calcium oxide. The purpose of the calcium oxide is to scrub off the oxides of sulphur. The reason we want to do that is, especially with coal when you have high sulphurs, is if we didn't scrub off that sulphur dioxide quickly enough and allow that to pass along with the moisture, eventually we would form sulphurous or sulfuric acid and we don't want to do that. We scrub off the sulphur at that point. The gases are then being passed through both the H<sub>2</sub>O IR cell and the CO<sub>2</sub> IR cell. These two individual devices are solid state single chamber cells and we are doing this to monitor the combustion. We are not measuring the gases at this point. We are monitoring the combustion. The gases are then collected in this 6 liter ----- which is just a glass cylinder that has a sliding piston. The gases are collected and after a short mixing time, we then take a plot of this gas mixture and we ----- it into a helium carrier gas and this is to take care of the measurement for nitrogen by thermal conductivity. We then back fill the CO<sub>2</sub> and the H<sub>2</sub>O IR cells to measure the carbon and hydrogen. This is all going on simultaneously. Obviously for your purposes, we are interested in only in the carbon. With the limitations of that, the temperature of the furnace, 950°C, is basically designed to meet the coal and oil folks needs. The infrared cells are not used on an ongoing integration, so there, we basically have to collect all the gas. Now if we fill that ballast volume up prior to getting the sample completely burned, we end up with what we call a C-burn incomplete or it might be a Hydrogen-burn incomplete. In other words the instrument would tell us that we haven't completely burned everything off. You have filled this ballast volume up, so we have a problem. In other words, you are going to have a poor recovery. What happened, too, is if you try to run to large of a sample or a sample that is somewhat resistant to combustion such as a graphite crystalline carbon, it will not completely combust in the time necessary. What we allow you to do is to control the flow rate into the combustion system with by the amount of gas we dose into that system. In other words, control the rate at which the gas of the ballast volume itself would go up. If we use the lowest flow rate, the ballast volume would fill up at the slowest rate obviously and take the longest time to burn. You may be starved for oxygen at the front end. We divided this up into three flow rates and we usually use 7 which is our maximum flow for 20 seconds and then we would drop it to 4 for 20 seconds and then a flow rate of 3 to the end. Now what the instrument does by monitoring these two cells here, if the system is, you see there is no more carbon coming over or hydrogen, it actually goes to the highest flow rate. That is the basic concept there.

Pinoli Is that built in to the CHN-600?

Lawrenz Yes, this is all built in. Now this is switched over to the combustion CR-12 system. This a real simplified flow diagram of that. We have an open end combustion tube. It is a ceramic tube. In the case of the 600, the CHN-600, we use a quartz tube. At 950 the quartz works quite fine. On the CR-12, it uses an open end combustion system and one end is closed and this has a liner in there. The liner is primarily to protect the outside of this tube that is made out of aluminum. We then pull the gases through this system all the way over to our IR cells. We actually have what is called a pull and a push system. We have a vacuum pump which you will see down here on the lower part of the IR cell actually pulling the gas from the combustion area and then

pressurizing it through a flow meter and then into the IR cells where we can control the flow at this end. Now what we do on the front end of this open tube is we purge with excess amounts of oxygen so we create basically an oxygen window there so we minimize any influx of outside air. Again the original concept was for sulphur which really had no problem, but carbon since it is a lower level, it would have a problem. The advantages of this system were that we could burn for a given element in a lot less time. In other words, with carbon, here, you can do a carbon analysis on a lot of materials in less than a minute, allowing us to do the temperature, but also the flow rate. We don't have to worry about filling up the ballast volume. What we are doing here is we are actually integrating the amount of carbon dioxide being produced on an ongoing basis. In other words, the thing is being combusted here, carried through the IR cell, monitoring that, measuring that, storing that data in memory and then the analysis prints out the weight percent carbon. Both of the systems, we weighed a pre-weight sample and the weight is entered into the microprocessor. Those are the two basic concepts.

Some of the problems exist in what kind of samples are you going to run in this thing. First of all in the CHN-600 we have been able to run a lot of your compounds, obviously, coal and oil, coke, the graphites which people have been running. Carbon fabrics are something that you run occasionally. It becomes a question of how you handle those materials, how do you weigh them? A lot of those things have been worked out over the years. In the meantime, we have been addressing some of those things in new instrumentation. I think what I wanted to do is indicate to you the two basic systems.

Personally, being involved in the lab for the last 16-17 years at LECO and working a lot of the different instruments, I would recommend or prefer to use a system such as the CR-12 for carbon fabric or graphite versus the CHN-600, if that were the type of material I was going to run routinely, because of a couple of things. One, I have a lot higher temperature to work with. That means I can burn things up more effectively, more efficiently. Number 2 is that it is much easier to weigh a sample. You don't have to try to get into a small capsule area. The crucibles are about 2½ inches long and a good ½ inch wide. You will have much more latitude that way. You can basically reuse these crucibles several times and you don't need an accelerator, so the system becomes one of running a lot of samples and being able to reach the crucibles. It takes about a minute or a minute and a half for the analysis. That is really the type of the system that I would prefer to use. Although the CHN-600 has been used in the past which points out some points that I would recognize. If you are running a material on the CHN-600 and it is not completely combusting with the last parts of the analysis in question, very slow where the instrument has a threshold set where it is looking to see what is coming over from the CO<sub>2</sub> or from the combustion area and you reached quite high of a peak. In other words, if you have a very high carbon peak, you have a maximum rate of carbon delivery to this detector and then it looks at what it sees now and that peak level there was so high so it said there was just a little bit coming through and shuts it off and continue on. Where the CR-12 has a similar system, but we have much more latitude there by -----the temperature we are going to burn a little faster. In our case on the CHN-600 would be made within the instrument specification and get lower recovery on certain materials and even if they are the same carbon level because of their burn characteristics, so it is extremely important that we recognize that or that whoever is operating the system recognizes that.

The other point that has to be made is that we are dealing with, basically in this case, pure carbon. Therefore, we are shooting for 100% and when you are doing that, the weighing of the sample is extremely important. I know that the CR-12 has a built-in balance and the balance was designed for ±1 mg. Obviously, if you are weighing 100 mg sample size and you have a 1 mg weighing error and you are at 100%, you can calculate off quickly what the weighing error is going to be as far as carbon. You can have a relative error of 1% or absolute error of 1%, just by the weighing alone. I think people have to recognize that the weighing of the sample is

extremely important, primarily because of the size of the sample you are dealing with and the amount of carbon. The same thing holds true for the CHN and that is of number one importance.

Another thing on the CR-12 which I think gets overlooked sometimes is the ceramic crucible. The ceramic crucible, by design, is, it weighs about 35-40 grams, okay, and it is a porous material made out of a different type of ceramic so that it can take the thermal shock of going from room temperature to high temperature. One of the things that happens is that it absorbs atmospheric contaminants and also CO<sub>2</sub>. Typically, in an analysis like this we are not worried about ultra-low carbon, but if that crucible has only 1 ppm of carbon contaminant on a weight basis and we are dealing with even a 1 gram sample, you can see that the crucible if it weighs 35 grams, you have 35 micrograms of carbon there. The next crucible may not have much in it. So on that crucible, since you have to weigh the sample into on a room temperature basis, place it in a furnace, go ahead and analyze it. The crucible itself is a concern. That is primarily because the precision that you are looking for. It is not going to affect the overall absolute amount, other than it may bias your numbers, somewhat, depending on that blank, what's in that crucible. Just to give you an idea of that, on a one gram basis or micrograms per gram, I will run "blank" crucibles, say 10 of them, telling the instrument it is a 1 gram sample and this run will be called "blank" analysis. What I will get on there, is I will get numbers from maybe a .001% right on up to .007% on a 1 gram basis, something like that. That would be 10 micrograms to 70 micrograms. That is on a 1 gram sample. If I am running a 0.1 gram sample, what that means is the instrument is going to see numbers that would range from .01 to .07 variability, just on the crucible. That is why it is important. What do we do? We basically take those crucibles and we bake them off in an oven or in the CR-12 itself at 1000° for an hour or 1350° for a couple of minutes and we place it in a desiccator and that will eliminate or reduce greatly that variability due to that aspect. That in conjunction with the weighing of the sample are probably the two most important things you can do with the CR-12 to improve the precision to its maximum capability.

The CHN-600 uses a crucible that is inside the system and is replaceable about every, depending on the type of sample, 50-100 analyses. We are using a little tin cap so that it has virtually no carbon, measurable carbon in it, so that is not really a major problem for us. The CHN-600 would not have that same type of problem associated with it. Again, in normal analysis, as most people look at it, that is not important. I think as you try and get this thing at the best percentage of accuracy, obviously, you have to do those types of things. Those things should be done, if you are really interested in that accuracy.

On the last pages of this I took preheated crucibles in a CR-12, our lab unit which is about 11 years old, and I analyzed some pure graphite. What I did was take some graphite and we outgassed it one our inert gas fusion analyzers at 3000°C in an inert atmosphere. Normally what we do is we ----- gases in a helium environment in one of our fusion analyzers. We took the graphite and let it cool down to room temperature and put it into a bottle. Assuming 100%, and obviously, it is not exactly 100%, but for purpose of combustion or calibration, I did that and then I ran that 10 times and I gave you the results there. The weight varied there from 138 mg to 265 mg. I took another sample which is one that we have had around the lab for many years, BCR coke standard, which was basically a European standard that was done by ----- analysis in the old gravimetric combustion carbon train and there were 17 labs involved with this particular standard and it was certified at 92.58% and it had a range of 91 something to 93% which gives you a little indication of the difference between the labs with the old carbon gravimetric system. Now what I was trying to show you here is what the CR-12 should be capable of as far as precision. Of course the accuracy of any of these systems is directly tied to the accuracy of the standard that we use in them. They have to be calibrated, but what we can do with this on the same type of calibration is I can run things like calcium carbonate which is 12% carbon and get within 11.95 to 12.05, in that range. We can take things like sucrose, 43% carbon and -----

, and all those different things and run them. There is a variety of types of materials that you can run. The same thing can be done on the CHN-600. That is really the type of thing that we could expect. Obviously when you are dealing with the carbon fabric or you are dealing with a non-uniform sample, 100 - 200 mg sample, these particular instruments can give us what we call macrosamples because if you look at a lot of other CHN determinators that only use 1 or 2 mg depending on the application. These particular samples, you should be able to run 100 mg typically.

Pinoli

Do you recommend using the larger sample?

Lawrenz

Yes. On the CHN-600, you have a little problem with that because as I mentioned if you try to run too large a sample, it doesn't all burn up in the time allotted to you. It will issue alarms, left and right. 100 mg or between 75 and 100 mg seems to be the normal sample size you can consume in that type of material. The CR-12, as you saw in the data there, I was running anywhere from 130 right on up to 270 mg and you could easily go on up to 300 mg. Unless you take care in getting the weighing down, your precision is going to be somewhat. Obviously, that accuracy will, too, but what we are able to do is show in the CR-12 that we have more flexibility because you can run a lot larger sample. You are not tied in to fill up any ballast volume on the CR-12 type system. We can actually burn that sample through 10 minutes if we want. You tell the instrument how long we want to burn minimum. We set a comparator level and again looked at the maximum peak to a certain level and we say before you shut this thing off, once it has reached the minimum time, you allow it to burn until this carbon level gets down or the detector gets below a certain level. We have that built in.

That is the two systems there and they are, let me say, they are somewhat different, quite a bit different in the way they combust the sample, but IR detectors, the IR cells themselves, are the same. One integrates the total signal and that is the CR-12. In other words, it starts out with just pure oxygen and as the CO<sub>2</sub> goes through this IR cell, it effectively absorbs the IR energy and that responsive detector is a loss of voltage. That loss of voltage is dependent on how much CO<sub>2</sub> is in there at a given time. Since we know the flow rate and the flow rate and the flow of the CO<sub>2</sub>, we measure that at the actual data points and at the end of the analysis we calculate it out.

The CHN system does not really integrate that over that period of time. What we do is collect all the combustion gases in this big jar and we take that and we take a sample of that and we just squirt it back in the IR cell. What you are measuring is a level ----- between the pure oxygen and the amount of CO<sub>2</sub> in there. Basically it is saying you don't have to integrate this, you can just fill it up and let it equilibrate and it is higher voltage under pure oxygen at 8.5 volts and the voltage when I put this gas with the carbon dioxide in it, it drops down to 6 volts and we measure that difference and that is basically a straight forward analysis. That has taken about 3 or 4 minutes to collect this gas and equilibrate it and bring it back to the system and that is the length of determination. The CR-12 is combustion, measurement and -----.

That is really the crux of the different systems and they are totally different. We are looking at different temperatures, 950 on one and 1350 on the other. You can run the CR-12 on 950°, if you prefer, but it would take a lot longer to burn at that temperature, probably about 30 - 40 seconds. Again those things that we have looked at, we prefer to run the higher temperature because we get more efficient combustion. We don't want a sample if it is a very volatile sample, say a coal, sometimes. You could have a problem of the sample blowing out the crucible. The same thing can happen on the CR-12 if you have a real light fiber material and a ceramic lance that sets right above the crucible and if you inject that lance too soon or too high of a pressure, you can actually blow some of your material out and if it sets in the back of the combustion tube, it would just burn a lot slower. The back end of the CR-12 combustion tube is about 1000°.

I have a few brochures to pass out so that you will have a picture of both instruments. The CR-12 family is a bench top model - the electronics, the combustion system, and the furnace. The CHN-600 and 800 are floor units. I didn't bring a whole bunch of those. I didn't want to try and act like a salesman, because I am not a salesman, but I would like to give you an idea of what we have.

Pinoli           How do recommend we handle moisture in the fiber. We are dealing with activated carbons which significant amounts of have moisture in them. Would you prefer that we dry the sample before we run it or do we calculate the amount of moisture in the sample and plug that into the calculation?

Lawrenz        You can do it either way. Technically it should work either way. What we have done in the case of coal, we normally dry it before we run it or coke. We may do that, but in certain cases, especially in carbons, you have to be careful with that type of deal with all the hydrocarbons you could actually drive off in the drying process. In a carbon fabric like this, in a coke sample, graphites, we just dry them right before we run them. In the case of your sample, depending on the moisture amount, that is a problem. If you are dealing with 0.1%, obviously, in a 100% weight, 0.1% is going to affect it. I would recommend drying the sample at 105°C for at least an hour. That is an old standard ASTM method. We use it for carbon depending on the moisture level. Now we have an instrument that will be able to determine, or should be able to determine moisture. We have not looked at that one, the RT-412. The RT-412 uses the resistance furnace concept which is another in our line of our carbon and moisture instruments, but it is designed for another purpose of being able to measure directly moisture by infrared and not be weight loss. In other words, you heat the sample up. Say in a case of a carbon fabric, you heat it up, start it out at room temperature and take it up to maybe 105°C and hold it there for a while or just ramp it all the way up to 1000 and completely burn it up. For moisture we would normally just use a nitrogen environment, therefore we would get moisture as H<sub>2</sub>O and we wouldn't be picking up combustion hydrogen products. Obviously it wouldn't burn the carbon up and if you have CO<sub>2</sub> absorbing in your samples to measure. That is a technique we have used for another piece of instrumentation. We normally don't promote that instrument for ---carbon, like in graphite, because what it was designed for was to do the low to high levels and maybe midrange of carbons in inorganic samples with organic ----- on it, but also in geological samples that had moisture not only inherent in absorbed water, but also water crystallization. There is also some controversy there whether or not you have water crystallization in the structure. I know with graphite we have found, especially for our work that we do part per million levels of oxygen and hydrogen in our graphite crucibles is that we have a problem with the carbon that is activated actually giving us water or small amounts are being baked off at the ultra high temperatures. In the case of this, it shouldn't really affect it that much, but we can dry a sample at 105 and as soon as they react with the air, they pick up a certain amount. I would say that determine how much moisture is in there and if it is consistent. The BCR coke called for not drying the sample, but letting it equilibrate to the atmosphere so it is pretty much a calcide product so it doesn't really react or absorb moisture.

This is the new design of the CR-12 upgrade. We have added some automation to it. This is for our customers who don't want to stand there and put one sample in there. We put an auto----- which can actually weigh up to 36 samples ahead of time and let it run. We have also improved the resistance furnace to allow us to run up to 1450°C quite readily. We changed the combustion tube to be more durable and we went to a concentric combustion system and this has improved the performance of the combustion tubes dramatically. We have gone to a 16 bit processor. We also have a full blown computer in the system now and you can see it has the touch screen display and the whole nine yards but one of the things that these new systems will do and again, we are on our line of new series of instruments, a new generation, is that it not only improves the short



term precision, but we found that with the advent of the new processor that we have been able to improve the medium and long term precision. One of the problems you have even with the CR-12, if you calibrate it in the morning, it can drift and all those things being considered, they drift a little bit and so you will see this calibration or small calibration change. If you have 10% or 5% carbon, it is not even noticeable, but when you are at 100% carbon and you start to recalibrate, what is it going to be like when I ran 100% carbon sample on that 5 hours from now? You will see a little shift with that type of a system and the CHN is somewhat prone to the same thing. With this new electronics we are able to minimize that. Resolution has been improved and with that we are able to get better precision and accuracy. These systems are out now. We have sold, the primary market on this one, the sulphur version which has sold to the coal industry and some of the graphite producers. We have a carbon - sulphur version simultaneous now. This is the first time we have done that. We can run your graphite or your carbon for not only sulphur but also for carbon simultaneously. We have a carbon only version which is the CR-412. In this brochure, you will see the combustion system. The computer has allowed us to also utilize a little different way of calibrating the system. Right now the CR-12 and the CHN work, is you run a series of samples and you usually have to run one particular material and then you just calibrate that to that material. What this particular new system will allow us to do is you can run 5, 10, or 20 different materials or different standards and do a multi-standard calibration curve. You can do a linear fix calibration which is what we have on the CHN and the CR-12. In other words, a single point but the cells have been adjusted by gas dosing at the factory. On the new system you can run this multistandard calibration curve in a linear fix or in a non-linear type of regression program. It just depends on what you want to do. You can also add a standard weight to these things, so the technology is taking quite a lead from the way we were able to do this. It has a 20 megabyte hard card and all the good stuff where you can actually store up to 32,000 data points on these systems. You can do statistical process control. In other words, if you are running something and you are running it through out the day, you can run your control standard. Set the control limit and it tell you when you are out of control. All of these things are built-in functions with this type of system. The contents are the same. They have been targeted for other markets, but the graphite, carbon, pure carbon we have run and it should work quite nicely. We are actually 10 years down the road from when the CR-12 and the CHN-600, and we still market those machines, we have taken a leap ahead with some of the technology.

Peasley                      What is the stated accuracy on the new improvements?

Lawrenz                    On the carbon, we have again kept to the  $\pm 1\%$  of the accuracy. I don't like to use the term accuracy as much as I do precision. Accuracy to me is only as accurate as the standard that was put in. We can determine accuracy by gas dosing and this is what we have done. We have taken known volumes of gas and dose it into these systems and that is how we calculate out the accuracy. When this brochure was put out, or when this was first introduced, since we just brought this out this spring, we kept the 1%, but based on the data that we have done, we have not only improved that range capability, but we have improved the precision and accuracy. I like precision. Again we did some data on this and I think the best thing we can do is take some of these products that you have and run, not just a couple or three numbers, but run it 10 times and then let the thing set, have different operators, different days like in a normal round robin and compile all that data. In terms of short term performance, I think you probably won't see a real big improvement on short term. By that I mean that if you run 10 in a row, this instrument will be as good or just slightly better than the CR-12 but if I don't do anything different between the two units and just run the CR-412 versus the CR-12, you will notice that the CR-12 will float around a little bit where the CR-412 will be much more stable and you won't have to re-correct and recalibrate. The CHN-600 has the same type of a processor as the CR-12, so it is very comparable to it. The CHN-600 has one advantage in that the IR cells are in an oven. Since the IR cells are in an oven, so it is above ambient conditions, so it isn't affected by room temperature

and we also made corrections for barometric pressure there. The CR-12 does not have that. It is basically has a chamber below the combustion area but it is not at a controlled temperature environment. The CR-412, we have gone to a controlled temperature environment, plus we have gone to a better monitoring of the system. We have improved in these areas, too. The one thing I ought to mention, too. One of the problems you will have because of the open ended tube is sometimes the air getting into the system on the CR-12 and that would sometimes cause some variability problems, although typically it is not a major problem. The CR-412 series or the SC-444 series, we have put an automatic door on there where the door is actually closed, sealing off, or partially sealing the furnace, keeping a positive pressure in the tube and it's open when the sample is slid in and closed right after that. That is to prevent during the analysis, small amounts of air getting into the system.

Pinoli Dennis, to my understanding of how these devices operates, chemisorbed oxygen will not influence the actual measurement of carbon content.

Lawrenz Typically, yes. Again you would have to say that you have a problem, in other words, we talked about if you use a standard and your standard has 0.5% moisture in it....

Pinoli No, I am talking about chemisorbed oxygen which has reacted to carbon atoms.

Lawrenz Oh, okay.

Pinoli Are you testing carbon specimens with 19 atomic percent oxygen on the surface. That oxygen is going to come through as CO or CO<sub>2</sub> and isn't going to affect the analysis. Quantitatively, the carbon assay value determined by the LECO apparatus is accurate.

Lawrenz What we do in our analysis and again, we are dealing with graphites, we measure the actual oxygen content by inert gas fusion and in inert gas fusion what you are doing is taking that sample and heating it in a helium or argon carrier gas and up to 3000°C and oxygen in there reacts with the carbon. We use a graphite crucible and then we can actually produce CO in that reaction and we convert the CO<sub>2</sub> measured by the same type of infrared system or we can measure the CO direct. Typically we deal with anywhere from 50 - 100 ppm of oxygen and in petroleum products, petroleum cokes, you are much higher than that obviously. When you have water involved, see that system doesn't care either if it's H<sub>2</sub>O or oxygen. The same thing holds true for other products in there, like sulphur. Even though you bake a sample off, you may not reduce all the sulphur. Typically we will see, if you look at some of these, even the pure graphite that we are supposed to have and completely heat up to 3000°, we will still see 30 - 50 ppm of sulphur left in there.

Ismail Do you have an instrument that can determine oxygen, nitrogen, sulphur and hydrogen in carbon? I think that is what you need, Pat. I think you are coming at it backwards. In other words, if you try to determine the carbon, the gentleman allows himself 1%, and if you give him another 1%, then you are at ±2% out of 94, so if your technician says 96 is accepted or his says 92, I think what you really want to do, Pat, is determine the remaining, or the balance which is not carbon there. That balance to me would be oxygen, hydrogen, nitrogen, sulphur. I can't think of anything else. If you do a good job on that, you can determine carbon.

Pinoli You are bound and determined to bankrupt us, aren't you? We are trying to keep things simple here.

Ismail Just by listening to the gentleman, you cannot get any better than ±1%. That is the best you can do and if you tell me the difference between you and Myles is 2 - 3%, to me that is acceptable. You cannot push the instrument any further beyond that and expect the whole community to give

the same number. If the whole group runs it at  $\pm 2 - 3 \%$ , then I would say they are doing a good job. Therefore, I don't see where you would want to push the instrument to the limits. There are some limitations.

Pinoli Before we get to much further into that, I think what we want to do is clean up our act as best we can. Let's address the carbon calibration media and then address the carbon test preparation procedure. Let's see if these factors will help us get reproducibility. Don't you agree, Dennis? We also need to determine if we give adequate time for combustion. This could be one big error factor. Let's try to clean up each of these aspects. Maybe if all these factors don't help, we are just trying to get more out of the apparatus than we should expect.

Ismail I am sure that Dennis can give you damn good numbers because he has been working with the equipment for fifteen years.

Lawrenz There should be, the ability of these instruments at that level, because of all the parameters that come in, the weighing, and the crucible and the instrument itself. Right now it is at about 1%. You saw with the CR-12 under ideal conditions in the lab, I am able to run about 0.25 standard deviation. If you take and multiply that by 3 for  $3\sigma$ , you are right at that 1%. But if you take, and you are able to run enough data points statistically that you are able to the differences, I think what we have to determine, there should be no reason for a person on a LECO CHN 92% and somebody else to get 95%. That really shouldn't happen. Round robins that I have seen have been closer than that and in some cases if you repeated that, it may reverse itself. I think there are some things we can do. If you are going to try to determine the difference between 99.99 and 100, there is no way. The point about the other determinations, we can do, to answer your question on the oxygen. Yes we can do oxygen and nitrogen simultaneously on the product that you have. We use, basically, a graphite crucible and it is an inert gas fusion system. We are going to be measuring oxygen and nitrogen down to the ppm level. The graphite we run because of the density of that, we can run half gram samples. Typically on this carbon fiber we are lucky to get a 100 milligram sample. We still should be able to see the difference between 5 ppm and 10 ppm of oxygen, whole oxygen and nitrogen and the other gas, hydrogen, we will get that out in another system, because it is done a little differently, we separate the hydrogen, so we can do that. Of course right now we are talking about a close to a \$55,000 - \$60,000 instrument to get that type of performance. Again that was targeted for the steel industry. As far as sulphur, we could do carbon and sulphur simultaneously or sulphur by itself. Sulphur and graphite, the kind of stuff we run, we are down to around  $\pm 5$  ppm, so you should be able to tell the sulphur to a very low level. You add those others along with the carbon and you should come up real close to 100%. If you really look at it, just like on a typical C, H, and N, the H and the N, for instance, that you are seeing there with the size sample that you have are really below the catch limit or at the catch limit, so those numbers you see on the C, H, N are designed for doing weight percent. It is not easy to do all at once. We can do oxygen and nitrogen simultaneously. We can do hydrogen by itself and carbon and sulphur simultaneously with the macro sample. We have C, H, N, S simultaneous systems, but they are for 2 milligram samples and pure compounds. That is really not adequate for this.

Pinoli Dennis, on calibration - the easiest material to use for calibration is simply one that is high in purity. WCA fabric is a real good example. It is heat treated above  $2500^{\circ}\text{C}$  and must be of very high purity. If you are going to do single point calibration, why would you want to use any other carbons than something of a extremely high reproducibility and a known factor of 100%? Why would you want to do something like the 96% that has a variation spread?

Lawrenz Well, there normally isn't except that if you are looking for a certified standard. We make instruments, there is a certified National Bureau Standard out there and people want to here that

NBS or NIST when they call in their order. They say this is a good, round robin sample. In other words, it is well characterized and taken all these, but as you can see in a BCR standard, that is using the old -----metric, combustion gravimetric method where they combusted it in a carbon train and they did both hydrogen and carbon on that sample with that type of system. You get a variability on the carbon between labs, 91 to 93%. That was with the supposedly the -----metric system. There is no calibration in that at all. It is just a gravimetric with calibrated balance. I would recommend a very pure carbon compound. Now again, if this point is around 100% why should I run 50%, or vice versa? What you have to remember is that even though we are at 100%, what we are dealing with is milligrams of carbon in that, how much CO<sub>2</sub> is being produced? If I have a 100 milligrams of 100% sample and 100 milligrams testing for carbon, I can burn up that much. If I have 50 milligrams, obviously, it is half as much. Well, if I take 150 milligrams, it is 50 more. That is why in the newer systems, we actually show you milligrams of carbon and milligrams of salt per second that are being delivered and also total milligrams. You can see how to calculate it that way, instead of saying percent. People say I have a 50% sample, but I am burning 100% carbon. Well, if I take 200 milligrams of a 50% sample and then that is the same amount of carbon as 100 milligrams of a 100% sample. You just take the amount of carbon and multiply by the sample weight, and that is really the amount of carbon. To check linearity, what would I do? I would take a pure compound. That is the best way to do it and use fractional weights. We take 20 milligrams, 30, 40, 50 milligrams of sample and we can calculate it out and the leave the weight compensator at one gram, so it is doing milligrams.

Pinoli            Your recommendation is to calibrate for WCA (which is 100%) and cross check wiht something like sucrose of a known carbon content. With the sucrose however, how do you deal with moisture?

Lawrenz        No. There is not enough moisture in that, typically, to worry about, but again this is a situation that you don't have to that. I think what I, one of the things that I worry about, was the carbon. You may calibrate with one that is 100% and all of a sudden you wind up with 101%. The one that was 101% was probably due to the fact that what we done we biased our calibration up because the combustion was good on this sample, but not as good on the other sample or vice versa. Do you see what I mean? That is where you have to be real careful. By running different types of compounds, in other words, carbon black or lamp black, that versus graphite, theoretically they should come in to the same, real close to the same calibration and they do, but they burn quite differently because the amorphous carbon burns much quicker. I would suggest a pure compound, in this case, since you deal with carbon, if you can find a pure form of carbon, then that would be the ideal thing. Then you have to establish what is the precision on that, short term, long term, relative accuracy. When you calibrate to that, then you can start out on a small scale and take selected samples. Everybody runs 100 samples, that means they have to do it over more than one day. We have to be able to control these parameters. They should be run, they should run the test, well what we normally do in the metals business and ASTM, and Larry is involved with coal and D5 analysis. I am more in the metals right now. We run our round robin, where you would protocol, you run your test, Day 1, Day 2, Day 3 and everybody is using the same standards and we do use, a lot of times, more than one standard, even though we calibrate with one standard, we always shoot for all the data points and then you look at the research report. Everything is compiled and you do a preliminary first and then you come out with a better protocol. I think that the biggest thing you are going to have to do is get a better standard. Get something that everyone is agreeing on, for instance a sample that is ideal, pure compound that doesn't oxidize readily. By the way, I did run on this calibration, we didn't have a lot of your sample. I had enough to run 1 analysis on just after I calibrated the CR-12 and it averaged 100%. This sample I got 100.2% on your sample just on one analysis. The reason that I put that BCR standard in there was to give you an idea that the difference is a carbon based material, but it is a certified sample done by round robin analysis and just to give you an idea of the percentage of

accuracy. One other thing we have to be careful of is that you have to, if you only pick one standard and then say you get 100% and this guy is only getting 98%. Maybe this guy had bad combustion or a leak in the system, then you go ahead and run something that is 92% and then that might be 95%. It is a bias error, but it can also be differences in combustibility, so it is always good to maybe have 100%, but to have a check sample, something a lower level which you may run into in the process. Another question is now often you should calibrate. In these systems with our protocol, you calibrate for use, you run after every 10 samples, every 10 analyses, we run a standard. That has to be within a predetermined limit and then we continue on. If not, we find out what is wrong and then try to recalibrate. This is done in our quality assurance program. It is a little bit more difficult obviously, when you have 100% samples, you have to know the standard and what you are doing. We do it more frequently than they ask us to. We don't find a problem, but if we do have a problem, I can't have a whole day's worth of work with a guy and in the middle of the day something shifts on us. We have real tight control on that. That is where the newer systems would be, you would actually get a screen plot of the actual data and you can actually see where your control is and typically, you will see a nice scatter. We can do the same thing on the CR-12...

Pinoli            On these, you'll have the same trouble. We don't want to spend the whole day testing and find out we have a problem at day's end.

Ismail            Pat, I want to tell you that it is very hard to find a standard carbonation material with 96% carbon and 4% junk. That is very hard to find.

Pinoli            Let me read you a describing the procedure used on some data provided:

"The LECO carbon analyzer was first calibrated with a standard coal sample, which is coke, traceable to NBS. (I think this is about 95% carbon assay) Then the WCA fabric was analyzed 6 times by 2 technicians. The average value was then used to calibrate, used as calibration standards for the fabric, and the yarn samples will be tested." Does that mean that initially you calibrated with a coke and then he ran WCA fabric (By the way, WCA came in at 99.1 and 91.2) after which, did he push a calibration button on the CR-12 to recalibrate up to this higher level to change it? The average value would then be used as the calibration standard.

Rubin            Yes that is what he did.

Pinoli            He pushed a button for calibration then, so that in essence then removed the previous calibration that was in there for the coke. Is that what I read?

Rubin            That is what I read.

Pinoli            Okay.

Lawrenz           What you are doing is calibrating with the coke and then you run your product and it comes in at 99.1 so I use the 99.1 as the calibration of value, so therefore everything I, when I run this, I expect to get 99.1 instead of 100. That is going to bring all of your numbers down accordingly biased and again with the data that you have, if you take the average value of that particular material and you just say 100% divided by the 99.1 and then it is just a linear, so there is no problem with integration or anything, so you are all covered.

Pinoli            So, it would just be a matter of recovering all the data with that conversion factor.

Rubin            Pat, I thought the game plan was the WCA was 100.

Pinoli When they reported out 99.1 and 99.2 for WCA, I said where did that come from? What it suggests to me is they ran their NBS standard for calibration and underestimated the carbon content of WCA fabric.

Williamson You have used the term, 100% graphite. What do you mean by 100% graphite?

Lawrenz I guess it is something that we use as a carbon crucible, okay. It is 99.99% graphite. We use it in our system where we take the rods of highly purified gas and machine them down in to little crucibles. What we did was take the ----, the stuff that was right there in the center of that and outgassed it at 3000°C and let it cool down. We assume that it is not really 100% carbon, but we take the same test for lamp black....

Williamson I am going to ask you a question. You have taken this to 3000°C and still call it carbon?

Lawrenz Again in our business here we run carbides and of course we are using the graphite crucible and we do volatilize some of the product. We also take carbon black. You see in a lot cases we will use a crystalline carbon or amorphous carbon and some of the people that have used instruments say that ----- That is where we get a lot of this. You could actually take a diamond and run it through the system. We can burn diamonds in the CR-12.

Pinoli George, do you have any questions?

Peasley A lot of accuracy things about the reliability of the instrument, beyond what we have covered here.

Pinoli You have had some downtime on your equipment?

Lawrenz What instrument do you have? Is it the CHN or the CR-12?

Peasley The CHN-600.

Lawrenz The CHN-600, we have had some problems over the years. I think we have addressed a lot of them. It is something that, an instrument, because we collect everything, we take the thing apart about once a month and clean it out. The CR-12, you don't really have those problems. Over the years, we have proved that. Right now we are working in another direction and Larry will you respond to that?

O'Brien Well, I think in terms of product development, and I know it doesn't do any good for you if you already have one. One of the things we look at is the response we get and we have a data base of every service call we have ever made on every product. For new product development, the very first thing we do, before we start the new product process, is to identify problem areas and address those. As an instrument manufacturer, I think you always have that kind of dual tug-of-war with how much you are going to do for a past instrument and how much you can do for the next project. Some of the problems have been addressed for the older, one of the best things, I am sure you have already incorporated, is to make sure you follow that recommendation ----. If you are talking about a CHN, for example, I know the ---- is probably not the top priority problem area. We are trying to avoid getting into the product area. I tell you though, there will be a new macro CHN this year, but you didn't hear me say that. I would encourage any of you to continue the conversation with us and the application lab to help work your problems out. We would appreciate the opportunity to work with. I won't mind a phone call.

Lawrenz On the other hand, too, as Larry said, if you want us to work as far as a round robin, we the instruments and the facilities there and we are more than willing to do that. If anyone would like to come up and visit our facility, no problem. We are more than willing to work with you. We have a lot of other areas of concern, obviously, metals and everything else, but we are more than willing to work with any of our customers. As an analyst, I can help in some things as far as techniques go, but instrument to instrument you will have some variability. That one percent that you see in there was done because we took three or four instruments, some may be a little bit better than others, and that is slightly better and some of that is due to combustion and everything else. The balance on that is a really important aspect of this. I think this is overlooked a lot. Even a five place would be best to take care of the nearest fourth place, because if you start messing around with that weight in 100% carbon especially at 70. Okay. Any other questions for me?

Pinoli What I wanted to do now is review where we left off at our last meeting. This series of round robin tests were reported out at the last conference. NBS calibration coke was provided by Tom Paral at Polycarbon for round robin testing at three laboratories. The laboratories were Gene Rubin's, Myles Towne and Tom Paral. The variance is roughly 96, 97, and 95 and based on what we have discussed today. Maybe that's what we should expect from this equipment.

The other previous work that we have done is round robin testing at the three facilities on a series of parametric fabric produced by Polycarbon. In this case we are comparing the vendor certification data with current data generated at three laboratories. Laboratory A is Polycarbon and Laboratory B is Gene Rubin. Laboratory C is Amoco's results. A couple of real outliers came in when we compare 10B data. It originally certified out at 96% or 97%. On this go around, it got 89 or 90%, 95% and 94%. My original feeling was a test procedural problem. I now feel the more likely reason is not procedural but fabric aging. The fabric has chemisorbed about 6 weight % of oxygen since being manufactured.

The standard RSRM fabrics also show signs of aging, originally testing 99.5, 98.3, and now exhibit 96%, this is a 3% difference. This suggests RSRM grad fabric is subject to aging starting from the time of manufacture.

Rubin They are all 96. It may not give you much confidence that there has been a change...

Pinoli The lower values look consistent to me.

Rubin Right.

Pinoli An aging effect showing up in the data is more pronounced in lower carbon assay fabric.

Ismail Pat, I don't see any problem with this data. I see everything is fine and dandy, except the 89.6. Other than that I would say, it is more or less the same. No problem.

Pinoli That is what you should expect. I am glad you said it and I didn't have to express the same point.

Beckley But, Pat, your original feeling was that we want to maybe work in the 99 - 100% range and want to have a lot of assurance of that and right now my understanding would be we can have a 99 carbon and it will occasionally show up as a 98 and put the vendor in a highly rejectable condition over something this simple. I think that is our concern about this, is that we should erect a spec wall that would .....

Pinoli If we are talking about setting a lower limit, say 98%, the aging effect will be much less than current RSRM fabric. However, with the kind of variability we're seeing here, good material could end up being rejectable.

Beckley Myles, just a refresher. WCA never comes out lower than 99. Is that right, but VCK does?

Towne VCK does. WCA ...

Beckley WCA is our state-of-the-art.

Towne Yea.

Rubin Could we have Myles, very quickly, tell us how he is running his carbons, because it is different than what we have heard today.

Towne Okay. We use the carbon-hydrogen train, weighing and typically we run one WCA at the start of the day to make sure that the whole system doesn't have a problem.

Williamson WCA is your standard.

Towne Yes. We just run it to make sure the system doesn't have a problem. It is not a calibration.

Pinoli This is the new data that has just been generated at LECO by their tech service organization. Carbon samples were submitted to LECO for analysis with both devices. We wanted to use the CR-12 and CHN-600 to develop data on the same samples. Dennis tested the samples on random bases. By that I mean, he didn't try to put the samples in any order. The data was just completed and this is our first review. I hope we didn't make any mistakes on data reduction.

In general, the CR-12 and CHN-600 data looks very similar. There is good correlation between test results in both pieces of equipment. In some of the analyses, you may see a little bit of skewness offset on the CHN-600 versus the 12, but that is not a consistent pattern. The previous chart presented values about 96%. The last time we ran this material, the  $\bar{X}$  was in the neighborhood of 96 or 97%. LECO data is now down to 94%. On 10B, we had 89% and 95%. There is still a five percent difference which I don't understand. Now Gene Rubin's data is becoming an outlier. You are at 95 and Amoco is becoming an outlier.

Rubin I've got company.

Rubin How long was this between the time we did it...

Pinoli About a year.

Rubin Had we done it again now, we might have gotten lower numbers.

Pinoli That could very well be. It really makes me wonder if there is a significant aging effect on this material. The LECO results look pretty good as far as standard deviation. The general trends confirm previous round robin results.

Rubin . You are willing to accept the standard deviation being as high as 1/2%?

Pinoli I think so. We have to be realistic.



Thomas Which do you really consider the outlier, Pat? If you go back to the previous page on your blind testing....

Rubin I think the 89 was the outlier on the previous page.

Thomas Right.

Pinoli Now on this page, it's 95.

Rubin I don't know if you can compare the pages based on the fact that they are a year apart.

DeVane If in fact that is the case, then we have to discover what is going on with respect to aging. It seem to be affecting a lot of our numbers in a lot of areas and it is really going to screw us up.

Pinoli We only run the 10B because it represents a product we are concerned about.

Rubin For curiosity, why don't you send us all a sample of the same material LECO just ran and see what we get?

Pinoli All right. We have plenty of material.

Towne These are the same materials that we ran before.

Pinoli Yes.

Towne I think that I still have a few little pieces left.

Pinoli Can you supply the pieces to Gene?

Rubin No, give us all the same.

Pinoli Okay, I will sample the original roll at Lockheed.

Moving on to major program needs. We are going to review ASRM Task 1 material and this gets us more into current activity. What is the new generation need for carbon assay testing? For those that are not familiar ASRM Task I carbon fiber is heat treated to three temperature ranges, low temperature, a standard, and high temperature. Fiber is being processed at Polycarbon and Hitco to similar fiber properties exhibited by a low, standard, and high temperature. Samples of all these materials were sent to the LECO facility in Michigan. Samples of the same fiber was sent to Polycarbon for analysis on their CR-12 and to Hitco to be run on their CHN-600. In light of what Dennis is telling us, a  $\pm 1\%$  test precision will allow all of the data to falls within an acceptable band. When we get to Don's comment that in the real world, we have to set a carbon assay minimum requirement; I was thinking in terms of about a 98% to allow for a  $\pm 1\%$  precision tolerance.

Devane The goal was 99.

Pinoli Minimum is 98.5 for the standard yarn or fabric.

DeVane For the yarn. The fabric was a 99, wasn't it, Pat?

Pinoli I want carbon assay values for yarn and fabric the same. Polycarbon has sent us some that was reported at 97. I hope that is test procedure variance and not product variance.

DeVane Is that run from Polycarbon using that technique you mentioned?

Pinoli This data suggests Polycarbon values are generally slightly higher.

DeVane Is the one where they used WCA...

Pinoli I am not sure how WCA was used. That issue may very well bring all these numbers up a small %.

DeVane In other words, the true number was a bit lower by possibly a percent.

Pinoli No, I think these numbers are low because WCA measured 99.1% at calibration. Discussions with Jim Ferrito indicated he wasn't sure how the WCA calibration affected the results.

Towne If they concluded with WCA, with 99.1% then this was lower.

Pinoli These results should be a little higher.

Towne They weren't running WCA at 100%. It was 99.1

Pinoli Yes, 99.1%.

Towne If they were all somewhat lower on the WCA, they would be somewhat lower than 100% by that same amount. If you take 100 and divide it by 99.1, you would get the factor.

Pinoli If I add 0.8%. This value would now be 97.8% and the value would now go to 98%. If that is the case, we are not nearly as bad off as we thought we were. It still makes you wonder a little bit about trying to use 98.5 as a minimum value.

Upton I think we need something closer to 100% to calibrate with.

Pinoli Is there a consensus on this committee that we would like to adopt WCA for calibration? When I say WCA, I mean WCA or equivalent. I am willing to accept that it is 100% carbon assay.

Beckley I would recommend that the program pick up some WCA and keep it as a standard and dole it out.

Upton I agree.

DeVane What if it ages? We have just been sitting here talking about aging.

Ismail WCA does not age.

Rubin Don said, and he is right, why are the CR-12 standard deviations so much higher than the CHN-600?

Lawrenz I think if you look at all the data we did, I noticed that, and one of the things that they didn't do in the lab was preheat the crucible, but again three data points. I think what we looked at is all the results and the overall standard deviation. The CR-12 and CHN were pretty comparable.

Typically the CHN will have a better blank and I think that is what is showing up. I would suspect, I would like to see, quite frankly, what our CR-412 would do with the new combustion system on that standard that you have and run. What we would normally do is on three different days with different operators, run set data points per day and compile the data and we can include the CHN and do sort of a round robin in our own lab and get some of these data points and then you can look and calculate. When you get down to a few data points, you have a problem. We can project what this thing should be. That is really what you need to accomplish what you want.

Buechler Can it give you that on the WCA?

Lawrenz As I said, we are willing to work with that. No problem, no charge. We can give you hard data on your material based on our three different types of instruments that we have.

Hall One of the advisement tasks that this committee has had on its books for quite a while is to come up with an acceptable method to measure resin advancement. Cindy Upton of Marshall is going to give us an update on a course that she took last week on NMR and how it can be the answer to what we have been looking for, for quite a while. Cindy?

Upton This is some work that I am already familiar with from graduate school, but our application can be quite different from what I am used to doing, so we may be doing some developmental work. I am working on this with Tony Day of Thiokol. He also is experienced in nuclear magnetic resonance spectroscopy. From now on I am going to call it NMR.

What we are going to do is go a little bit into some theory, but I will try to keep it very simple because I want you to get a good feeling for why this going to be a good technique for us to be able to determine a mechanism from the reaction of the cure.

If you remember from quantum mechanics, electrons are considered to spin and some of the purists don't like this argument and in fact in our class they said that instead of thinking of it spinning like a top, what you should do is you should go and get any of Stephen Hawkins' books and read up on his discussion on time-space continuum for electrons. We'll leave that as an exercise.

Pinoli Is that an assignment? Do we have to do that tonight?

Upton Yes, before dinner.

Upton I still like to use the top argument because it is very easy to visualize, but if you think about nuclei spinning, and you put these in a magnetic field, you are going to generate a magnetic moment and the nuclei will behave like a tiny bar magnet. Not all nuclei possess this property and this chart entitled "Nuclei Which Have the Property of Spin", will illustrate where NMR is effective. This just basically goes through and tells you when we can use NMR and when we can't. In this case, when you have a odd mass number and then, up here is the mass number, the spin integral constant,  $I$ , is  $\frac{1}{2}$ . If you have an even mass number, but an odd charge number, then  $I$  would be one. In either of these two cases we would see an NMR signal because of this spin property. However, if you have an even mass number and an even charge number,  $I$  is 0, you don't see the signal. You don't get spin and you don't get an NMR signal. This list is not exhaustive, but from it you can see that to see carbons we have to go with the carbon 13 isotrope probe.

If you take one of those nuclei that I just told you would be suitable for NMR and place it in an external magnetic field, it can align itself one of two ways. As it is spinning in its magnetic field, it can align with the magnetic field. This is the most stable orientation or it can be flipped requiring the input of some energy and go against the field and this is where we look for our NMR signal.

Just to differentiate a little bit between something that you are probably used to in NMR, when you look at IR and UV spectra, you are changing the frequency and you are noting the absorption as you change the frequency and that is how you get the overall spectra. In NMR it is quite different. You are keeping that frequency constant but you are changing that magnetic field. Now at some point the magnetic field is going to be equal to the frequency. Energy is going to be absorbed. The spinning top is going to be spinning and it going to flip and you are going to get a signal. This is called the effective field strength.

This is a very crude drawing of NMR spectra and it is just to give you an idea of basically what we are looking at and if what I just said was all that happened, this is all the NMR signal we could every get. You would have an effective field strength. We would get all the little tops flipping at the same time and you would get one huge peak which would be great, but you wouldn't have any resolution. So how do we get resolution - through absorption of the nuclei at the applied field strength.

Something slightly different happens. This is why NMR can be used as a molecular component elucidation tool. There is a different type of field strength that is very slightly different and very significant. It is applied field strength and it takes into account the particular environment that the nuclei "feel". When you take NMR classes and you learn about how to discern between different atoms in the molecule, they tell you that you are in the molecule when you are sitting on such and such an atom and which nuclei and who are your neighbors. You have the carbon over here, you have a proton over here and that is very important because that is what leads to your signal splitting. You have to know this to know what peaks are where on your spectra, in other words, their unique chemical shifts.

The applied field strength is very unique, very individual for each nuclei in each environment. So it does look around itself and see who its neighbors are and it is those neighboring interactions that places it on a certain place on the graph here. So it might be moved upfield or downfield from its neighbor. That is how we get the resolution, in a nutshell.

Now, obviously, if absolutely everything was different that would be bad, too, because then we would get peaks all over the place and we could never discern Peak A from Peak B, especially if they look quite similar, so if you do have the same chemical environment for a nuclei, it is going to have the same field strength and it is going to absorb at the same place and those are going to be equivalent peaks. See the chart entitled "Equivalent Nuclei". This is to illustrate how this works. I am going to use ethyl chloride as an example first. If you notice, you get two NMR signals and if you look at this methyl group here, it is very obvious that is very different from the methylene group and the chlorine group. This is going to be using protons for our example, using proton NMR here. The protons on this methyl group are different than on this methylene group. The next example is isopropyl chloride. Here if you redraw the center carbon like this showing all four hands to spread out these groups, here you can see that these two methyl groups are indeed the same because they are both seeing a single carbon with a hydrogen and a chlorine attached. When it is written like this, it is a little difficult to see because you might not be able to tell where those bonds are. Here you see the methyl groups are equivalent. Next, using propyl chloride as an example, we can see that none of these are equivalent even though we have two methylene groups that look like identically the same, neither a nor b of this group is seeing the

chlorine, only the methylene group c is next to the chlorine. So, C. has a different environment than b. The point here is that it is very difficult to use any other method that I can think of to differentiate between these two methylene groups. Hopefully you are beginning to see just what level of resolution we can obtain.

Now before we start looking at some NMR that has been gathered, I wanted to take a brief review of the resin. This was gleefully lifted from Dr. Hall's Volume I of his report. This just shows you the different types of compounds that can form from the phenol-formaldehyde reaction in the resin. If you follow the phenol as it is reacted with base, we can either get ortho-methylolphenol or we get the para. These two can go on and form different types of methylene groupings. These methylene groupings are very important in our study because this is one of the most important things we are going to try to qualitatively and quantitatively define in the cure reaction mechanism.

If both of the phenol-formaldehyde are para then we get this type of methylene bridge. If one is ortho and one is para, then we get this type of methylene bridge. If you have a combination of these in the reaction, which is usually what we have, then you are going to get a highly complex product with combinations of these two. In the past, this has messed us up because we haven't been able to differentiate kinetic data. We haven't really been able to tell about the structure of the cross-linked resin. Is it growing in chain length or is it cross-linking and thus becoming more bulky. It is very difficult for us to tell this.

Some preliminary NMR work has been done by Dr. Robert Wardle of Thiokol/Wasatch. These spectra still need some work and I'll explain why, but it does give us an idea on where we are going with this and what we can already see. The first example is a proton NMR and we are looking at the proton in these molecules. What we want to do is measure and compare the aromatic protons from the methylene bridge protons and we can do this in a qualitative and quantitative way. We also want to be able to determine what the solvent is and if it's pure, and also what our catalyst is. You notice, though, in this proton NMR spectra, the aromatic hydrogen here is an unresolved clump. We may not be able to differentiate or resolve these peaks any further. This is a good indication for us that we need to go to C-13 NMR and that is what we are about to do.

Before we look at this plot, I just want to show you that at about 2 ppm is the solvent that was used, d-6 acetone. At about 1.4 ppm is isopropanol, again at about 4 ppm. Now the underlined hydrogens are the ones that are represented by that peak so remember when we talked about different neighboring groups. In this case we can clearly see that the hydrogen attached to the central carbon is very different from the methyl hydrogens. Next, here are the different types of methylene bridges that we talked about and note that one is a para-para linkage and one is the para-ortho linkage. Here at 4.8 ppm is our catalyst peak. The tall lines are the integration peaks and normally underneath the integration peak, you have a value of the area under the curve and that is how you get the quantitative data. You have to be very careful when you integrate because when you take that number as being quantitative, you have to be sure that the spectra has been run correctly. By that I mean, you really can't get an accurate area underneath the peak if the peak is not optimized. We would really want to resolve the areas of the spectra where there are several coinciding peaks better. You can do that several different ways. There are some useful special techniques in NMR. The most common thing to do and what I would do first, is to scan more times. This wasn't scanned very many times. This data was gathered rather quickly and like I said, it is just a first look. Obviously in our development, we are going to try to get these peaks more resolvable.

Bhe

What kind of catalyst are you using?

That is hexamethylenetetramine.

Now one point on this, too. As is the case with IR and UV, there are shifts that are fingerprints for different types of groups. It is the same case here. There are published tables to look up a certain methylene group in a certain environment, it might have already been studied by someone else and it might be in a table, so when you go about looking at these spectra and you are coming in cold and you haven't seen anything on it, frequently what you will do is run an IR and UV on it to try to figure out what region you are looking at and in what area. Then you might go to your NMR peak table and you will look up in there and see what range on the magnetic field sweep scale here and you could find that particular kind of a atom. You don't go into this thing blind and look at it and think that obviously it is this, this and this.

The next example is a carbon 13 NMR spectra and you can tell it looks quite different. We are looking at carbons now, not protons. It all just depends on what kind of compound you have, whether one is better than the other. I always like to run both because you can get good data from either one. In our case though, we had to go to this kind of a spectra to get better resolution and here again, this needs to be scanned several more times. As you can see, we still don't have really good peak resolution, but it is a whole lot better and we can tell a whole lot more about what we had. Here again you can see with the isopropanol, we still have 2 different signals at about 32 ppm and 70 ppm because, look, now we have these carbons that are quite different. At 70 ppm, this central carbon has one hydrogen, and oxygen group and two methyl groups on it and over at 32 ppm we notice these two methyl groups. See the central C-OH group - so the methyls are equivalent. At 42 ppm, we can see the ortho-para linked methylene bridge, and at 48 ppm, the para-para. Downfield at 160 ppm we see the carbons on the aromatic peaks that are connected to the phenol carbons and connected with the alcohol group. At 130-140 ppm is the region of unresolved aromatic carbon peaks and again I am going to show you a spectra in a second that shows a better way to resolve that. Now when you go to integrate these things, you are moving a cursor and so if you are not real careful, and if you don't know what you are doing, you could move the cursor incorrectly and integrate it incorrectly. If you run your spectra several more times and scan it several more times, maybe even overnight like Tony and I did, then these peaks should become more quantitative or more real.

There are different types of NMR spectra you can obtain. The next example is still a carbon 13 spectra. This is a special kind of carbon 13 spectra called DEPT. DEPT stands for distortionless enhancement with proton transfer. What this does is cleans up your spectra for you. In the places that I pointed out a second ago in the other spectra where the five aromatic carbons were still in a clump, you will notice now that we have five peaks. Yes, this could be scanned a few more times, but you can still discern five peaks and that would correspond with the five aromatic carbons on that ring. On this particular type of C13 NMR, the quaternary carbons don't show up. Those are the carbons that have no hydrogen attached. This is how it is cleaning up your spectrum. If it doesn't have a proton attached to it, it will not show up on here. As you see, some of these peaks are inverted, like the catalyst peak and our two bridge peaks are inverted. That is because on a DEPT spectra, the methylene peaks ( $-\text{CH}_2-$ ) are negative. These are the carbons with two protons attached. We can see the catalyst methylene peak are going to be negative to the baseline. The methine ( $-\text{CH}-$ ) peak, which is a carbon with one proton or a methyl ( $\text{CH}_3-$ ) with the carbon and three protons are going to appear as positive peaks. This is just a little exercise in carbon 13 spectroscopy that cleans up our spectra for us and gives us better resolution and it is just a technique, one of those things that you learn.

What can we get out of this? Why is it a good idea? One of the many things that we can determine by NMR study is bond length. Chain growth of ortho and para methylene bridges is very important to us. We can watch this grow as we watch the solvent peak diminish, so we are

actually watching desolvation as we are watching chain growth and cross-linking occur. I mention kinetic information because while you are scanning it, you can keep up with the reaction. We can run the resins through the cure cycle, and take a NMR spectra as strategic points along the way. As the resin solidifies, we can do solid NMR. We can also look at the prepreg. We can get structural information pretty much any time during the cure process. One very exciting thing that I think was talked about in the April issue of Spectroscopy Magazine, Lockheed Research at Palo Alto is studying a magnetic resonance imaging which is sometimes called MRI. MRI is what you hear about in the medical field so often and is when you put a person in a magnetic field and are actually running NMR on a person. When we were in the class, to illustrate the possibilities of the future for MRI, the instructor had a cartoon of a cow inside a magnetic field. Tony Day and I were sitting in class together and looked at each other and said, "rocket nozzle". It is theoretically possible that one could put a rocket nozzle inside a magnetic field and do MRI on the finished rocket nozzle, as a NDE test. That is what I am talking about when I say direct examination of pre- and post-fired materials. We can look at small samples of cured material in a regular NMR. You can look at the material at any time during its lifetime. A different type of NMR probe is used to look at a solution or at a solid. It is considered a normal research tool. It is not something that we will be proposing for an online qualitative analysis, quality assurance instrument, but it would be something that would give us information on the mechanism that would hopefully clear up a lot of our problems, such as the microcracking problem that we are experiencing now. By understanding the phenol to formaldehyde ratio exactly, and understanding the role of the catalyst exactly, and the role of the solvent exactly, then we should be able to know enough about the cure mechanism that at any time to predict certain properties and certain characteristics. This technique will help us understand fundamental properties.

Ismail                   How big is your sample and deep can it penetrate into it? I am talking about the current.

Upton                   Well, generally you work with a very small sample size because you are trying to keep as much of the room inside the instrument for the magnetic field as you can. Obviously, the larger the sample, the less room you are going to have for a magnetic field. There are two different types of tubes that you use for NMR. There are the 10 mm tube and a 5 mm tube and you make a concentrated solution, like the resin or extracted resin, and you have it inside that tube. If it is a solid probe, then you use long slender strips of material with current instrumentation. I am not talking about this MRI business. This is a regular NMR and you are talking about small pieces of fabric like we took up to Virginia to run with us.

Ismail                   You scanned the whole sample?

Upton                   You can. Normally you just look at a small place.

Schmidt                I was wondering why they don't use this technique to determine the chemistry.

Upton                   It is done in a lot of areas. I am a chemist. I am from an organic research background and it was an everyday tool for us. The instrumentation is quite expensive. Marshall wants to buy one, so I priced it at about \$2 million, which includes facilities and then you have to have a dedicated operator because it is very complex and very sophisticated and you are talking about hiring one person to do NMR all the time. We are lucky because Thiokol has a guy who does NMR on propellant. Right now he is not too busy to help us. Sometimes gathering the data takes a long time. Some people cannot stand the kind of time lapse that it takes to run. One of the things that we are trying to do in this study is learn enough so that we can apply what we learn to other test methods. It is not just academia, and it is not just research. We are looking at direct application. However, it is not hard for me to understand why NMR is not a household instrument.

Bhe This is a solution where you dissolve your resin?

Upton Yes, but you can do it neat. You can put it in there with no solvent, too.

Bhe Does the viscosity of the solution have any effect -----?

Upton It depends on how high the viscosity is. If it is very viscous, a lot of times, people will go ahead and lower the temperature and increase the viscosity even more and then run it in the solid phase. The class I went to was the American Chemical Society hands-on class on NMR taught at the Virginia Polytechnic Institute and State University. One of the things that they told us was that with our carbon fabric, we would have to be adding silica to it because, obviously, if we put carbon cloth in a magnetic field and it conducted, we would get crazy signals all over the place. We would much rather develop a technique to look at it in the solid state. You can do solution, you can do solid, we are trying to figure out what is the best way.

Pinoli If you put that into a solution, aren't you going to run into the same problem we have with GPC- only the soluble constituent is analyzed.

Upton Well, we haven't run into any trouble yet. You are physically spinning the sample, too, and so we haven't run into that problem.

Beckley If you have to extract it, Pat, to get into the cell in solution, you have the problem you are citing, but if you have the material already there, then it is going to behave. It is somewhat coincidental, Cindy, but BP Research, which is in Warrensville, has NMR and they are beginning to work with us on identifying the relationship of the IR peaks which we have come to learn and love and even know a little more about with the NMR peaks and I think your track is good and there will be some falling out of it both ways.

Upton Great. That would be wonderful.

McCarthy I can see how this would work, but phenolic resin kind of resins up and if you can't dissolve it anymore, can you still get that?

Upton It doesn't have to be in a solution. You can do solids by NMR.

Beckley What will you do with the filler and the carbon fiber?

Upton Well, you would have to know enough about these characteristics to be able to discern it on the spectra and I think this is where your IR studies would come in because they are not going to shift necessarily, because you have gone from solution to solid. You should be able to still differentiate your resin and your filler if you really understood them. One thing about the solid probe, though, is that you do lose sensitivity. Generally what you do is run for days and days. You know that I was mentioning that you put the sample in a magnetic field, you keep the radio frequency constant, and pulse the sample. You pulse it and it causes that energy to be absorbed and all those little tops flip and then you have to let it totally relax before you pulse it again. If you don't you get that spectra I showed you with all those little peaks that aren't resolved well. This is one reason that our materials take a long time to run because we have to give a long time between each pulse for relaxation. That is why it turned out to be better to let it run overnight. With solid probes, you are already losing some of your sensitivity, so it is better to let solid samples run for a couple of days.



If you don't get the magic spinning angle spinning just right, there is always the danger of the their spinning sideways and that clutters up your spectra and especially the side bands. The spinning side bands is an anomaly that you get when there are inhomogeneities in the magnetic field and in the spinning tube. They are symmetrical about your main peak, but if they form and are eclipsed by another peak, they can throw you off. If you don't see that symmetry, you may not recognize them as being spinning side bands and you go ahead and identify them as something that is not right. That is a danger.

Thomas Cindy, you are talking about the examination of your pre- and post-fired nozzle. Is this with the magnetic field? What is your readout?

Upton Well, like I showed you that very simple diagram or something like this. You know this is basically the magnetic field sweep versus absorbance. It would read just like that, that type of data. Like I said the quantitative part comes in because when these spectra are done correctly, you can then directly measure the area under the peak and so you can get, say a 1, to 2, to 3 ratio of Peak A, Peak B, and Peak C.

Thomas Do you have to have just the ablative part? What form?

Upton Well, for MRI when they do a person, they don't take his brain and look at it. So I am thinking that we should one day be able to look at a rocket nozzle. With current NMR techniques, we would just be looking at the ablative part.

Ismail Are you talking about carbon-carbon composite or carbon-phenolic composites? What do you have in mind?

Upton Carbon-phenolic. I'm sure that, when you get into something that has mostly carbon, you have got so much carbon there, that your spectra is very difficult to resolve - too many of those carbons would be environmentally alike. I don't know what you can gain from it that would be helpful, so I am not saying that we would not be willing to look at carbon-carbon composites. Since we are trying to track the resin cure, then we will be looking at that. Since our resin happens to be a phenol-formaldehyde type resin, then we would be more interested in the carbon-phenolic.

Hall Thanks, Cindy. Next up is Jim Kirkhart to talk about electrical resistivity testing.

Kirkhart The objectives of this work was to determine the variation in method of analyzing or determining electrical resistivity and to look at the variation in test methods and look at the variations between test facilities at Hitco, Polycarbon and Lockheed.

Actually what happened is BP Chemical ran the first series of resistivity tests. The same fiber was sent to Polycarbon and Lockheed and then back again to BP Chemical to make sure the fibers hadn't been damaged. They used the NARC rayon fabric that had a special heat treatment. It started out with an inch and a half long cut here on the fabric about one and a half meters apart. The next step is to take one warp yarn and pull that out to see the alignment of the warp yarn. Then the fill yarns are cut to relieve the pressure on the warps so that they won't be damaged when they're pulled out of the fabric. They pulled out about 15 warp yarns and looked at them under a scope and decided whether or not they had damaged the yarns. Each facility used their own standard technique to measure resistance and measured it at 100 cm and 50 cm intervals with the ASTM technique that we'll talk about as a reference.

BP Chemicals method of test was designed with a flat plate that has copper pins at 50 cm and 100 cm intervals. The yarns were taped down at one end and a 60 gram weight was attached to the

other end to make contact. Polycarbon used a similar set-up. Lockheed uses copper pins, too. The yarn is clamped at one end and pulled taut over the pins by hand.

There were four different techniques used to measure resistance. The first was to check the resistance at the full 100 cm length, check it again at 50 cm, then take an average of it. You have all the 100 cm measurements and all the 50 cm measurements and then those are averaged. Amoco method was to do it essentially the same as BP Chemicals method, but at the lowest resistance of the two measurements is reported.

These are the raw test data. All fifteen are very uniform. These are the 100 cm measurements, done by Hitco, and so forth and then again by Hitco to verify that the yarns weren't damaged. The next columns show Polycarbon's and Lockheed's results using their techniques.

From the raw test data, all the data are very close. This one here is a little higher in resistance. This is just the same data plotted again but in a different way. As you can see, they are all very close.

This view shows the ASRM test procedure and this is Hitco, the first time through, Polycarbon, Lockheed and Hitco, the second time.

Pinoli Resistance of 434.6 and 434.7. Are you sure you did that work?

DeVane We did. This is just the  $\Delta$ . The 100 minus the 50, right?

Kirkhart That is usually the ASRM procedure.

DeVane Right, but that is the 100 minus the 50?

Kirkhart You take the 100 and you take the fifty and you take the other 50 and you average all those. You average all the 100's and you average all the 50's.

DeVane Right. Right. The reason that I am pointing that out is on the earlier chart where you say the BP method is the 100 - 50, another method is the minimum of the two. We were following what we thought was the ASRM method. It is not our method. We were following a procedure that said take the 100 and subtract the 50 and it leaves that value.

Kirkhart It seems to me that if you take the 100 and subtract the 50, get that number. Do that fifteen times and take that average, wouldn't you have the same answer that if you took all the 100's and all the 50's?

DeVane That's not what I am pointing out. What I thought I read earlier is take the minimum of,.....

Pinoli That initial procedure was provided by Amoco.

DeVane Okay.

Pinoli You ignored that issue from the start?

DeVane Yes, we didn't understand it when we read the ASRM packet and that is how we did it.

Kirkhart This is a graph evaluating the test methods and once again emphasizing the fact that there is very little difference.

The conclusions are probably very obvious. There is very little variation that exists that can be related to the test facility, test technique or the analysis method. Since the data is so close, it is hard to make a recommendation, but is recommended here that we used the ASRM-Y2 method and as I was talking to Pat earlier, I guess it is the most suitable to run, but this morning I was pecking on a calculator using this chart I showed earlier. I was looking at these numbers across here and it looked like it indicates that this method gives a higher resistance and is more or less an outlier of these other methods we were testing. I averaged these and the ASRM procedure did come closer to having the smallest  $\Delta$ . The ASRM method was derived from the ASTM method. It is on the last few pages of the handout. What I didn't notice on this, too, is it looks to me like it could use some rework. It didn't really tell you to use a 60 gram weight and it didn't tell you to use copper pins or what. I think something should be added to that.

Ismail            Why are we measuring electrical resistivity?

Kirkhart        Why?

Ismail            Yes.

Pinoli            We are using that as an analog to thermal conductivity of the fiber. Second, it is an easy characterization test to run. It should be directly related to the firing temperature of the fiber.

Ismail            But you have lots of other ways. Myles showed us oxidation, we talk about density which is much more related to firing temperature. Why are you adding a third parameter?

Pinoli            Your question is, how many tests are needed to characterize this product.

Ismail            Is this just to get some idea about firing temperature?

Pinoli            Yes. We are in a very sensitive range. Every test we run has certain shortfalls. You do need data overlaps. An example is a moisture adsorption test that can be tied back to the firing temperature and we know the test is also sensitive to post firing activation.

Ismail            Yes, but the moisture adsorption is a very valuable test.

Pinoli            Density is a good test, too.

Ismail            Density is good. I don't have a problem with it.

Pinoli            They can all be tied back to the firing temperature, yet they all have other sensitivity factors that could come into play. Three out of the four tests could fall into an acceptable range, but the fourth may not fit. We need complimentary data to freely characterize an activated carbon.

Kirkhart        When I worked at another place, we had to do a lot of testing on materials. The first thing we did was test density and if that is out then everything is out. Resistivity could be a good low-cost screening test for fibers.

DeVane          There is one difficulty that I can foresee with it and that is we have seen some evidence that the electrical resistivity changes as the material ages. If it is old material, pulled out of storage, tested against material that just been pulled out of the furnace, supposedly under an identical process conditions, whatever the process capability is, we saw a significant difference in electrical

resistivity. It may relate back to what we might be seeing with carbon assay. We have also done studies with densities that change with time. There is something there.

Ismail I would rather do thermal conductivity which is a lot more valuable number than electrical resistivity. We don't use this number. When you have a thermal conductivity number,.....Pardon me?

Williamson How are you measuring thermal conductivity?

Ismail I am not an expert in this area....

Williamson You can expect your ----- to rise if you don't measure it correctly.

DeVane What we are doing, Ismail, is looking for a test that we can use as an acceptance test and you can do electrical resistivity tests right when it comes out of the furnace. you have to impregnate, laminate and then to do thermal conductivity. What we are doing here, I think, is determining what test can we use to characterize raw carbon when it leaves the carbonizer to make sure it is where we want it to be.

Pinoli I would like to get that data in real time as close to manufacturing date as possible. This test is really capable of doing that.

DeVane We are even considering using that as an online test.

Towne You're say resistivity, but you are measuring resistance.

DeVane Yes, I mean resistance.

Towne I would like to take just a couple of minutes if I might to tell you about something that you will see tomorrow. This will be quick. I have two different systems to measure resistance. I have a portable system to test the three points, 100 cm apart and this is where we measure the 100, the 50, and subtract the 50 from the 100 and take contact resistance. That is the one that I carry around where ever I go. You will see another one that is not in operation yet, but it is in our fiber test lab. We will be putting it into operation here in a couple of weeks and this is a 3 meter long and has the same readings, 100 cm sections, and we will have, though it is not in place yet, additional points outside. At each of these points you will have a copper clamp that goes down on the copper bar. You line up your fibers, pull your tension at one end that is applied with a weight and then put down all your toggle clamps and the copper lines will read off into a computer which will then give us the resistances for all the sections. Presumably you will have already run the density on the fiber ahead of time, so the operator will plot the density, weight change and resistivity. This may seem a little bit elaborate to you, but we are doing a lot of work here on high conductivity fibers as well as experimental low conductivity fibers and then you have PAN and then rayon. We have a lot of interest in this technique and it tells us an awful lot about the fiber. That is what you will see tomorrow, so you may have some questions about it again when you see it.

Pinoli Myles, on those high oxygen content fibers, do you have a data base that shows the relationship between the electrical resistance? How about modulus versus electrical resistivity.

Towne No.

Pinoli Myles, I think I asked you this before. Are you still uncomfortable with the technique we are using; stipulating that we take 5 direct measurements at one meter, then take 5 direct measurements from the same samples at 50 cm, add those two series and divide by 5. Now we subtract 50 from the 100 to get a 50 cm resistance. That is a deviation from your procedure. If you look at the data that was generated at all three laboratories, every once in a while you will see a number after individual subtraction for contact resistance that is a little higher than the previous 50 cm. The question is why. I feel it could be nonuniformity of yarn over 1 meter in length, or it could be broken filament.

Towne I think that is possible. That is what I am hoping. We are not really going to measure resistance, with these two end points, I'm for putting in a standard 1 milliamp and measure voltage drop along the way and then the computer will be working to calculate resistivity. You will see at the end of this is a little motor that will be used for twisting the yarn. On the rayon, it doesn't make any difference. On PAN, it doesn't make much difference either. The filaments are pretty much continuous, but in pitch sometimes we have a number of discontinuous filament and we have to twist it up to reestablish contact.

Pinoli To follow up on my train of thought, Myles, what are your thoughts towards the accuracy of the numbers we are looking at. If we get a higher resistance value because of broken filament, would we rather take that high electrical resistivity value or should we take the lower number.

Towne When I see the numbers for 50 cm and if it is significantly different than the one for 1 meter, I'll do the other 50 cm and if they are different, significantly different, I'll throw that sample away. There is either damage to it or there is something else wrong with it.

Hall Okay, let's move on. Tom Bhe...

Bhe Some of you may recall that last year that the bias tape of the prepreg, that the thread that was used to stitch the bias tape together was contaminated with silicon oil. Since then we have been working with BP Chemicals identifying the suspect lots of prepreg that has the thread with silicon oil contamination. We traced it back to the hardware that was used in the tape wrapping of the prepreg. The status is that now BP Chemicals has cut off the stitching and restitched it with the good thread. Don can probably tell you more about this.

Beckley Okay, Tom, thank you. When I saw Pat's opportunity to talk about thread, I kind of thought it was a subject that was, in a way, last year's story, I have realized since then that quite a bit has happened and it is an opportunity now to try to fill you on where things are. To go back a little bit, to join straight tape or bias tape together, sewing thread has been used for quite a few years. There are two kinds of thread that have been commonly prescribed by our customers, a nylon thread or a polyester thread. Each one of them is bought to a respective government spec, BT-295 or BT-285. In those specifications they allow for lubricant to be used to enhance the sewability. Factually speaking, when we look into this situation, there has to be a lubricant put on it at the time the yarn is made. DuPont, the typical yarn maker, synthetic thread company is the typical thread manufacturer and spinner. Neither of them could handle the material if there wasn't a lube put on it as DuPont makes it. They use two things. First of all, the lube they put on is an oil. DuPont's oil though is never a silicone, so the problem doesn't really emanate out of DuPont. They put on coconut oil, vegetable oil, linseed oil, almost any of the natural oils that you can think of. None of us get a thread that is really free of oil. They limit it to 2%. Then if the selling application requires additional enhancement to ease sewability, the thread maker applies additional lube to it. This is very common practice. A lot of people that make canvas to sew up sneakers and shoes, etc. need a fair amount of oil, up to 20% is typical. The range between 2% and 20% is what the industry functions with and what specifications would

automatically allow. We had an incident back in the 60's where we made some prepreg, sewed it up and in spots, weeping began to show on the thread ends. As a result of that, we initiated our own internal control spec for the amount of lube and fed that into the system. The origin of this problem has, there is a lot of material with nylon thread with lube on it and there's a lot with polyester thread with silicon lube on it that exceed 2%. One of the most interesting ones, Bob Looney commented on how people in our business and what they do, this particular one strikes me as just the way life is. The buyer back at the thread company has been at his station taking orders for thread for twenty years and knows the business backwards and forwards and he got a call one day for a young purchasing agent who was in a hurry to get a lot thread and a lot thread to people in the business is 150 pounds. He was from a new company he never heard of, called BP Chemicals and they wanted immediate delivery and he could ship out of stock and that is the way the conversation went. He didn't realize that BP Chemicals was the old U.S. Polymeric that has this mean requirement not to have more than 2% lube on it and apparently our purchasing agent never said we couldn't use more than 20% on it. So it's a communications world that functions. The step after that was, over the years if you have heard about businesses that run well because they are trying to buy things on certification and just in time and first in and let your supplier to do your testing for it, this is a lesson in that there are some things that you just have to test when it comes in to be right about it because the consequences are too great the other way. The combination of having not tested the thread lot and having communications on the other end, the system doesn't usually fail when one thing goes wrong, but when you find two things going wrong, you get into this kind of condition. That is the story of how the happenings occurred, namely our customer specs. Several of you that I am looking at condoned the amount of lube that had to be prevented by a series of steps by a spec and that system failed, so siliconized thread got into the industry and I kind of had the task of determining the extent of the problem is. First of all, how much material was affected, what programs are affected, get out an information to each of the customers separately. At this point that is one of the things that I guess everybody has learned during the period of time. That is, if you open up and tell everyone what the problem is, people are very helpful to work with you and help you and to work things out. The end result is that right about now we have every program has looked at their problem and looked at the reports that we have published. In fact, I am sorry today that I didn't bring you the so-called white paper that we have written on the subject of the thread and it contains things like what the issues are, what the origin is, what the background is, the investigation regarding testing of the extracts infrared analysis with Aerojet. We learned how to clean out and decontaminate the silicone off of tooling and sewing machines and the technique is not really mysterious. We got a real good break in that the silicone that is involved in this is very soluble in ketones and very soluble in almost all the solvents and as long as your cleanup technique doesn't take silicone that is located on the spot here and you smear it over here and then you continue on. If you'll confine that to one area and clean it up, throw the cloths and the solvent away that you have rubbed that area with, then you won't contaminate this area. In a very short time you can have your facility back up and clean, so we have learned to clean and learned the extent of it. We used SPX and ESCA and SEMS to look for migration of silicone within the material. We found out, essentially, that the extent of the migration with prepreg is confined, generally, within 0.025 of the thread itself even under pressure of laminating later on. It will migrate a layer up and a layer down. It rarely goes past that distance and probably one of the most important things, some of our customers and ourselves did testing of laminate made with the thread and determined that there was really no structural effect that could be seen. With the structure not affected, weeping really becomes the most significant item that you look at. Weeping is kind of a strange phenomenon in that you can clean it up with solvent and some days that is all it takes. That is, it will never reappear. Other times you can clean it up and come back the next day and it is there again. You can do it two or three days and then it is essentially gone and there are some parts that as far as I know never cleaned up, so there is still thread lube coming out. I have tried to do one of those things that was referred to this morning. An inch of thread, a quarter inch of thread contains a

hundred micrograms of lube and you can start to figure how long does it take, how many wipes does it take for that to come out at your detection level and this is one of the things that was done. Our detection level is six micrograms. So we have a hundred in that yarn in a quarter of an inch, how long is it going to take and how many wipes is it going to take for it to stop milking out of the structure. For the most part, we think we are at the point now where I can list the number of programs that are off and going with it and satisfied that they don't have a problem. That's Delta, the Titan IV, The Titan IV-U. D5 and Intelsat are looking to complete a bonding study that we have made specimens for to ascertain that there is not a problem as the silicone might migrate to the tool surface or to the shell of the exit cone and then effectively be subject to an interference and with PK 2nd, I am still not clarified on just exactly where that will end up. Overall I think we have learned a number of things about the situation, things we should of never forgotten twenty years ago, but that had to be reinforced. The problem, overall, is just not as severe as it could have been by any stretch of the imagination. Anybody have a question?

Buechler            What were the actual results of the D5 bonding study?

Beckley            The status right now is that we have made 200 hundred specimens and we made them with flat panels and we put sewing thread of 4 kinds together, supposedly nylon with excessive lube on it, 15%; polyester with 5%; then nylon with no silicone and polyester with no silicone. We made these 200 specimens that are  $\frac{3}{4}$  inch and then if you will lay over on a 20° angle, you can get a  $\frac{1}{4}$  thick specimen that will form a 1 by 1 bonding surface and it will have 5 thread ends in it, so we have put the thread so that you get 5 thread ends on each surface. The status right now is both CSD on Intelsat and D5 are deciding how they really want to proceed with a step of bonding or a step of wiping the specimens looking for the amount of exudation that occurs and then effectively deciding what that wipe off situation is, and we have encountered one of those things that also happens. After our operators made the specimens, they did the thing that they usually do when they make the specimen. They wiped them and cleaned them with acetone and as it turns out now, there is no thread lube to be seen. It turns out then that one cleaning on a specimen with a quarter inch of thread length is enough to take it completely out of the picture. I see the probability that we will have to make a set of specimens or do what the program calls for and that is take parts to study the wicking phenomena. The bonding problem is probably more diminished in the fact that 1 cleanup with acetone cleans the specimen in one swipe. The bad news is that we may have to remake the specimen.

Drake                Who was doing the study on D5?

Beckley            D5 is being run by a combination of Kaiser and Hercules. Greg Warren is the contact on that. CSD's work on Intelsat is through Ed Mills. Ed is usually at this meeting.

Pinoli                Things are pretty much at rest then, Don.

Beckley            It is not totally settled, but I think after the bonding study is done that will be the extent of those programs' activities.

Pinoli                I have some data to present out and this data is related to carbon fiber density measurement. There are many reasons why measuring fiber density is important. I think this committee has a preference for a good density measurement on fiber for basis characterization. A good fiber density measurement is necessary to get an accurate electrical resistivity value. With regards to background and why we are studying the issue, just about all the carbon fibers we are studying are rayon based and sensitive to moisture adsorption. Water displacement doesn't provide a value that reflects the effective composite/fiber density. We need a bulk fiber density that will reflect the composite fiber density. The committee recommended that we look for a displacement fluid

which is environmentally acceptable. In order to do that, we need to stay away from chlorinated hydrocarbons as much as possible. However, one of the true and tried fluids that is strongly recommended by Amoco is ortho-dichlorobenzene and I could add my recommendation to it. The work that I have done with ortho-dichlorobenzene, has shown good reproducibility and comparable to density gradient values. Unfortunately, it is environmentally unacceptable to many of the people. Hexane would be far better. Cyclohexane really excited me because environmentally that should be acceptable and as far as its structure, cyclohexane is closer to benzene which I found to do an excellent job.

The test procedure I employed for this assessment used a 2 meter length of C-5 yarn. The reason we took C-5 yarn is that it is very easy to work with and was readily available. If we could make it work with the yarn, I felt the fabric would be easier to work with. For fabrics, it is just a matter of cutting out a disc of the fabric and suspending it in the fluid. In the case of the yarn, we had to tie it in to a bow. The specimen is vacuum dried overnight, given 10 minutes of ultrasonic agitation in the test fluid and then the volume measured by suspension in the fluid. The numbers that we measured are summarized in table form.

In each case I have compared the result with gradient column data. An example is a very low fired C-5 material yarn. This has a moisture adsorption number somewhere in the neighborhood of 12% or higher. Medium range will get you down to about 3 % adsorption, and high would be around 1% or less. The gradient column data exhibits very little difference in fiber density. A significant drop in adsorption capacity of moisture, however will follow a parallel drop in density as the internal pore structure closes off. We have recently had some additional data coming out of the ASRM program that clearly shows the densities we are measuring are being reflected in the composite density. If we go to three significant figures, 1.45 versus 1.44, the gradient column data agrees very well. When we round back to three significant figures, ortho-dichlorobenzene and cyclohexane might be acceptable fluids. If you look at standard deviation, you will traditionally see much wider standard deviations, with these fluids: like .39% versus .06%. The gradient column requires a certain amount of preparation time and uses benzene which is unacceptable environmentally. As far as all three fluids analyzed, the ortho-dichlorobenzene probably looks the best to us.

The hexane is, environmentally, a relatively safe material. The data, however, has some outliers and considerable variance. I can't account for that. If some of this variation is due to pore intrusion, then you will expect the results to be consistent on one side of that issue. These numbers are all considerable higher, then once we get over here that suggests that the hexane is penetrating into the pore structure deeper than the gradient column fluid. Once again after showing up in this area, in this case it is even greater and harder to understand because the adsorption capacity is much restricted in this area. To my way of thinking, hexane would be unacceptable.

The one that I was really hoping would look good is cyclohexane. Looking to three significant figures, 1.44 versus 1.43 is not too bad. In this case, the average number doesn't look too bad, 1.40 versus 1.42, but look at this run to run variance of 1.38 to 1.41. Possibly if we worked on test procedure we might be able to get better results with cyclohexane. Does Hitco have any data to report out, George?

Peasley

Yes, Ken has a few slides to present. I would like to preface his remarks by saying I'm glad you said that about standard deviation, because I was looking at the standard deviation from what my lab did. There the gradient column and everything else was in tens of thousands, so I feel a little better now. You have one that is .18 on hexane.



Pinoli

We did this independently of each other, so this is my first exposure to this data.

DeVane

First of all, I just want to let you know that what we did was part of the ASRM program. We took seven different fabric types and we made five different measurements for them and we are going to be doing a sixth in the future. This included the gradient column with benzene and the displacement method where again as Pat pointed out, we just spin the material and weigh it in the fluid. We used water. This is typically done for space shuttle today for RSRM. We used water with a surfactant, the ortho-dichlorobenzene, cyclohexane and we are planning on going ahead and checking with hexane. These are the results that we got. I plotted these in descending order of density and we assume that what we are trying to do is duplicate the type of data that we are getting with this one which is the benzene column. the water displacement method, typically you are coming in at about 1.85. That is lower temperature and you started to approach the type of numbers that we got with benzene at high temperature. The surfactant is basically identical. Some of this variation I will talk about in a little bit, but it really is in the technique followed by degassing. The ASRM Y2 method which is the ortho-dichlorobenzene, we have had a lot of difficulties with that and a lot of scatter in the data. Typically what we saw with the ortho-dichlorobenzene and the cyclohexane were standard deviations of about 10 times what we got with the benzene column. We attribute that so far to our technique and to degassing difficulties that we have. Incidentally, these are between 12 and 42 samples per test. There is quite a bit of data here.

Benzene standard deviations are typically about 0.003 grams per cc, but we might have had 0.03 and as high as 0.06 and 0.08 for all the other displacements. The one that we found promising was the cyclohexane. (We haven't done the hexane.) For cyclohexane, we have only completed three numbers to date. Two of them were identical out to three decimal points to what we had with the benzene. The standard deviation is still higher. It is still an order of magnitude higher. The other cyclohexane value was right there. The reason you only see two points connected is that the third point is right here and is identical to the benzene value. The issues that we have, our concerns, are again the technique. We have stopped our testing because of the high deviations that we are getting. We are going to be looking at the technique and seeing if we can improve it. Maybe we can go from ultrasonic degassing and follow that up with a vacuum degas and keep the material in the solvent the whole time and take it right over to the balance and transfer it. Even though these are safe for solvents, we'd rather not use them. Following is information that our industrial hygienist gave me. The benzene right now has an exposure level of 10 ppm and they are considering taking it down to 1. It is a known carcinogen. It is dangerous as a fire hazard. The ortho-dichlorobenzene has 50 ppm, moderate fire danger but what we are really concerned about is both skin and respiratory entry rate. We would like to, if we have to use a solvent, we would prefer to go to cyclohexane because its TLV is 300 ppm.

We also have an issue of solvent disposal. We prefer not to have any solvents around. I guess the question that we have to ask is, do we really need this? There are two aspects to that. One would be for R&D. Okay, we really need to know density. Yes it is important. We might be able to develop processes, procedures or other test methods using one of the solvent methods, but if we are going to be using the tests for ongoing production, checking material as it is coming out of the line, acceptance testing, I think we would be concerned about the volume of testing. There may be other tests that would be adequate. For example, a lot of things correlate with it temperatures. Moisture adsorption does. Electrical resistivity does. So does density. Possible we could be cutting down the number of tests that we do and only go to one or two of them. If we do need to have some sort of test with a solvent, we could reduce the test frequency. In other words, right now we test it every 5th roll. We do carbon assay on every roll. We do sodium on every roll that we produce. Maybe we can cut down and do every 20.

Peasley We are concerned about working with the carbon fiber. The technician was working with the solvents in the hood and in some vibrations got the solvent on the glove and was worried about cancer...

DeVane He did mention that he got a few drops on the glove and he walked away from the hood to do something and he got a whiff and off he went from a minor amount. This guy has a beard, too, so he can't wear a mask.

Ismail Why is your water density higher?

DeVane Good question.

Pinoli Water intrusion into the internal pore structure.

Ismail How did you measure the water density?

DeVane Same method, hanging the materials in water...

Ismail Oh, you mean density gradient column?

DeVane No, no, not density gradient column. The displacement method, exactly the same as Pat did with the ortho-dichlorobenzene.

Ismail Yes, well, Pat is having an advantage there.

DeVane We degas the material also.

Ismail You degas it?

DeVane Yes, and what we are thinking we need to degas more because the standard deviation has been so high.

Buechler Many years ago I had this same kind of thing and I used methanol. Is there any reason that methanol was not used in these studies, because methanol is very high?

Beckley It will do the thing about like the water does. It will give you a number that the polarity of it goes right to the carbon yarn. The fibers produce a number like that 1.85.

Pinoli Another issue is that methanol absorbs moisture so the fluid density must be measured after each run.

Buechler I think that was the reason....

Beckley It drives you crazy in the long term.

Ismail When you measure your density with benzene, you are getting benzene in the pore...

Pinoli No, it doesn't generally penetrate into the pore structure.

Ismail How do you explain that density goes up overnight?

Pinoli Oh, that is where pore intrusion does occur. Very low fired fiber exhibits this factor out properly fired fiber will not show significant pore intrusion.

DeVane These are potential firing temperatures.

Pinoli We are talking about something that is fairly low fired.

Ismail Yes.

Pinoli You will have overnight pore intrusion by those fluids.

Ismail It doesn't really make any difference whether it is pore or not pore.

Pinoli The way you get around that issue is to use a standard 60 minute reading. This is the value I report. I don't wait for pore intrusion to occur. Out in this region as you go to higher firing temperature, you get less progressive pore intrusion. The percentage of pore intrusion is almost nil. I don't think anybody is concerned about that issue at this point. What we want is a good, quick bulk density. We need a fluid that won't rapidly intrude into the pore structure which is very restrictive. Water gets in very quickly and that shows up in your densities.

DeVane One thing you are trying to do is eliminate bad guys down here.

Pinoli Don, I mentioned a long ago that I was willing to accept water as the displacement fluid provided you accept the value as an upper limit, say 1.55 That would provide a go-no go test to screen out water sensitive fiber.

DeVane That would be acceptable from the point we are talking about.

Pinoli A problem now is what do we use now for the electrical resistivity measurement. Are you going to use the phony water density? If so, the electrical resistivity value is useless.

Beckley Can I give you the number of 1.55 as what the fiber is in phenolic resin? I think that is the number that would be nice to have.

Pinoli You would like to have a composite fiber density to reflect the moisture that is trapped in the fiber. That is why you are talking about a little bit higher density value than the gradient column provides. The gradient column does not include water in the fiber. That is why there is a little bit of a variance in what we measure in the fiber dry state and what you see in the composite.

Beckley WCA produces a number of 142 in phenolic and basically in water and in ortho and so that one is inert to variation.

Pinoli Your composite should reflect the lower fiber density.

Beckley It does. 142 is the right number for it as far as phenolic composite goes.

Ismail Pat, this is very discriminating here that if we just use water density....

Pinoli That is all we want.

Ismail I don't think that is a very good idea because you have a second decimal point here.

Pinoli I agree if that is what you want out of this test, but we also need a good bulk density for electrical resistivity and you can't use that number.

DeVane But that is where the issue of using a procedure for development to come up with a product, versus what we want to do during production. If we can correlate things well enough to show the relationship between temperature, moisture adsorption, carbon assay and resistance measurement and drop resistivity, then we don't have trouble with solvents.

Pinoli Okay.

DeVane For discriminating without having to have chemicals.

Pinoli I think a good acceptance test works both ways. A good acceptance test screens out products that should not go into the end product, but it helps give you some insight as to how the end product should perform. I see the electrical resistivity doing just that because if you get an inadvertant high resistivity number; it can be cross-checked to fiber density. Property data should be interactive. The data I have seen on resistance versus resistivity suggests that when you see a resistance variance in these products, you generally see a corresponding shift in fiber density or yield. Therefore, before your reject a fiber due to electrical resistivity, you must verify which property has shifted; resistance, density or yield.

Beckley Pat, would you use the 185 number and still come up with an incorrect resistivity reference?

DeVane Aren't there enough other tests? In your resistance, if anything goes out of whack, then you go back and look at it. You have your moisture adsorption there, you have your carbon assay...

Pinoli Being a conservative, I like to consider testing costs somewhere in the equation.

DeVane The bottom line is if the test has to be done, it has to be done. We will find a way to do it.

Pinoli I would like to keep pursuing the cyclohexane.

DeVane I agree.

Hall We need to close out several of these items that we have been working on for a couple of years. One thing, about a year ago, we finished up on the rayon specs, the items that we thought should be evaluated and of course along with the old items, we have added wet elongation and wet strength. They have been incorporated into these specs for NARC. Unless there are any objections, we are going to close out the rayon advisement task. I think that was number 2.

Beckley There is the caveat that some of us haven't seen the revised values.

Hall We are talking about the requirements, not the limits. Now Bob Looney has the limits if you are interested. In fact, I don't know of any reason why we can't show them to anyone who would want to see them. This is not part, our recommendation is what items to evaluate and they are the same as they have always been with the exception of wet elongation and wet strength and this has been written into the new specs.

We are going to write a letter through Hercules to SPIP office saying that this is the recommendation of the committee. Since Hercules is the prime contractor for the SPIP, the letter will go through them to Ron Nichols. We are going to try to get three or four tasks, out of the way this morning. The first one is rayon which we really finished up a year ago. Dr. Turbak,

ken Wilson and Tony Day from Thiokol all agree that we should add wet strength and wet elongation.

Pat, what do you want to do next?

Pinoli Let's let Jack present the code identification work.

Hall Jack's not here yet.

Schmidt I have a question. Are there any things on test methods that have been closed out? Have any been closed out or improved?

Hall What time period are you referring to?

Schmidt Over the last three years.

Hall The only one that we have really closed out, and this was not really closed out because we did not take it through the proper channels was the resin content of the prepreg.

Pinoli While we are waiting for Jack, let me pass out the ballots that are a part of Jack's presentation. This ballot designed to get a response from the committee, the product suppliers, the product users and product designers as to what criteria they feel is appropriate for changing your product identification. We recognize that each one of these groups has a vested interest. The end user will probably like to see a product change made at the slightest change. The product manufacturer would probably not like to change anything. He would like to think that his product is always consistent no matter how many changes in supplier or basic spec change occurs. Case in point is MX4926. Somehow we have to acknowledge that code a change must be made. If changes make a difference or not in the product, we would like to at least have a reference point to track. Case in point, North American Rayon is now being used as the standard precursor. All future products should recognize this so that we can easily track it through to hardware. the hardware.

Let's go over some of the items that we have established. Under carbon fabric and yarn, fiber precursor is a must to identify. Precursor source - you may look at that from a different vantage point, but as an end user, I definitely think it should be identifiable. How you identify this with a change, I would leave that up to the manufacturer. Heat treatment temperature might be a little difficult, Myles, from Amoco's standpoint a product such as VCL can cover a multitude of different products. There is no finite temperature at Amoco for VCL. You have indicated that Amoco procedures meet the customer acceptance tests. If Titan comes up with a spec then the product will be produced to meet those requirements. Postwoven versus prewoven - I think is natural that if a fabric is being produced, it should be identified as to whether it is postwoven or prewoven. I think we always identify the fabric weave anyway. The filament count - if you change the filament count, obviously the product will change. Yarn construction really involves things like twist and sizing which most of the manufacturers describe. In other words, on T-300, Myles, you stipulate how much twist you are going to put into it?

Towne It is either NT or ST.

Pinoli So you already have a code for that factor. Is there anything that we have missed on this sheet that we should identify?

Ismail Sizing.

Pinoli I think the intent here, if the sizing changes, Ismail, you change the connotation of the fiber. The T-300 is something else. We are not going to change the T-300, but sizing is a call out, a subscript call out. I think that probably falls under yarn construction.

Towne Pat, just to review here. For products like T-300, the designation is s 3K or 6K, and then it is 309ST. That would be 309 sizing with standard twist. That is incorporated into the label that goes on to the package of T-300.

Drake What was the last letter designation?

Towne ST or NT for standard or no twist.

Beckley One of the ways of looking at none of the above another way is to recognize that a prepreg gray code really only means one set of characteristics at that time and a contractual no change clause locks that qualification to that specification, in other words a no change clause in the spec and the qualification locks all that together and you get everything set with one number.

Pinoli The specifications that you are referring to are customer specifications.

Beckley They are the qualification spec for a given program and factually that is really locked together that way and it is a violation of contract to essentially make a different product later on. You have listed some of the potential differences, but the only way you can really do that is to go back to the customer and say that this is the change we are proposing. Is it satisfactory? The customer has the prerogative of accepting or denying your change.

Pinoli Are you at the same time saying that this is FM5055G/WS119153. That is your product.

Beckley Yes, you are because the contract puts those two together. Sometime in the past it used to be commonplace that a spec would always contain a QPL on the back that tied and locked in the qualified product to the spec and a thing that we have found in the past that is really useful is to list it with the lot number that serves as the qual for that date. That lot number, that qual is what it is made up of. When all that is done, you have a snapshot of what the ground rules are.

Pinoli The end user tends to drop off any connotation to the actual test methodology that applies to that product. The only thing that seems to carry through all the literature will be the FM5055. Everything else is lost along the way.

Armour What makes you think that this is going to be any different?

Beckley I think, are we trying to approach this the long way around rather than the short way.

Pinoli I think that I understand where you are coming from on this, but what you are inferring, Don, is that if we respond back to NASA and tell NASA that there is an obligation on the part of the end user to clearly identify the specifications that were employed in the manufacture.

Armour This industry is notorious for shortening everything. If you have a product code that is 18 letters long, somebody is going to shorten it.

Pinoli I tend to agree with you.

Larson I think this is an age-old problem, though, where we have all used the numbers 4926 and 5055 and have not really known what were the specifics, what really went into that product. We have

talked about that a number of times. It is true that you can go back into the lot, certification and all that sort of thing, but it takes a lot of effort to be able to go back into the records and dig all that stuff out. What I think NASA wants is a user-friendly type of code. Not a 13 letter thing, or 19 letter thing, or whatever that might be, but they want something a little bit more specific so that it goes a little bit beyond the 4926 and the 5055 level of description. They don't want a big long thing that tells the whole history. They really do want something that is a little more descriptive and breaks it down beyond where the 4926 and 5055 is. I think that we can come up with some reasonable code. They still would like to know whether it is CSA, or whoever the carbonizer is, and would like to know a little bit more beyond that. There are a lot of people who look at these codes who are not as familiar with them as we are. I can look at a lot of our leaders there in NASA and they are not that familiar with them. They recognize numbers, but still they don't always know the product. They need something.

- Thomas        If you look at this, you are trying to code 18 different things, 18 individual codes. Do you really want to carry, I don't think you are asking for this, if you identify each one with a code, would you carry that all the way up and ....
- Larson        I don't think that 18 is a user-friendly number.
- Thomas        We have got 5055 or 4926 per ASRM spec.
- Armour        That is the key right there.
- Thomas        That is the key right there or for RSRM, that spec says I want it twisted and kinked, etc., and if our 4926 doesn't meet that then it is not 4926.
- Hall           We just had a meeting with ASRM up at Iuka, MS about a week ago, and Fiberite and BP made presentations. There were a bunch of new numbers there, but they were all 4 numbers. With those four numbers is a product sheet and on this product sheet, it had every bit of this information on there. One of our problems was that maybe, and I don't want to pick on anybody, 4 numbers was not unique, but under the new system it is unique. It has a product code sheet that goes with those 4 numbers and it says everything on there that needs to be said. I think we are already there, really.
- DeVane        As one of the carbonizers, we do, in fact, change the code on the carbon when anything is changed and that includes everything that you have there on your list and we have done that since CCA-1. Each one is a different version and has a different precursor, etc.
- Hall           In the ASRM program there is going to be at least 8 new products and all of them have different numbers and all of them will be well defined. Is this not correct?
- DeVane        That is what we have always said.
- Thomas        I can vote to control all of these codes and I think we should and we do, but then do you say none of the above because I don't want to carry them all the way through the system and I am not sure now how I should vote. I am for the codes. We have codes, but how far do you stack them up.
- Johnson      Let me ask a question. Everything we have done has had a number on it. Now when it goes to the carbonizer, it is up to you guys as to how you want to identify it before it goes on to the prepregger. It seems to me that it is implied and realistic to think that a lot of these things are done, but they may not be translated into that 4 digit number you are talking about. Even when

we got into the surcharge issue with Avtex, every time we had a new price, we put a new number on it. It may sound silly, but it helped the customer identify what he paid for.

Beckley It was carried through the contract, into the configuration control system that is set up. It was independent of changing 5055. The fact that it had a different price, another way of getting at some of those things, you have resin specification, filler spec and you may as well put down prepreg spec which implies resin vol and flow. We had a 30 specification on 30 different programs for 5055 and essentially the things that differ are the vol and flow call outs that tried to get a material that fabricates for one product, one part differently than another, so you get down to a level where you just cannot include a vital thing that is going to go in another part of the definition or in this case, in the spec. There are 30 different ones for the same product. That is the control level and you want to purposely want to leave it open.

Williamson What is the real objective of the program?

Pinoli The objective, as I understand it, was driven by the fact that a lot of material in the past has been produced with one broad code identification that ended up with different products being out there that the engineers could not define into a definitive box as to what it was. There were variations in the product and what they were asking for was that the manufacturers recognize that when a significant change, well, they have to be defined, they want a different number associated with product. ASRM has already picked up on it. Right from the start, they said these are new products. They have new codes and everybody has jumped on that and I think has responded and I think in many ways, part of the problem has been solved. The next generation of material will be well defined and the product numbers that are out there are in response to the new code. Some of this activity may be water over the dam. We can't go back and correct faults that have already been put in place

Beckley Even in the instance that you cite, the engineer, after the fact, may not know for certain what he had with the gray code number, but I feel confident that at the time the order was placed, all of that information keyed off of the things that we talked about. The spec, the contract, the product gray code were known. You just can't carry all that on one piece of paper as a matter of fact.

Williamson You have to cite these things.

Beckley Well, the spec does, if you go to the trouble of having a qual lot register, but even so, the information was available if the engineer really wanted to know what it was. There never has been a case that I am aware of a documentation that, going backwards, didn't find who, what, when, where. The records are there. Why waste the time and the agony for every time, when you are going to write out 18 letters instead of 4 is also a time and a cost.

Thomas But your lot number is what controls what went into that material. We deliver 4926 and use Hitco material, or we can use Amoco material, we can use Polycarbon. Our lot number will tell which one it is, as well as our resin, our filler, and so forth. What you have on the list, we do that each and every time.

Pinoli What's the feeling if we use, what if we go back to NASA and say that our recommendation is that any time a product is identified, by the specific lot must also be included. What if you have 3 lots in an end product?

Beckley The lots don't have the problem, the hardware does. It is reality that those three lots are in that part.



Towne I think that if it doesn't take long trace back, but there was one instance, I think, where this really became a problem. You didn't know if it was something you wanted to trace back or not and it was the issue of whether 4926 was made with a five harness satin fired at a high temperature or an eight harness satin fired at low temperature. That was a pretty significant difference and you just didn't know whether or not you wanted to go looking for it.

Beckley With all respect to my colleague sitting on the left, you know we as prepreggers have different philosophies on that and I would really ask Fiberite to be willing to say that henceforth that they will only use one gray code per one combination and then put another number on the next product. I think we have all come to recognize it is a necessity.

Pinoli Is that a given, Jim, that Fiberite is going to take some steps toward doing that?

Thomas We are doing it on ASRM.

Williamson Ed Mills concern is when you order 4926, is it VCK or something else?

Beckley Frankly, Jack, he could control that if he was the controller going in on the purchase order. We both know that.

Williamson You know people get lazy writing out quotation requests. They want to make it as short as possible. 4926, 5055 and that doesn't do it.

Thomas But, 4926 with three different carbonizer is in the spec unless you want it tied down to the carbonizer...

Williamson Ed Mills has got a spec and all he has to do is 4926 and cite the spec.

Thomas Right.

Kirkhart Maybe add something to this. I bought a Chevy pickup and on my dash it has a VIN number. It tells whether it is made in Canada or Dearborn, axle ratio, and so forth. I ordered it by make and model, not the complicated VIN number. GM cares about that number, but not the buyer.

Thomas But that VIN number is an 18 or 19 digit number. It is not 4.

Drake I want to go back to the gray code. In the first column here it says that carbon yarn, carbon fabric code, normally refer to that as a three digit, three character number, WCA, CCA3. Does that not include all the things in that column?

Pinoli Yes. That is my interpretation of what that means.

Drake How far should we carry that, through the prepreg.

Pinoli I want to know if WCA, if they change the precursor to NARC, should that be called WCA-1.

Thomas You have to have a code to identify what 1 and 2 is.

Pinoli Hitco has already recognized the precursor change, CCA3 to CCA8.

Williamson Here is the rationale for that. If the material doesn't get on there until it has thoroughly gone through a qualification on the major program...

Williamson      How many times has a phenol supplier changed, or formaldehyde supplier changed?

Pinoli            A good question but where do you draw the line on changes?

Thomas           Pat, you were talking about precursor. We have only had Avtex. There has only been one precursor as far as the rayon is concerned.

Beckley           There was industrial rayon.

Drake            Well, if you go back to the original purpose of the identification code, such as FM5055 or FM5014, what is the purpose of segregating that stock from something else. If you look at WCA for the Titan program, ala Avtex, and another one from NARC, you certainly want to be able to identify the difference because the government is spending many bucks trying to requalify individual rayon precursors.

Pinoli            My personal feeling is that if you have a fiber precursor supplier change, you should change the code. I know what Jack is saying. We have qualified the material and it is equivalent and that should put an end to any future thought, but these concerns persist. There is always going to be, "Well, what about the precursor in that part?" It would be nice to have traceability built into the system right up front. Now is it going to be WCA-1, WCA-2, WCA-3? I personally don't think that is going to be a big effort on the part of the manufacturer to meet that requirement.

Thomas           I think we are meeting that requirement.

Pinoli            I would ask Myles, are you going to change Amoco's fiber identifications to reflect NAR precursor?

Towne            I am not the one that can say that, Pat. One of our problems is that we already have a number that follows WCA and it is part of the lot designation. We have numbers up front that are part of the lot designation, so we can easily pick out when a material was made and also which lot in that time frame. If you add another number in there for the source of the rayon is something that we have not addressed. As you probably recall, we tried WCA-1, WCA-2, WCA-3 which referred to the structure of the WCA and then we decided that was too much at the time. I think we will address it and see what we can come up with internally.

Thomas           I can assure you that if we order material from Amoco to go on the RSRM program, it would be AVTEX material because NARC is not qualified. We would not order NARC material. When the time comes on ASRM, we will order NARC, not AVTEX, because there won't be any AVTEX anyway. I am assuming he is going to be honest and deliver me what I want or I won't deal with him. He may put an A or an N in there or 1, 2, 3 or something like that, but I would be able to go back to him and say, "What yarn did you put in there?"

Pinoli            I haven't heard any arguments out of NASA with respect to how this issue is being addressed for ASRM. The feeling I had was that they were absolutely content with code identifications on new products under study. The only problem that NASA was trying to bring to our attention is the fact that historical data is difficult to trace and track because there isn't enough identification code attached to existing product. Testing done at SORI refers to MX4926 and without a lot number, we do not know what is in it. You have to find out who made it into a part at CSD and trace it back. I don't think SORI publishes all products' case histories. We can fault SORI, and say "Hey, you guys do a better job". If you are going to be doing any testing on a composite itself, then you should impose stricter guidelines on SORI reporting.

Stokes            We generally do try to do that. We try to get as much information on the product as we can get so that we can put that into the report. It is not always freely available.

Thomas           I don't know why it is not readily available. I don't understand that statement. We can tell you what we deliver by lot number. Like Jim says, you can take vehicle identification a VIN number, an 18 or 20 digit number with letters and so forth. We can make a material identification number. We can put all the numbers out there, but then you would have to have a dictionary to interpret the code. That can be done.

Pinoli            I think a lot of the emphasis has been on the engineer that supplies the material for a test and he would have the responsibility of the traceability of individual lots. In some cases he can and in some cases he can't.

Thomas           Eric called me three months ago with some numbers. Wasn't Eddie able to run those down for you.

Stokes           Yes. That was generic information, though. The more difficult thing to do is to get the information from the prepregger all the way back. It is just difficult to trace all the way back.

Williamson       Ed Mills had a paper to give and couldn't make the meeting because he had a conflicting business date and we have gone through it basically already and his principal concern was when he called out 4926 what was the definition. If his purchasing department sends that out, he has no assurance that he is going to get VCK. I think Mr. Mill's responsibility is to cite the appropriate CSD specification and then there isn't any question. I am sorry Ed isn't here and we could argue about that.

Thomas           If he wants VCK when he puts in his order he could always...

Williamson       Cite his spec. That is all it takes. Put 4926 on his spec and specify VCK.

Larson            We have a similar situation on the old C4 program at Hercules. Our spec was written calling out for the qualified material 4926 and we assumed that it was CSA, the lower fired material, and it wasn't until a number of years later that I got to looking back at the data, and in fact reports from Southern Research, and right there they called out VCK themselves. Unbeknown to us, they ordered VCK in lieu of, and I can't imagine that because it is a higher price, rather than the CSA. It was all again under the 4926 designation. When we had our executive meeting back in January, we came up with a recommendation for consideration and again we wanted to recommend some sort of a user friendly type of code where we wouldn't be involved in a 15 or 18 letter designation. We felt that we wanted some kind of a code referring to the resin, filler, and the fabric. In the fabric we were concerned with fiber type and source and the weave construction. We talked about temperature but I think we agreed that was proprietary and we didn't have information to describe that. Anyway, with those three things, we realize we are going to have to do some research. It would be very helpful, I feel, to at least have a letter or a number that would give us a clue as to which fabric we get. I think that is what Corky and John Koenig and others have been pushing for, also. I think personally, even as a user, that is would be very helpful to have 3 additional letters on the end of the main designation to describe it. I don't think we could possibly consider a 13 letter designation.

Bhe                Do you have different references for FM5055 or 4926?

Larson            If you want more detailed information, then you have to do research.

Bhe Do you have that information for lot numbers?

Pinoli I want to go into a little of the background on this particular task. We had an open forum up at North American where we spent about half an hour to an hour discussing the attributes and problems associated with stipulating an SPIP-type code. We outline a couple of different approaches to both to the fabric and to the prepreg. Most of them seem rather unwieldy, long, and a little more detailed than the people were happy with. The executive committee sat down and discussed this amongst ourselves as to how best to handle this and the net result was that the executive committee didn't feel that it could arbitrarily make a decision for the whole committee. We recognize that there are differences of opinion on this thing and that is really what the ballot was designed to do, evolve a consensus among the committee. Our approach now is to look at the ballot response and develop a response letter to NASA stating our position on specific areas that we feel that we have a consensus. We wanted to bring some of the dialogue we have discussed here and indicate future programs, such as ASRM, have already incorporated code changes into the prepregger operation. All of these future products are more well-defined and we have an agreement that if those products do change in the future, they will respond with an appropriate change in their code identification.

Buechler How are they doing that?

Beckley We did not change anything from our internal policy on gray codes except to say that this is a new product. It will be this reinforcement, defined by the first 8 things on the yarn.

Buechler Do you think you could put it on a view graph and show exactly what you are talking about. Give us a sample of how this can be done.

Beckley In our system, that stands for phenolic and it is not a P because we use P for polyester. The M part of the number stands for material and that becomes FF if we have a filament product. In our system the number with the 5 in the first digits also denotes phenolic, the 6 is polyester, the 7 is epoxy and the 8 and 9 are miscellaneous materials. The next three digits really restrict the system to what is in our gray code book, a master register, as to what that product is. In the case of the new ASRM materials we have FM55939, that in our gray code book turns out to be USP 95 which is the resin system that is in the current 5055 but ASRM has asked for some changes so those changes are built in to this particular gray code. It is made up specifically of resin, filler and a given amounts of material. That is built in to the number and it goes in to our gray code system. We internally cannot change that. We get an order for this thing and that is what we go and make. It infers with the three digits that we will have a particular fabric and a particular resin and a particular filler. They are a consecutive series of numbers and then as the product modifies and customers want to change things, we will not change this product at all. That is the system that we follow.

Pinoli Have you published this information?

Beckley It was set up specifically in our own gray code book by somebody who was very orderly in his mind.

Bhe Do you have this from Day 1?

Beckley Yes. It hasn't changed from Day 1.

Buechler This is the kind of knowledge that isn't out in the community in terms of being able to reference these kinds of changes that are occurring. If we could provide this gray code information to the

engineers, it would be much more simple to trace down and then you wouldn't have this discussion about coding.

Beckley Would this group like a summary memo doing a better job than I have done now to say how this is done?

Drake Would Fiberite cooperate, also? Just for conversation, suppose a change from NARC to BP rayon, would it change the number then.

Beckley It is a suffix letter. Let's see if we can do one. FM5055 is the product and essentially in shuttle, they have forced us to modify our system by their preference. They want that product called B, 5055-B, and they don't want to change all of the paperwork in the shuttle system. That is the reason that letter has stayed there. 5055-B in our system is also J because that is the time that the last changes came into the system. When we get up to the point of moving 5055 from AVTEX to NARC, the product is K, L, or M and the one that I remember 5055-Q is Cydsa. You can see that this flows along with letters, A, B, C, up through Q that I know of and when a customer as formidable as the shuttle says they don't want their product changed, we have to make our system adapt to their wishes for them, but everybody else buys the same product as the J.

Schmidt Have you changed that filler designation number?

Beckley We have changed it in our own internal system, and depending on whether the customer wanted it changed, they didn't. They gave us an effectivity date that essentially we moved from 333 to 27 and then to 28 and we were controlled by effectivity. These are examples of where you have a system and make it do what somebody needs done.

Drake If I understand, Don, in the case of shuttle is 5055-B, when you go to NARC, it will remain 5055-B because of that.

Beckley Just because of that. Everybody else will buy that product as an M or an N. I have forgotten which letter it will turn out to be. In the gray code book it is logged in as that one particular thing. To accommodate a number of people, if Ed Mills was here, there was a time when people ordered 5055 and they wanted Myles' reinforcement. We did this and it worked out okay. 5055 (VCK) was okay for everybody. The resin was okay, but they wanted that reinforcement.

Drake This particular kind of designation becomes important when you have a program like the IUF which doesn't follow along the mainstream and they may be using AVTEX for 10 years. It would be important to them if you change the product. It is important to maintain the identity of the product.

Pinoli Maybe some verbiage should be put into a response document to NASA that there is responsibility on two sides of the issue. One is the user side, to identify what they want, and the vendor side, to re-identify every time they make a change.

#### BREAK FOR TOUR

Pinoli Let's go through the action items that we are going to take, in order to close our specific tasks.

Under Advisement Task 5, which is rayon specification. There are new specifications coming out for the North American product. I don't think there is much more that we can do on that particular task. We had Mr. Turbak in; we have had a visit to North American; we have had presentations on the variabilities of the North American product and the attempt to move

specification limits to more closely align the spec with North American's production. I think all of these efforts have been positives. What Bill and I are proposing to do is write a formal letter back to NASA management that we are closing the task out. We will enclose new specification limits and summarize the work that was accomplished on this task.

The next one is oxidation mass loss.

Drake Pat, does that include the test methods?

Pinoli Yes, we will reference those that are going to be implemented.

Drake I guess what I am concerned about is will the test methods and specification limits include both 1650 and 1100 denier rayon.

Pinoli Did you get a copy of those?

Drake No, but I have seen rayon specification test methods and Aerojet adopting it to their facility and by process of evolution...

Pinoli You have adopted the new specifications whether you like it or not. And the reason you have it is DOD programs have not implemented has specification control. Only the NASA/RSRM program has imposed specification control at that level.

Drake I understand. Even within NASA, you have two contractors buying it...

Thomas If it is bought for NASA it is bought to the same spec.

Drake Does Aerojet buy to the Thiokol spec?

Thomas That is the Thiokol spec that they put out.

Pinoli Thiokol is the main contractor in both programs, RSRM and ASRM.  
Bill, I am sure there is going to be a different designation on ASRM specs.

Drake I guess I am concerned that if I wanted to adopt the procedure for electrical resistivity, what would they go through to do that?

Pinoli Resistivity is not an issue for the precursor.

Drake What about carbon assay?

Pinoli Carbon assay isn't an issue in rayon specification. The system is designed for traceability however from carbon fabric back to yarn produced at NAR.

Peasley When are those test methods and specifications going to be published?

Pinoli We have specifications that we submitted about a year ago. We could send them out to those who would like to have them.

Thomas It might not be a bad idea.

Hall I have the copies of the properties. The limits we don't put on there because it has not been signed off on. As I mentioned yesterday, by the first of June the new limits are supposed to be signed off on. At that time we will give you the spec limits. At the present time all we are saying is these are the properties that should be measured to qualify. When you look at these, there is really no really difficult test to perform on these. The test methods are pretty straight forward. We did add wet strength and wet elongation which was not previously required. This was a recommendation of both Turbak and Thiokol.

Thomas Ken, I have accepted an action item to explain our gray code system, except we don't call it gray. It is either white or black. Did you decide to close out the oxidation mass loss test, too?

Pinoli Yes, we kind of got sidetracked. Have you got that down, Bill?

Hall Yes.

Pinoli Myles, what do you think about writing up your procedure and put it out as our recommended guideline procedure. Is there a consensus here that the procedure we have outlined would probably do the job of discriminating a product that is very susceptible to oxidation. That was the task goal of the effort. To go much further on this might not be that profitable. We have a sophisticated procedure using the TGA apparatus that will do the job and we have used that procedure very effectively on the ASRM program. We have a simplified procedure that Myles has used and has done a reasonable job for those people that want a go-no go test. I don't think that necessarily that we should be in a position to cross all the T's and dot all the I's in a procedure. We want to move on to some new ground. My recommendation would be to write a letter back to NASA with the proposed procedure with some of the data that we have gotten.

Carbon assay testing, I think what has come out of this today, or yesterday's discussion, was a clear indication that the LECO equipment was never designed to be used in the capacity that we are using it. It was designed for coal, coke, etc. We can't push it any harder than  $\pm 1$  or 2%. That is the best you are going to do. In doing this work, though, we have seen some trends that I think the Hitco people recognize as probably true. That is the aging effect on the very low fired material. The fabric is changing with time. This has given them some concern that in the future if any problem develops, and they are forced to go back into their historical pile of fabrics. They are going to find it is different than the product originally certified. Rather than hang Gene Rubin and saying you didn't do the job right the first time, now we have some insight as to why data on retest is not the same. If you carry that through the composite, it is another basket of snakes. One of the things that we did on the D5 program, we stored carbon fabric 10 years before we used it all up. That fabric was put in storage and after about 2 years in storage, I had some concerns about the aging effects. We initiated a program at Lockheed to look at what the potential changes to expect downstream on fabric that had been stored and that long we estimated that maybe in 6 years, you start to develop some problems passing hardware acceptance tests.

Thomas This was black goods in storage?

Pinoli Yes and we got down to the end of production and experienced density problems on the hardware. We didn't pursue it any further. We thought 6 years at that time was more than we needed. Unfortunately we had so much overhang that we moved into a new program and required about 10 years to consume all of that fabric.

Peasley We have some evidence that aging rayon may be better than raw rayon. It was the stuff that was made back in 77 or 78 in Nevada and that stuff that was turned out is comparable to AVTEX material.

Pinoli We all wish that Avtex could produce the same product again.

Peasley We thought it was like fine wine, you had to age it.

Towne Do you feel that it was due to aging or because it was just made better at the time?

Peasley We figured that it was the same plant, the same materials, but that may not be accurate.

Pinoli When they first started up at AVTEX, I think they were very cautious. We watched them like a hawk. These guys at Burlington were watching them on a daily basis. I think that is the reason, the yarn was so good. We monitored that operation for 2 or 3 years. Every month we had samples coming out to or Lockheed. Wayne was looking at it with a heavier surveillance and he showed good uniformity.

Towne Pat, yesterday you said something about renewing that round robin on those same samples to see what the aging effect would be a year later.

Pinoli Would everybody like to see that done? Myles, do you want to run those again?

Towne Yes, I would like to do that.

Thomas Is it a consensus of opinion of the group that the low fired materials are the only ones that change with age. Do we have enough data?

Towne There is VCX-13 and a WCA in that same group.

Thomas Did anybody indicate that the changes that have been seen that they are significant enough to associate with aging.

Pinoli There has been no data to suggest that VCX-13 or WCA are subject to aging effect. From the ASRM program, that is where we are trying to go. We feel pretty confident that they will behave the same.

Hall On this one, Pat, we agreed to use WCA as the standardization material.

Pinoli Is there agreement on that?

Hall There was yesterday. I think we need to talk about the weight of the sample because LECO indicated that this was extremely important and maybe even talk about the gas flow that they use at LECO. We need to write up a test procedure and close it out using WCA as our standardization and using their recommended weight.

Pinoli How about a preferred procedure for CR-12 and CHN-600?

Hall Right.

Pinoli I'll get with you, George, and with Tom Paral and we'll work the issue of calibration.

Towne I trust these will not be written up for the LECO equipment.



Pinoli We are just going to ignore you Myles. You have an ASTM procedure and it is well defined. I don't think we have to get into that. Does anyone know of equipment that maybe better than the LECO as an alternative?

Ma Pat, I am aware of some scanner technology that will analyze carbon and sulphur. I heard about it a long time ago, but I will dig it up and send it to you.

Pinoli Do we want to move this off the table or do we want to follow up on it with round robin testing?

Buechler I think LECO offered very generously to run some of those tests. I think they ought to be incorporated into the round robin.

Larson I would suggest that the committee write a letter to NASA and propose that we continue on based on what we found out with the new equipment.

Pinoli I'll buy that.

Larson It is something that we ought to keep informed on and this has been going on for quite a while, but it is something that has come to light just recently.

Pinoli I am concerned about the LECO devices. They just won't do the job that we would like to see it do. That is to give us reproducibility within about 1/2 %. Frankly if I can't reproduce within 1/2 %, then I don't think we should run the test.

Thomas Pat, I think you are going to have some variability in the material that will overshadow the 1/2 %.

Williamson I don't think you know that.

Thomas No, but it is a good gut feeling.

Ismail Pat, what is the objective of the carbon assay? What do you want out of it?

Williamson Maybe Myles can answer that better.

Towne Well, one of the things runs through my mind is carbon assay, my understanding of it was to be sure you used a firing temperature that was sufficiently high for your application. I think that we have also identified a couple other tests that do that same thing and that are a hell of a lot easier, resistivity for instance. Oxidation is also good, but you do have the sodium as a possible deterrent in that.

Larson This committee also has to recommend some additional replacements. Maybe this is a good one here.

Pinoli Maybe we could open up a new effort that explores the relationships. That allows us to study them again and look at the relationship of carbon assay testing and resistivity testing. What do you think about that?

Larson I don't think the electrical resistivity should be part of the task.

Pinoli We'll just make the task to define the relationship between those two properties.

Thomas You said three earlier. You mentioned electrical resistivity, carbon assay, and what was the third one?

Pinoli Oxidation.

Towne Oxidation would do it, but it does have the potential of sodium effect.

Thomas I think when we establish a new task, we need to be as specific as we can rather than going in with another 3 years of shopping. I don't they want us to do that. Have some specifics in mind and go test them.

Pinoli That is why I like electrical resistivity and carbon assay.

Pinoli Finally with regard to product identification codes

Hall Pat, that has a task number. Do you know what that is? Number 7?

Thomas Let me back up to Task 4. If we are going to identify new task are we going to recommend that Task 4 be closed out?

Hall Yes.

Pinoli Under the product identification code (Task 7), my thought is we have to document, in writing, a lot of the dialogue that went on at the last meeting and this meeting. Action has already been taken by the prepreggers to improve identification code. They are being implemented on new products. I don't feel that it is even possible to go back and correct problems that have occurred in the past. The only thing this committee can do is make recommendations for the future. Hitco is incorporating just about all of the recommendations and requests that are coming out of NASA on code issues. At present I don't know where Fiberite is on this issue. Maybe now is a good time for someone to say a few words on the Fiberite code? Can you provide something that is similar to what Don has promised?

Thomas I took the action to discuss the gray code system. Until I talk with Eddie on exactly how that is done, I really can't say anything. I think we are working with Aerojet, Lockheed, and Thiokol on a new code based on the ASRM standpoint. I don't think there is any question. If there is in Bill Armour's mind, then we will address it. I think we are doing what is required. The only thing that I would ask Bill to make sure of is that when he writes a spec and puts down with what he really wants and we will comply with that.

Pinoli Can we say if changes are made, and A designation will be added to your code?

Thomas I just hate to see us get a large identification code system that you will need a book to interpret. It is not the intent to cover anything up. We can provide anything you want.

Schmidt I have a suggestion. I think it would be useful if they would put in writing proposed changes and then have those that are responsible for changing the code make everyone aware in writing. I heard Beckley say when I change the code, I change the number, but when I asked what he changed, he changed the number. That is what I heard him say.

Pinoli Don, I was going to ask you what happens when you get to the end of the alphabet?

Hall            You know this is one of things that was solved about 3 or 4 years ago. At the time there was no spec to do with filler whatsoever. Since that time there has been a spec and back then there was no reason to notify us.

Thomas        I am afraid that Don may have been leading up to something that there is a lot of misconception out there. I can only speak for shuttle.

Pinoli         My only comment, Don, is if we are going back in history and covering old ground, we cannot affect the past, only address the future. What we have heard from both of the prepreggers is that they recognize the problem and will make some changes in the future. You can be assured that in the future, if there are subtle changes, we are going to notify you. There will be more interfacing.

Larson         I think we have to begin from today's date and establish our relationship, even with the new code, but let's not go back into the past.

Thomas        Why don't you let Fiberite respond to the gray code inquiry.

Johnson      I would imagine that Fiberite has something similar to what Beckley described. If you have this thing where you want it, don't get into a confirmation number and make everybody go crazy. If you go back 20 years, you won't prove anything.

Pinoli         I think they are getting the message. I think that is one of the reasons that Corky wanted to bring it up. He doesn't want to go into any specific new code.

Thomas        Corky's argument was that when I get 4926, I don't know what I have, CSA, WCA or VCL. It is just 4926. When you look at the lot number, and go into the details of that lot, the data is there.

Larson         Speaking from a user standpoint, however, I have been through this trying to unscramble this before. You have to dig out old records and I think that if we consider the basic elements, the fiber, the filler, the resin, we won't have to undo the basic number, 4926. Just add something to that, a couple of letters, and I think we are covered. I was on the phone for one hour with Don Nichols and Mark Stucker and they were drilling me on this very subject. They are really serious about wanting something done. They don't mean to jam something down a prepreggers throat. They want something that will be accepted. A 15 letter code is not what they want. They really are serious. They want it for ASRM and RSRM.

Towne         I may get shot down internally on this. You expressed a concern that WCA is always WCA, no matter what it is made from. We talked about maybe WCA-1, WCA-2, we had a problem with that. One thought that came to my mind is if we had WCA followed by parentheses 430. Now we had internally, 400 was IRC precursor with WCA, 410 was INCA, 420 was AVTEX, 430 is NARC. Internally, we handle that. We know that, but that is never out to the industry. That does define the precursor.

Pinoli         You have a trace number on Amoco products?

Towne         Yes, but the precursor is internally traced.

Thomas        My question to you is if I deliver you 4926, do you want me to add 430, etc. to it? We already put that in our lot number.

Larson That level of detail should remain beginning today and going forward.

Pinoli Myles, would you be willing to share your designations with the community?

Towne We identify them by those 400 numbers, now whether it would be worthwhile to anybody else, maybe it would just further complicate things.

Pinoli If we have to respond back to NASA management, we can say this is the situation as it exists today. Here are the codes used to controll and monitored within the organizations. This is how Amoco does it. Here is their code. This is the way Fiberite does it, etc. Maybe that would go a long way in to making every one feel more comfortable. These things are being traced and we are maintaining control.

Thomas Would Myles be willing to accept part of that action item and let him describe his numbers.

Towne Yea, I'll do it.

Buechler If you could summarize this information in a packet, so that it could be used at all levels, it would be more helpful.

Johnson You're not talking just about NASA, but the whole industry.

Pinoli It'll probably go to the whole industry. That is what the committee is supposed to represent. There shouldn't be any secrets as far as I am concerned. Whatever you put in there, try to make it non-proprietary. Tom Paral out at Polycarbon will be called, too, to contribute their input.

Johnson Do you want this information sent to you?

Pinoli Yes, or to Bill Hall?

Hall Bill Armour, on the ASRM material that we are looking at, only the improved solution could have anything except a unique set of materials, right? This should go into the report that as we move into ASRM, 4 numbers means exactly 1 unique material.

Pinoli Yes, that is right. It is being evaluated as a unique product all its own.

Drake Couldn't we extend that same action item to Polycarbon?

Pinoli Yes, I did. I'll talk with Tom on that and I'm sure he will participate in that. We will have everybody represented on that this issue.

Drake From what was said, what if Titan 4 makes some new hardware out of the NARC and some more hardware out of AVTEX, and it gets mixed up and shipped. Is that still a possibility?

Thomas The numbering system won't prevent that.

Drake If he put WCA 420 and shipped it, or shipped it as just WCA.

Thomas I can only send AVTEX certain places and I can only send NARC certain places. Not everyone has qualified NARC.

Williamson Myles, when you ship out AVTEX WCA and NARC WCA, how do you differentiate those?

Towne Externally, I guess I am not sure, Jack. Internally, on is 420 and the other is 430.

Williamson When a shipment is going to the prepregger...

Thomas There has to be something that says it's AVTEX or NARC. There's got to be.

Towne It is shipped for a program and one program is requiring North American and one is requiring AVTEX.

Williamson Do you have a piece of paper that says that?

Towne When it goes out, I guess I am not 100% sure.

Thomas It may be shipped against the purchase order number, and the purchase order states whether it is AVTEX or NARC. But he would ship it back against the purchase order. Maybe that is where it is.

Rubin What is going to give the worker on the shop floor notification that the material is this WCA or that WCA.

Thomas Well, he's not going to know the difference between 420 and 430.

Rubin He will if your paperwork states the difference.

Thomas A purchase order can do the same thing.

Drake He didn't see the purchase order. The fabricator may have 4 or 5 different prime contractors. We had a problem with Hercules getting material, some time back, for the PAN program. If everybody along the way can't identify the material and they can only identify it by lot number, the shops don't operate like that.

Buechler There is a traceability problem. In such issues as foreign PAN versus domestic PAN in Titan 4, for example, Hercules has now got it going, is sure that they have the control to distinguish between foreign and domestic produced PAN. That is another aspect of this whole control problem. How do they do that? It is the same thing that we are talking about here. Out on the shop floor, how does that person receiving that material know whether it was made from domestic PAN or foreign PAN. There are huge consequences in the way control is being set up and implemented and ultimately recognized by the workers.

Pinoli That is why, if you put an A, or a B, connotation on it, that will carry through.

Buechler Not every single body, not every single purchaser, etc. is cognizant of that. That is the problem of implementing it.

Rubin But if it has an A after it, your shop paperwork is going to call for an A and if it says a C on the roll, the worker will not use it.

Larson Once these letters are submitted to the prepreggers and so forth, what is going to happen then, Pat?

Pinoli Bill, I and Cindy will sit down and put some dialogue together to summarize our efforts.

Larson Are you going to write and make a recommendation as to how it is to be used?

Pinoli Yes.

Larson And that will go back to the prepreggers and all of the suppliers?

Pinoli No, I think what I would like to do is take the response back from the prepreggers, carbonizers, weavers and pretty much say that internally, these people have done their job. They are maintaining control. What may be necessary is the people that are purchasing these products are going to have to specify an A, or B, or C attachment that is associated with changes made. I know that specifically for the D5 program, anytime there has been a major change, they will send a document out to the prepregger directly new identification. It is handled as a program directive.

Larson And you say only recommend one letter in addition to the regular code.

Pinoli Each program will probably have to handle it themselves.

Larson Is that going to be controlled by 1 letter, the fiber, the filler, the resin?

Pinoli Any change that particular program wants to monitor. If indeed they change the source of the fabric, ASRM will direct them to identify the change on their products.

Williamson You have a change order, don't you?

Larson In other words, with a letter A, each one of the suppliers would have the information on what letter A means? And then for B?

Pinoli Each one of those changes can something distinctly different. It could be a filler change, a fiber change, or a resin change.

Larson I don't see anything wrong with that.

Williamson That would change the gray code procedure that Poly has that I set up originally 28 years ago, but I would like to see that change made.

Larson There would have to be a separate legend sheet for each...

Williamson That is right. You will have the change order.

Larson Well, again, it can be made available by each one of the prepreggers and that updated legend sheet would identify all these different combinations.

Williamson If you have a specification and you change it, you have a specification change. It's the same thing.

Larson Yes.

Bennett It seems to me NASA is complicating things by insisting that they don't have to change their ---- of 5055B. If they allow a change...

Johnson I would like to ask a question. Why?

Hall                    Okay, are we talking about getting back to Ken, like the WCA, instead of 420 or 430, is going to be WCA-A, or B, or C, right? Is that what we are agreeing upon.

Towne                We haven't agreed upon anything.

Johnson            I think where you are coming from is you take 5055 and you are saying it is B or it is 5055C, or it is 5055D or whatever. Bill has classified it in his shop the way that it is classified in yours, I would think that you are going to make your people aware of this.

Larson                We would do that through this legend sheet.

Johnson            When you go out for a new change, a prepregger comes to you and says we have a change here that you should be aware of. You are going to accept it or reject it or whatever. Are you going to set up with a new letter?

Larson                A new letter. That should do it.

Thomas              I don't think it can be a simple A, B, or C because I think you are already got individual codes. Pretty soon you are going to have the 18 letter code and trying to describe everything you are trying to control.

Larson                For instance, letter A could be WCA, or whatever it is, and it would give the resin, it would give filler, etc. A would describe the whole, but if anyone wants to change the material in the future, this will change to B and you would give that new description in the legend sheet.

Rubin                What if you have 5 or 6 different specifications? What if 4926 here in the handout has six different specs for one batch of material specifications?

Larson                I don't know about specifications.

Armour                This group cannot change an Aerojet spec.

Rubin                What I am saying is, if you are looking for FM5055B, and you call it A and A has 4 different specifications that call for this material, but each one is different. How are you going to identify that?

Larson                I don't think really...

Pinoli                That is the manufacturer's problem.

Larson                That is right.

Pinoli                He has to identify the product that those specifications dictate. Case in point, say MX4926 and MX2994. We have a whole range of what that product is. If there is any change in the suppliers or materials, I would think that the easiest way to handle them would be to re-identify it as B.

Bennett              This is part of the problem though, Pat. You have 4964A, 4964B, 4964C, 4964D, all going out to the same program

Pinoli                The program is trying to stay away from that.

Bennett              No. NASA wants to be able to say....

Pinoli We are getting into equivalency.

Thomas Rather than try to solve it here, because I don't think we can, at least give us a chance to respond. Let Pat and them put it together and go from there.

Pinoli I think we ought to get it down in writing and see where we are coming from. I might make one final comment, the next meeting has been tentatively scheduled for Sacramento. Gary Brown has graciously committed to sponsor the next meeting at Sacramento in November.

Hall The first week of November is the JANNAF meeting, the Nozzle Technology JANNAF meeting. Our meeting will probably be the second week in November.

Pinoli We will try to get a notice out well in advance. Bill and I talked about putting together a small committee to work this issue of sizing and whether we approach it by using alternate methods of removing the sizing. We would like to put a committee together which will be constituted by someone from Polycarbon, Hitco, and Amoco, to work this and Bill Armour has offered to be the sponsoring organization. Hopefully we can get it accomplished by the time NASA/ASRM goes into production.

Towne This is the sizing of the white fiber?

Pinoli Yes. We want to hear all the viewpoints and options that we have available and try to pursue a solution.

Larson Is this a new task, Pat?

Pinoli It is not a new task under SPIP; we started it at NAR. Is this one that we want to continue sponsorship or do you want ASRM to sponsor it? I think we will get more action if the ASRM program handles it.

Larson I don't think we will be able to do that. I think that if we handle it in this committee, then it ought to be an SPIP program.

Pinoli To be reported out, yes. Let's put it this way, Jay. Are you prepared to pay the expense of supporting this effort in addition to the other on-going activities?

Larson Maybe I didn't understand. Are you saying...

Pinoli We are putting up a separate committee to work this issue on a direct program basis, as opposed to this committee with up to 10 different advisory tasks under study.

Larson So you wouldn't necessarily use this committee here then?

Beckley Clearinghouse.

Pinoli Yea, clearinghouse is a good word. I think that is what we can do. When it comes to being program specific, we will move it into the ASRM program to get the job done.

Larson Please keep one thing in mind and that is we have to justify our existence, this committee, and if we put the time and effort into it and charge our time to it, then we have to provide a report.



Pinoli We will report it out to the committee. As far as SPIP funding, the only funding that will be required will be funding for myself to sit in on the meetings. The other option is to say that SPIP will sponsor this but you better be prepared to handle the cost of bringing these people together. I don't have the money.

Thomas You mean that if I send him a bill, he will pay for my trip over here?

Drake Did you pay for anybody's trip to come over here?

Thomas I didn't know that. I have been coming to these meetings for two years and I haven't gotten a penny.

Larson Let me explain a little bit. If we want this committee to handle say, five or six ongoing projects, and they want to give support and they want this committee to give support to those five or six projects, we have to show progress. Progress is measured in their eyes by reports submitted and so I am hoping that whatever things that come along like this are not going to push us away from doing our regular tasks.

Pinoli We are wiping four advisement tasks off the table today.

Larson The only reason for my question is I am wondering if maybe that is not a worthy project to be a new task to replace one of those.

Pinoli It will be an advisement task that will be reported out. It is a cooperative program between ASRM and our committee. Just like some of the resistivity data has been generated as a cooperative program between ASRM and SPIP. I don't have any heartburn putting these two programs together.

Larson Well, I hope that before we dismiss, we will be satisfied by having some additional programs to replace those that are being closed out.

Pinoli I think we need some ongoing dialogue on density measurement, which is a new task. Along those lines, I think one of the problems that I want to avoid is getting too many things on our plate at one time. I think cutting back to three or four to concentrate our efforts on is more appropriate. Let's not bite off more than we can chew, unless more budget is made available.

Larson We are committing ourselves to close out a minimum of three per year as we were talking last night.

Pinoli I think we started out with five tasks under advisement and with that many you can only do a little bit on each one.

Thomas I don't think this group should recommend this morning a new task, but I think this is probably one of the most premier groups that have been put together in the carbon cloth industry. I would like to see this group continue and work along common goals. We have good communication between suppliers and the users and the end users and I would like to see that continue, but I don't think we can continue spinning our wheels. We are spending a lot of money on this and going down and beating the same dead horse over and over. I would hate to see this group disbanded for that kind of thing, but I think they have to be worthwhile tasks.

Towne I would like to suggest one right now. This has the potential of bringing NASA some money and that is to get rid of the damn sodium test. I think that is an area where NASA could really save some bucks.

Thomas I support that 100%.

Towne Whatever we need to do to move that along, I would like to see us working on it somehow.

Ismail It seems to me that here, this committee has really achieved our goal of straightening out the rayon fabric business and really whatever we are trying to add to the next phase, say phase II, is really the same old stuff we have been talking about. I think one should ask whether we could get really some real problems from NASA and solve them. I appreciate the oxidation tests, but I guess we are done with it. I mean you have been doing density for twenty or thirty years, Pat, and we are doing fine on density. I don't see any problem with carbon assay. Electrical resistivity is something to determine.

Pinoli What Cindy is bringing in on NMR...

Ismail NMR is something new. Helping NARC is something we are all obligated to do, but I don't see that there is a real place for, I am sure if NARC needs help from any of us, we would help, but it is not a full item for the agenda simply because I didn't see much of NARC being said yesterday. Everything is fine and dandy. My question is can we get some real problems from NASA and work on them instead of just going in circles?

Williamson Non-destructive testing in process needs to be addressed. It is a major problem. There are many, many dollars of material going through there and the time delay before we get a readout as to what you are doing is unacceptable. There are several approaches to it and I think that it is something that ought to be looked at.

Thomas Jack, I think that is an excellent suggestion and we should be working with Bill Armour and Aerojet an NDE type scanner to measure and evaluate at real time. We have been working on that and some strides have been made. I don't know that I would recommend that it be a task of this committee because I think that it is something that we could accomplish real time. I think we have to accomplish for the ASRM program, and we have to do it real time rather than putting it...

Williamson ----- has an ongoing program of doing just that and I think...

Ismail You know there is a meeting held by Ames Laboratory every year and it is called "Non-Destructive Testing of Materials" and it is a huge meeting. I agree with you that it is very important, but on the other hand I would rather work on problem that NASA is having today. I just don't know what their problems are. If we could get some way to NASA and say "what are the current....

Williamson I will bring up a question. What is the current rejection rate on RSRM hardware being fabricated today? It is higher than it has ever been in its history. You don't think that is a problem?

Ismail Yes, but that is not well defined enough.

Williamson There is a variation in the prepreg.

Ismail I think maybe even Phase I of our, or the first part of Phase II, should be sitting with NASA and trying to define problems. I think defining the problem is probably 30% of the job. I don't think

NASA is able to say, "We have this problem, work on it." I think they will just keep telling you that things when most of us would rather hear the real problem.

- Pinoli This committee was never set up to have definitive time elements, i.e. three months to solve this problem. Individual programs have engineering staff to solve immediate problems. What I thought our charter covered is to look at long term issues and basic problems that take time and don't have a definitive schedule.
- Larson The concern that I have had with Myles' request a few minutes ago to get rid of the test for sodium, is not, I don't think, left to us to say let's get rid of it. It is up to us to recommend how you test for it. Is that not right, Pat, Bill?
- Pinoli I think it would be appropriate for the committee to say that we have communication here.
- Towne I think those two statements up there of the objectives at the start of the meeting...
- Pinoli I think that is appropriate to say there is a consensus on the committee to say "this is a better test, this is a duplication. Why don't you save your money?"
- Thomas Myles has done a tremendous amount of testing on that and reached a conclusion and has presented it at least the last three meetings that I have been in. Why can't we take that and make a committee recommendation to NASA and the rest of the world.
- Pinoli If we are ready to do that, I will support it.
- Thomas He has got a pretty good set of data.
- Towne Pat, when Fiberite or Polymeric request fabric and you look at the cost, you can come up with \$X and then you add X and X. You come up with that sodium test and a few other things. By the time Fiberite and Polymeric do the tests that they have...
- Hall As ASRM comes on line, we are going from a 1-type prepreg to maybe 3. You have hot melt, you have post woven...
- Pinoli You have that new product, LDC.
- Hall Right. No we have cut it down to just two.
- Pinoli NASA may force us to cut those two into two. That is yet to be determined.
- Hall We know we are going to have new materials to be looking at and that is coming up very shortly. We have things in front of us that we know are going to be new and different like the test methods that we are going to use to qualify this new stuff.
- Drake I think this committee should be involved in round robin testing and standardization of the prepreg properties. There is a wide variety of techniques and methods used and that is getting into a broad problem area.
- Pinoli I will take that as an action item. What do you think, Bill, to identify those factors and get recommendations from the prepreppers.
- Drake Do some round robin testing.

Armour As you know we have put together an ASRM test methodology. It is a draft but we are heading down that road.

Hall Since we are going to be out at Aerojet next time, maybe we can get a copy of it and get it out to everybody and that will be one of the items that we discuss there.

Pinoli My thoughts on that, Bill, is to make the ASRM program focal point of the meeting.

Hall Ken, that will support what you are saying.

Drake Another area that seems fruitful is tag end round robin testing. Each contractor has his own tag end testing.

Pinoli That is not part of our charter. Our charter is only to pursue up to prepreg. However I agree with you, Ken. We should not stop at prepreg. We should work up to tag end testing.

Hall I don't see any reason why we can't. 3.1.1 is not active.

Pinoli That might be justification to recommend tag end acceptance testing be added to our charter.

Hall If 3.1.1.1 is not going to be active, we may work all the way through.

Drake You have a valuable group of people with the capabilities to follow it through with prepreg and tag end round robin testing.

Pinoli 3.1.1.1 was never concerned with acceptance testing. Its only concern was the fundamentals of testing composite materials. I separate that activity from acceptance testing. SORI does a lot of testing of the materials for the manufacturers and the end users. I think they are two separate issues and we should be free to add tag end testing to our charter.

Hall Myles, I want to thank you again for a very enjoyable visit. You did a good job.

**APPENDIX A**

**ISMAIL ISMAIL**



# Non-Isothermal Oxidation of Carbon Substrates in Air

## Part I: A Comparison Between Isothermal and Non-Isothermal Oxidation

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### INTRODUCTION

Carbon fibers and fabrics (CF) are essential materials for fabricating the carbon composites used in aerospace applications. When exposed to high temperatures in air, the CF gasify and the mechanical properties of composites degrade. To understand the oxidation kinetics and mechanism, the reaction may be performed under isothermal or non-isothermal conditions (referred to here as IC or NIC). The first objective of this work is to address how some experimental parameters can affect the results obtained under NIC. Then a comparison between the oxidation kinetics under IC and NIC is made. Finally, a summary is given on the advantages and drawbacks of isothermal and non-isothermal oxidation (IO and NIO) of carbons.

### EXPERIMENTAL

Several CF, chars and carbon blacks were examined. The present article focuses only on two substrates; Saran (a microporous char), and WCA (a graphitized rayon fabric). The physical/chemical properties of the two carbons and their kinetics of IO are outlined elsewhere [1,2].

Using a thermogravimetric analyzer (TGA), Cahn system 113, the as-received carbon (8-10 mg) was placed in a quartz pan suspended on the balance beam. While flowing air at ambient pressure over the sample at 50 cc/min, the TGA reactor temperature was increased at a heating rate (HR) maintained linear above 300 C; 1, 2, 5, 10, and 20 C/min. The decrease in sample weight due to gasification was recorded as a function of time and temperature until the entire carbon gasified.

### RESULTS AND DISCUSSION

The oxidation under NIC is sensitive to the experimental parameters including heating rate, sample size and flow rate. The latter is not critical in affecting the kinetics, as shown in Figure 1 for the highly microporous Saran char. Increasing the flow rate by a factor of 4 slightly affects the rates and raises the apparent activation energy ( $E_a$ ) from 47.1 to 51.8 Kcal/mole. The rates under IC, reported earlier [1], are at least one order of magnitude higher than those computed under NIC. Further, the values of  $E_a$  for IO (42.6 Kcal/mole) and NIO are close, indicating that the oxidation mechanism is essentially the same in both cases. Thus, for highly microporous reactive chars oxidized under either condition, the reaction takes place exclusively in Zone I [3]. That is, the oxidation kinetics are controlled by surface reactivity; chemisorption of  $O_2$  on active/reactive sites, located inside the micropores, and desorption of  $CO_2$  and CO to yield gasification products. With the present setup, air flow rate has little effect on Saran oxidation.

The NIO data can be presented in several ways. Figure 2 illustrates the burn-off (BO) curves which relate the percent of ungasified WCA fabric to oxidation time. Increasing HR shortens the time required to gasify the entire carbon or 50 % of it,  $t_{0.5}$ . When the HR rises from 1 to 20 C/min,  $t_{0.5}$  decreases from 140 to 13.5 min. The empirical relation

between the two is:  $(HR)^{0.78} \times t_{0.5} = 135 \pm 5$ . Figure 3 shows the dependence of BO on temperature, increasing HR displaces the thermograms to higher temperatures. A second empirical relation was developed:  $T_{0.5} = 750 + 115 \times \text{Log}(HR)$ , where  $T_{0.5}$  is the temperature at 50% BO. Combining the two equation gives:  $T_{0.5} = 1064 - 147 \text{ Log } t_{0.5}$ . The relation between time and temperature required to gasify 50 % of the CF is independent of HR.

Figure 4 illustrates the oxidation rate profile (ORP) taken from Figure 3. The ORP is a relation between the differential rates of oxidation (based here on the starting CF weight), and sample temperature. Increasing the HR not only shifts the ORP to higher temperatures but also raises the rates. This trend was verified for all the carbons studied (CF, Saran and blacks). With a lower HR, the carbon "sits" with  $O_2$  for longer periods of time and gasifies slower at lower temperatures. The product of "lower" gasification rate times "longer" interaction time yields a "large" amount of carbon gasified. This is not the only legitimate interpretation for the data. Heating under NIC is also associated with a lag between the sample and furnace temperatures. As the HR increases, the lag becomes larger. Using calcium oxalate as a standard with the present TGA, the largest lag for oxalate decomposition temperatures between HR of 1 and 20 C/min, was less than 35 C. Therefore, the results in Figures 3 and 4 are not only dependent on the carbon/oxygen system but also on the temperature lag imposed by the TGA setup.

A comparison between the Arrhenius plots of IO and NIO is shown in Figure 5. While the IO yields one line with an  $E_a$  of 40.9 Kcal/mole, the NIO plots are not linear. They show a continuous curvature; the slope starts high at the lower temperature then declines with increasing temperature. That is, there is a slight continuous drop in  $E_a$  as the oxidation progresses. Yet, for practical purposes, at least two linear regions could arbitrarily be defined on each line. The first is computed at BO below 5% and the second is between 5 and 55 % BO. The corresponding  $E_a$  values are 108-112 and 32-44 Kcal/mole, respectively. The first linearity can be attributed to sample activation and opening its micropore system. This step enhances the WCA surface area by as much as two orders of magnitude [4]. Once the structure is opened, the oxidation continues inside the micropores (second region) in a manner similar to that of the IO. The overall kinetics for NIO continues mainly in Zone I with minor contribution of Zone II which becomes increasingly significant at higher temperatures.

In Figure 1 and 5, the rates of IO are higher than those of NIO; the trend has been confirmed with many other samples. There are three possible explanations for this discrepancy. First, the pretreatment procedures used in each case are different. With IO, the samples were degassed at 1000 C and cooled to the projected isothermal temperature in  $N_2$ . Air was then introduced to the clean carbon surface which had fresh active sites. For NIO, the samples were heated in air

without treatment. The active sites were occupied and the surface was preserving the original impurities. Second, the rates of oxidation are calculated in different ways. The IO rates are computed on a global bases when the BO/time plot showed a constant rate of gasification. The oxidation rates below this linear region (beginning of oxidation) and above it (when the micropore structure collapses) are lower than the maximum rate of the middle linear region. With NIO, the rates are instantaneously computed at small temperature segments; they represent the rates encompassed by all different events occurring at a given time and short temperature range. Third, the structure of the carbon during IO is not the same as NIO. While with IO, the micropore system of WCA is opened at one temperature, it is opened gradually at multi-temperatures during NIO. As illustrated earlier, there is a large effect of activation temperature on developing porosity of this fabric [4]. The higher the temperature, the lower the extent of developing porosity. Micropore entrances are considered as the gates to the internal active sites.

In summary, both IO and NIO techniques are valuable tools to study the kinetics of carbon oxidation. The IO is more traditional and perhaps more fundamental than NIO. However, IO relies on obtaining a single oxidation rate that is normally computed either at a given BO (usually 50 %), or at the linear portion of the BO/time plot. Generating the Arrhenius plot for one sample requires several days or weeks. By contrast, NIO is a faster way for observing continuous trends, it is more realistic than IO. When a carbon composite, for instance, is exposed to high temperatures in aerospace applications, its temperature gradually increases and the recession likely occurs under NIC.

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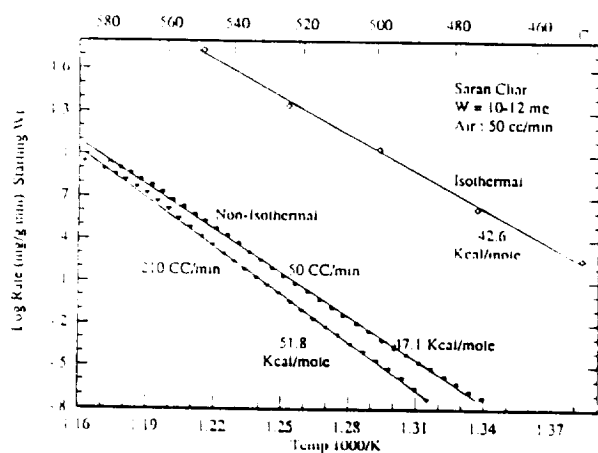


Figure 1: Isothermal and Non-Isothermal Oxidation of Saran

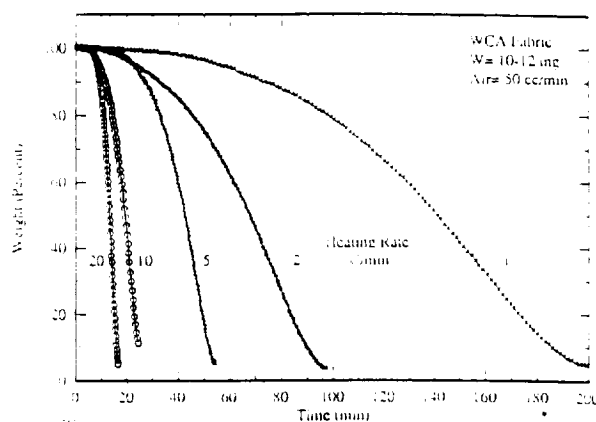


Figure 2: Non-Isothermal Oxidation of WCA - Variation of Weight Loss with Time.

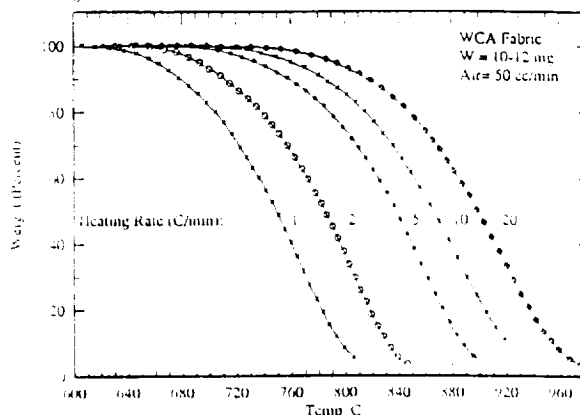


Figure 3: Effect of Heating Rate on Non-Isothermal Oxidation of WCA Fabric

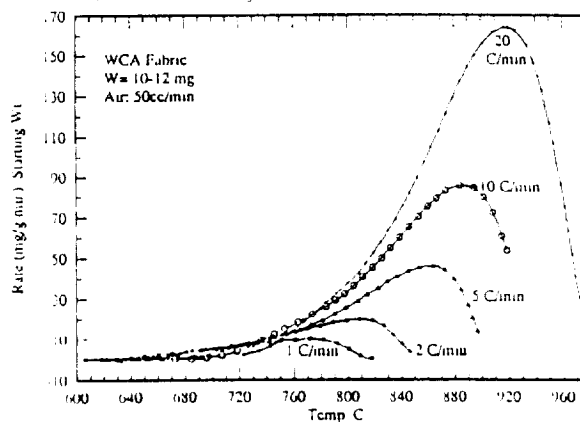


Figure 4: Dependence of Oxidation Rates on Temperature and Heating Rate

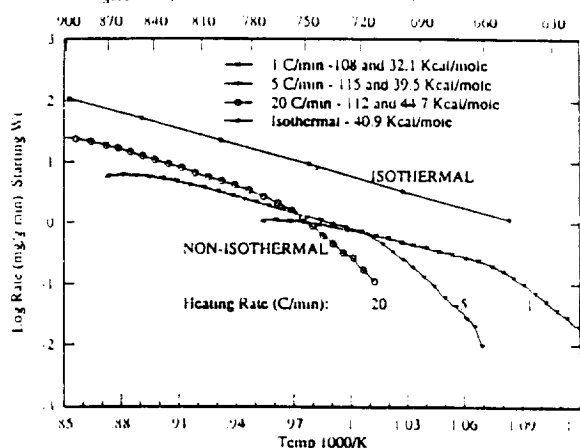


Figure 5: Arrhenius Plots of WCA under Isothermal and Non-Isothermal Oxidation



# Non-Isothermal Oxidation of Carbon Substrates in Air

## Part II: Relative Reactivity of Fibers and Fabrics

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### INTRODUCTION

In part I, a comparison was made between isothermal and non-isothermal oxidation kinetics of several carbon materials. The advantages and drawbacks of each type of oxidation were outlined. When performed under comparative experimental conditions, the non-isothermal oxidation (NIO) is a fast, informative and realistic means for evaluating the oxidation kinetics. In this article, we start with a brief illustration of the concept, using well characterized carbon blacks. Then we address some critical issues and drawbacks that considerably affect the results. Finally we apply the method to compare the relative reactivity of several types of carbon fibers/fabrics (CF) obtained from different sources.

**Concept:** The experimental procedure for NIO is simple and only requires a thermogravimetric analyzer (TGA). A known weight ( $W$ ) of the CF is placed in a quartz pan suspended on the balance beam. Platinum pans are avoided because this metal is an excellent catalyst for the  $C/O_2$  reaction. With air flowing above the sample, the TGA furnace temperature is raised at a constant heating rate (HR) until the entire carbon gasifies. During gasification, the change in sample weight as a function of temperature and time is stored (in this work, the three variables were saved every 15 seconds). The data can be presented in several ways (see part I), but the most informative ones are the oxidation rate profile (ORP) and Arrhenius plot. The ORP yields a temperature corresponding to the maximum oxidation rate,  $T_{max}$ , which is characteristic of the CF. The Arrhenius plot predicts the oxidation mechanism. Further, either plot can compare the relative reactivity of different CF over a wide temperature range.

### RESULTS AND DISCUSSION

Figure 1 displays the Arrhenius plots of five carbon samples which have been well characterized by several authors over the past three decades. The NIO was executed with  $W=40$  mg,  $HR=10$  C/min, and air flow rate (AFR)=100 cc/min. The values of active surface area (ASA) of SP-1, V3G, Graphon, V3, and Saran, as determined by oxygen chemisorption techniques [1], are 0.05, 0.20, 0.22, 11.3 and 37  $m^2/g$  respectively. ASA may be taken as a reasonable index for the reactivity of carbons [1]. Looking at Figure 1, we note that for the five carbons, the sequence of reactivity is the same as their corresponding order of ASA. At one extreme, the highly reactive disordered Saran char, occupies the right side of the graph and is displaced upwards. The char gasifies with high rates at lower temperatures. At the other extreme, the least reactive well-ordered SP-1 graphite is at the far left side of the graph and slightly displaced downwards. SP-1 is one of the hardest graphitic materials to gasify. The V3G was prepared from its precursor V3 by

graphitization at 2800 C. As expected, V3G is less reactive in air than V3, this is also evident in Figure 1. By applying this concept to several CF, we can predict their relative reactivity, as it will be discussed shortly.

The data displayed in Figure 1 show two distinct regions with the graphitic materials, and a curvature with V3 and Saran plots. At the beginning of oxidation, the rates increase sharply with temperature then decline to almost constant values independent of temperature. With graphitic carbons, the oxidation kinetics starts in Zone I then "jumps" to Zone III [2] until the carbon is completely gasified. Zone II is either absent or only present for a short time during the transition from Zone I to III. At the beginning of oxidation, carbon gasification rates are solely controlled by the chemical reactivity of the surface (Zone I). Then suddenly, the rates attain a constant value independent of sample nature. The rate limiting step becomes the diffusion of air to the external surface of the carbon (zone III).

With the TGA, the apparent oxidation mechanism is very dependent on the experimental conditions selected for the run. Figure 2 illustrates this point. By changing  $W$  from 40 to 10 or 5 mg, and  $HR$  from 10 to 5 C/min, the shape of the plots and their locations change. Reducing the starting weight of the carbon (lower bed height) and reducing the heating rate, not only yield a more linear plot but also gasify the carbon at lower temperatures. Using a small value of  $W$  and a high AFR with moderate  $HR$  is probably the best combination to perform the NIO. Yet, if  $W$  is too small and AFR is too high, the error in measuring oxidation rate is significant due to particle entrainment and the noise in balance signal. For these reason, most of the study on CF reported here was executed with  $W=10$  mg,  $HR=5$  C/min, and  $AFR=50$  cc/min.

Figure 3 illustrates the ORP for three graphitized CF namely, T-300 polyacrylonitrile (PAN) fiber, VSB-32 pitch fiber, and WCA rayon fabric. The relative reactivity, based on  $T_{max}$ , is  $T-300 > VSB-32 > WCA$ . Values of  $T_{max}$  for T-300, VSB-32 and WCA are 764, 824 and 862 C, respectively. The corresponding ASA are 0.067  $m^2/g$  for the graphitized T-300 [3], 0.029  $m^2/g$  for the VSB-32 [3], and 0.068  $m^2/g$  for WCA [4]. These values do not completely support the ORP of Figure 3, as it was the case in Figure 1 with the carbon blacks. For example, the ASA of T-300 and WCA are the same but the T-300 gasifies faster than the WCA. This indicates that the ASA is not always a good parameter for indexing the reactivity of CF. Perhaps the values of  $T_{max}$ , taken under fixed TGA experimental conditions, are more appropriate for this purpose.

There are two remaining features in Figure 3 that need further clarification, the height of the peak and its width. From the

limited data, it appears that there is a correlation between the width and height. While with WCA, the peak is broad and short, it is narrow and high with the VSB-32. The WCA gasifies over a wider (and higher) temperature range than the VSB-32. It is possible that the physical geometry of CF has a large effect on ORP. With the weaved WCA fabric, the accessibility of Air to the internal surfaces is somewhat restricted. As a result, the rate at  $T_{max}$  is suppressed. The VSB-32 fiber has a larger filament diameter (11 micron) than the graphitized T-300 (5.8 micron) [3]. Therefore, with the VSB-32 fiber, the volume of voids/gaps between the filaments is larger, and the accessibility of air to the internal surface is high. Possibly this is the reason for obtaining the sharpest peak in Figure 3. At the present time, these speculations are offered until verified experimentally.

Finally we consider the NIO data on carbonized and graphitized rayon fabrics. For the sake of clarity, only typical examples, representing the limits of each group of fabrics, are shown in Figure 4. At the left side of the graph, two (graphitized) WCA samples represent the limits of 15 other WCA fabrics. They are the least reactive CF. In the middle of the plot are curves for four carbonized rayon fabrics: CCA-3, CSA, and VCL. In this case, the activation energy is 36-43 Kcal/mole, which is close to that of Saran (see part I). The oxidation is taking place in Zone I where the surface reactivity controls the kinetics. Even though these fabrics are highly microporous materials, there is no diffusion limitations on the oxidation reaction. That is, Zone II is absent [2]. There are two reasons to explain this: either the oxidation temperature is low for imposing a diffusion barrier, or the micropores are converted to larger meso- and macro- pores during gasification.

The last class of rayon fabrics is shown in Figure 4 by the data of CSA-4671. The behavior of this fabric in air is unique. To the authors' best knowledge, this is the first time to report this peculiar Arrhenius plot for a typical C/O<sub>2</sub> reaction. It was reported on coals and was attributed to loss of volatiles [5]. In the present work, the oxidation rates of the fabric increase, then level-off, and finally increase with temperature. This behavior will be further discussed in part III of this series. Since the oxidation characteristics of this class of fabrics is not fully understood, and because of their high reactivity in air, the utilization of this group of fabrics is not recommended for manufacturing carbon composites.

**ACKNOWLEDGEMENT:** The financial support of Air Force Office of Scientific Research under contract number F04611-83-C-0046 with the Phillips Laboratory OLIAC is highly appreciated. The authors acknowledge Mr. Pat Pinoli for graphitizing the T-300 fiber.

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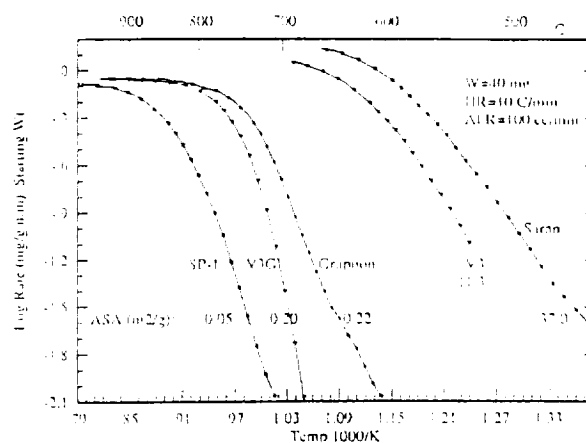


Figure 1: Arrhenius Plots for Non-Isothermal Oxidation of Carbons

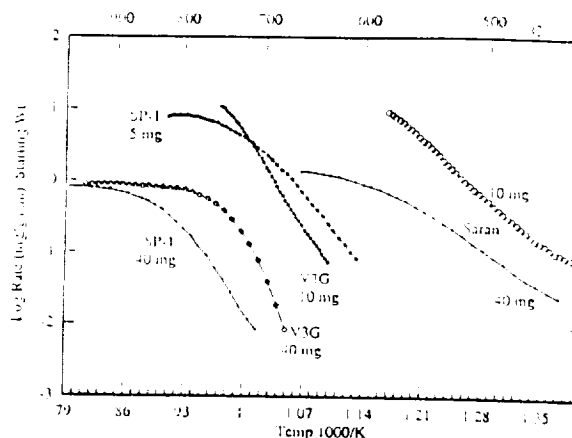


Figure 2: Effect of Sample Size on Non-Isothermal Oxidation Rates

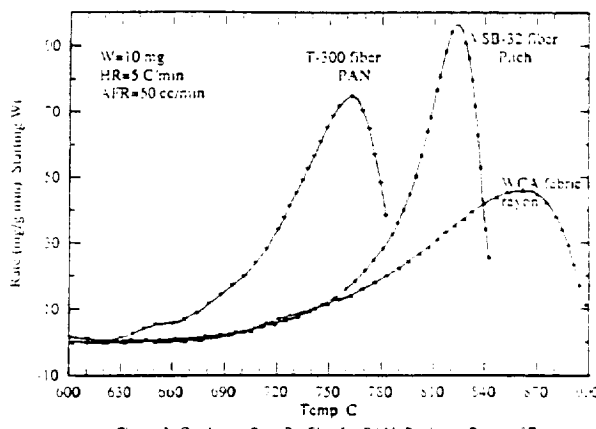


Figure 3: Oxidation Rate Profiles for PAN, Pitch and Rayon CF.

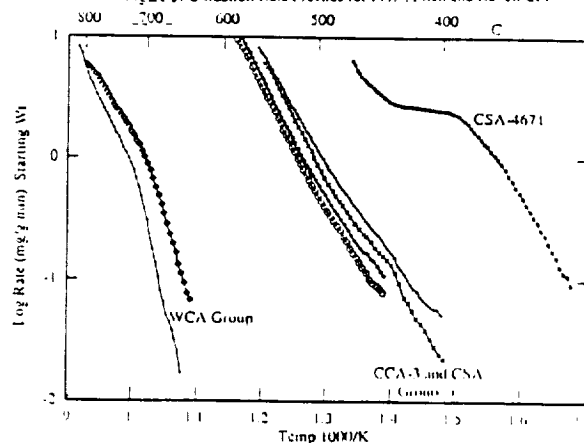


Figure 4: Comparison between NIO Rates of Different Rayon Fabrics

# Non-Isothermal Oxidation of Carbon Substrates in Air

## Part III: The Unusual Behavior of Some Rayon Based Fabrics

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### INTRODUCTION

In part II of this series, the non-isothermal oxidation (NIO) of several carbonaceous materials, including carbon fibers/fabrics (CF), was discussed. The Arrhenius plots of most carbonized rayon CF, belonging to the CCA-3 and CSA series, showed a distinct linearity over a reasonable range of burn-off (BO); 10-60%. Yet, in the case of CSA-4671 fabric, the Arrhenius plot showed the peculiar behavior illustrated here in Figure 1-plot A. The NIO rates, based on starting sample weight, first increased with temperature (or BO up to 12%). The Arrhenius plot in this (first) region was slightly curved, showing a continuous decrease in activation energy ( $E_a$ ). Then the rates leveled-off during the next 50 C temperature increment, yielding the second region. Finally, the rates increased with temperature until the complete BO of the fabric was achieved (third region). The objective of this communication is to address this peculiar behavior.

### EXPERIMENTAL

Four CF were examined; their properties are reported elsewhere [1]. While sample A (CSA-4671) has the highest Na level (3153 ppm), sample B (CCA-3 1641 B) has the lowest (13 ppm). Samples C (CSA-96813) and D (CCA-3 K15 D) have the nominal level of Na noted for other carbonized rayon fabrics (100- 500 ppm) [1]. The NIO kinetics was studied with a TGA apparatus, Cahn System 113. Prior to oxidation, most of the samples were evacuated to  $10^{-5}$  Torr at room temperature (RT), flushed with ultra high purity Ar to ambient, heated under Ar flow (50 cc/min) to 1000 C, held at this limit for 30 min, and finally cooled to RT. This treatment is designated here as (O) for outgassed. Air was then injected at 50 cc/min to replace Ar, and the furnace temperature was raised at a designated heating rate (HR), kept constant above 300 C, until the complete carbon BO was achieved. Additional experimental details on HR and sample weight (W) are given on the graphs and in the text. In a few cases, the NIO was carried out in "one shot". That is, starting from RT, the CF was just oxidized in air (50 cc/min) at a constant HR without prior evacuation or heat up to 1000 C in Ar. The experiments performed in this manner are designated as (AR) for as-received fabric.

### RESULTS AND DISCUSSION

Figure 1 displays the most puzzling, yet interesting, finding. The peculiar Arrhenius plots, with their three oxidation regions, were only obtained for the samples with the highest and lowest Na levels; CSA-4671 and CCA-3 1641 B. Yet, all other rayon CF examined, with nominal Na levels, yielded a reasonable Arrhenius line with  $E_a$  close to 40 Kcal/mole. Typical examples in Figure 1 are samples C and D. The values of  $E_a$  are in line with the published values for C/O<sub>2</sub> reaction.

Let us focus the attention first on sample A. The peculiar behavior can be attributed to two possible explanations. First, the catalytic effect of Na may be more pronounced at the beginning of oxidation (first region) and diminishes at higher temperatures due to particle agglomeration (second region). This region could be representing the beginning of the uncatalyzed reaction which continues through the third region to a complete BO. Since in the first region,  $E_a$  decreases with increasing temperature, this explanation is ruled out.

Second, the peculiarity may be somewhat related to the effect of pretreatment (O vs AR) on fabric surface prior to NIO. From Figure 2, the ORP plots after the outgassing (O) treatment are shifted to higher temperatures. Using the as-received (AR) samples without pretreatment not only lowered  $T_{max}$  but also yielded a different ORP especially in the first and second regions. Thus, the presence of functional groups and/or other surface impurities enhanced oxidation rates. To separate the effect of functional groups from that of impurities, the CSA-4671 fabric was first cleaned (O treatment). Then it was exposed to an air flow (50 cc/min) for 24 hours at 50, 75, 100, 125, 150, 175, and 200 C. This procedure removed the impurities but "loaded" the surface with functional groups to different extents, depending on chemisorption temperature. Figure 3 shows that as chemisorption temperature increases to 150 C, there is an increasing weight gain because more functional groups are added to the surface. The maximum uptake was 0.28 % O<sub>2</sub> (at 150 C) which corresponds to an active area of 8.75 m<sup>2</sup>/g. This computation was based on the value of 0.083 nm<sup>2</sup>/active carbon atom as proposed by Laine, et al. [2]. At 200 C, the rate of gasification, occurring concurrently with chemisorption, was significant. After 10 min of exposure to air, the net effect was a weight decrease. That is, the sample was activated during chemisorption.

Figure 4 displays the ORP of the CSA-4671 fabric before and after chemisorption to different levels. The introduction of C-O functional groups displaces the plot and  $T_{max}$  to the left, this trend is qualitatively similar to that of Figure 2 with one exception. The shape of all plots in Figure 4 is not similar to plot I in Figure 2, which was taken on the AR fiber. This suggests that the external surface of the fabric is contaminated with some impurities that are removed by heating to 1000 C. For chemisorption at 200 C, however, there is a distinct dip (Figure 4) in oxidation rates at 430-440 C. As shown in Figure 3, this sample has been activated during the chemisorption reaction. The activation process, together with the high population of functional groups, are clearly responsible, in part, for exaggerating the peculiar behavior. It may also explain why the CCA-3 1641 B fabric, with the exceptionally low Na content, showed the same peculiar behavior (Figure 1). Apparently sample B went through some purification process that removed the Na to a level well below the nominal. With it, the fabric was activated and its active area became higher. It is also

possible that the external surface of the fabric has acquired additional super active sites [3]. Thus, the "penalty" for removing Na which catalyzes the C/O<sub>2</sub> reaction was to end up with a fabric that was very reactive to O<sub>2</sub> due to enhancement of active area.

The reason for the peculiarity of the CSA-4671 fabric is different, it is the presence of high levels of Na. Figure 5 compares the ORP of the CSA-4671 fabric before and after washing with double distilled water (DDW). Both oxidation profiles were executed after the normal outgassing (O) procedure. Washing with DDW was carried out overnight and reduced the Na level from 3153 to 1773 ppm, the process removed essentially the Na present at the external surface. Removal of Na displaced the ORP to the right (less reactive fabric), and it considerably suppressed the first and second region. The shape of the ORP for the washed sample is now less peculiar and similar to those obtained with other fibers.

In conclusion, for carbonized rayon fabrics, neither a very high nor a very low level of Na is desirable. At one extreme, the C/O<sub>2</sub> reaction is catalyzed by Na. At the other extreme, the surface is activated and the rate of uncatalyzed reaction is high. A compromise has to be made between the two effects to obtain the least reactive fabric.

**ACKNOWLEDGEMENT:** The financial support of Air Force Office of Scientific Research under contract number F04611-83-C-0046 with the Phillips Laboratory OLAC is highly appreciated.

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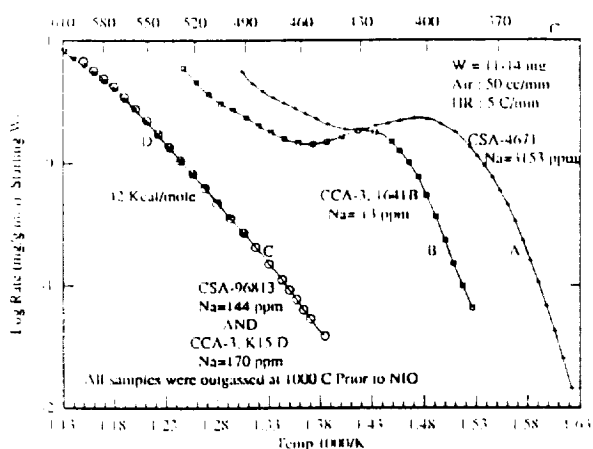


Figure 1. Arrhenius Plots for NIO on Rayon fabrics in Air.

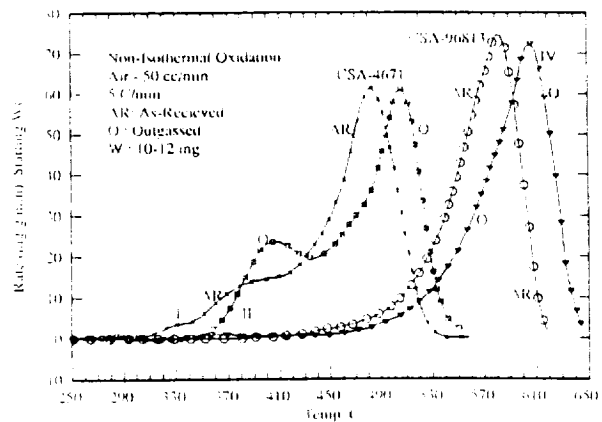


Figure 2. Effect of Outgassing on Kinetics of NIO.

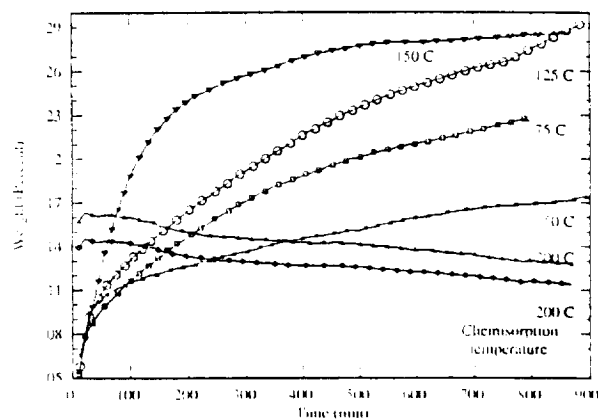


Figure 3. Oxygen Chemisorption on CSA-4671 Rayon Fabric.

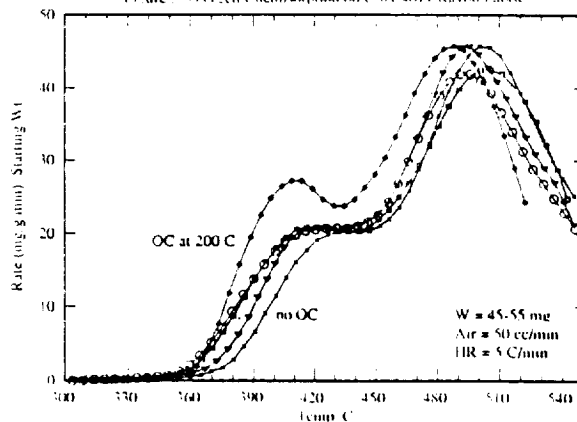


Figure 4. Effect of Oxygen Chemisorption (OC) on Fabric Oxidation.

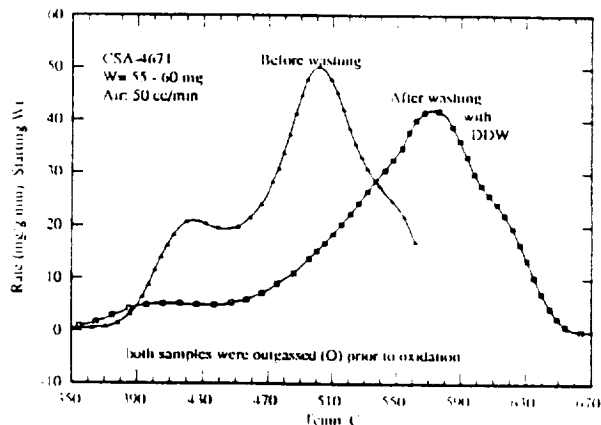


Figure 5. Effect of Sodium Removal on Oxidation Rate Profiles.

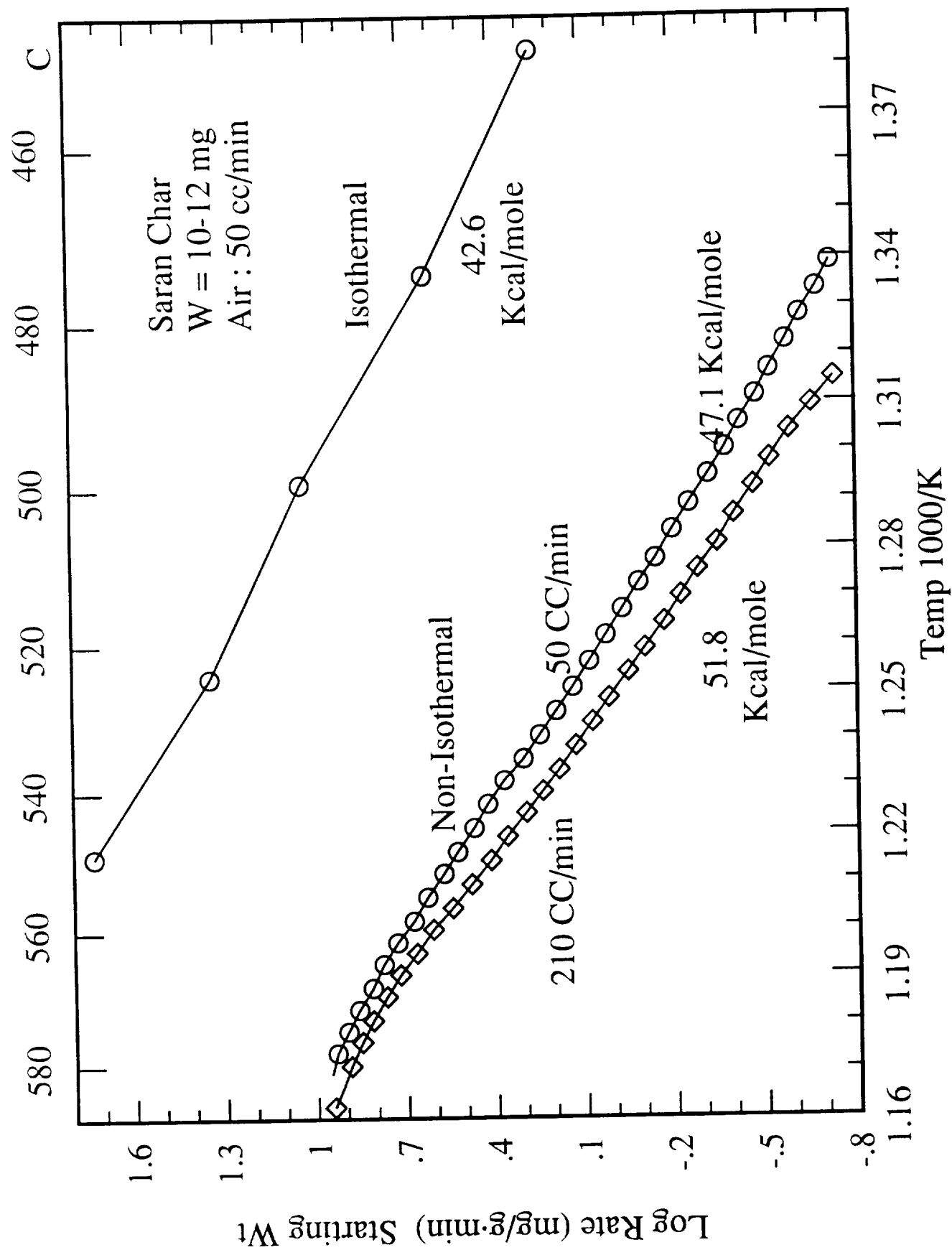


Fig 1: Isothermal and Non-Isothermal Oxidation of Saran

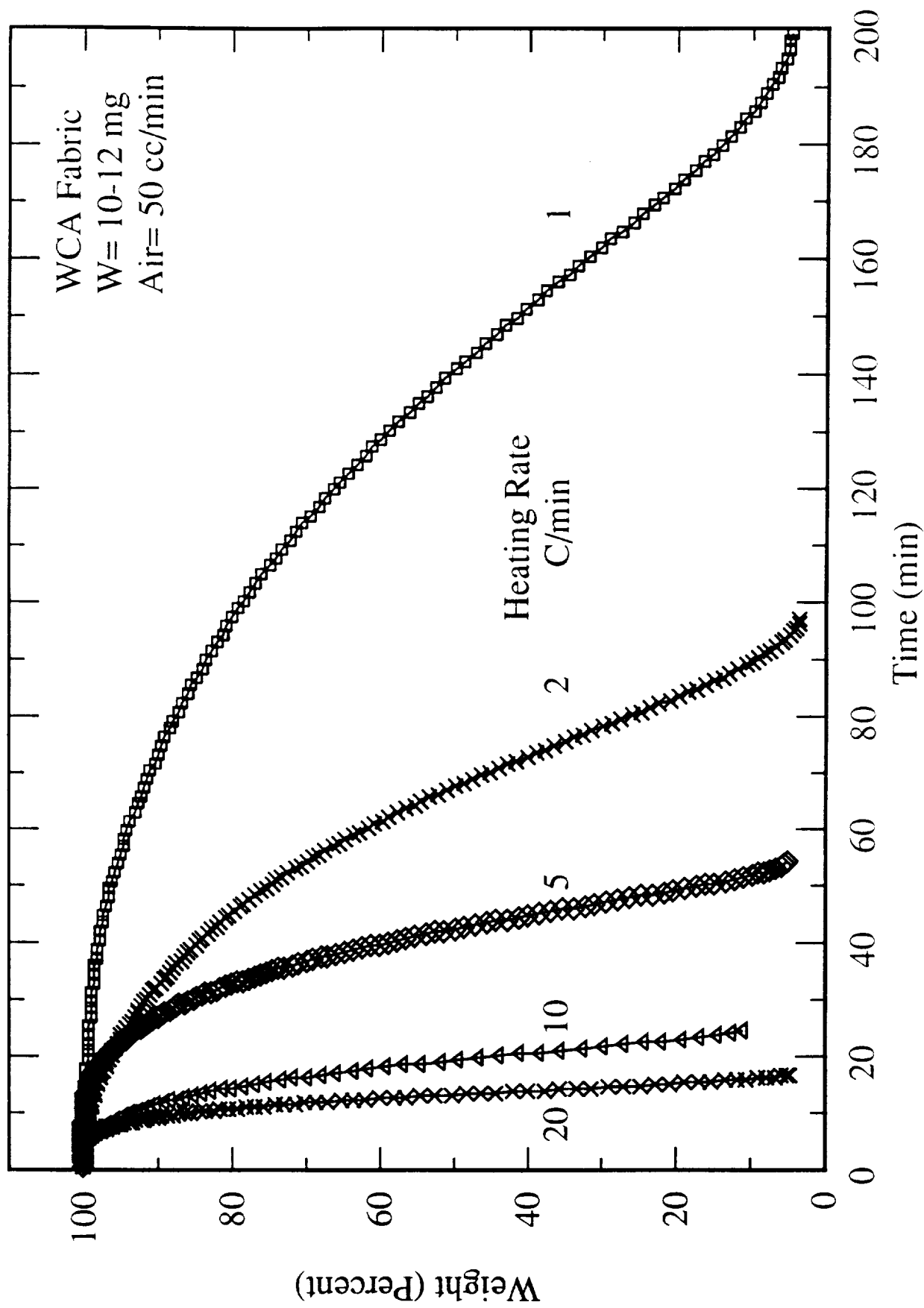


Fig 2: Non-Isothermal Oxidation of WCA - Variation of Weight Loss with Time.

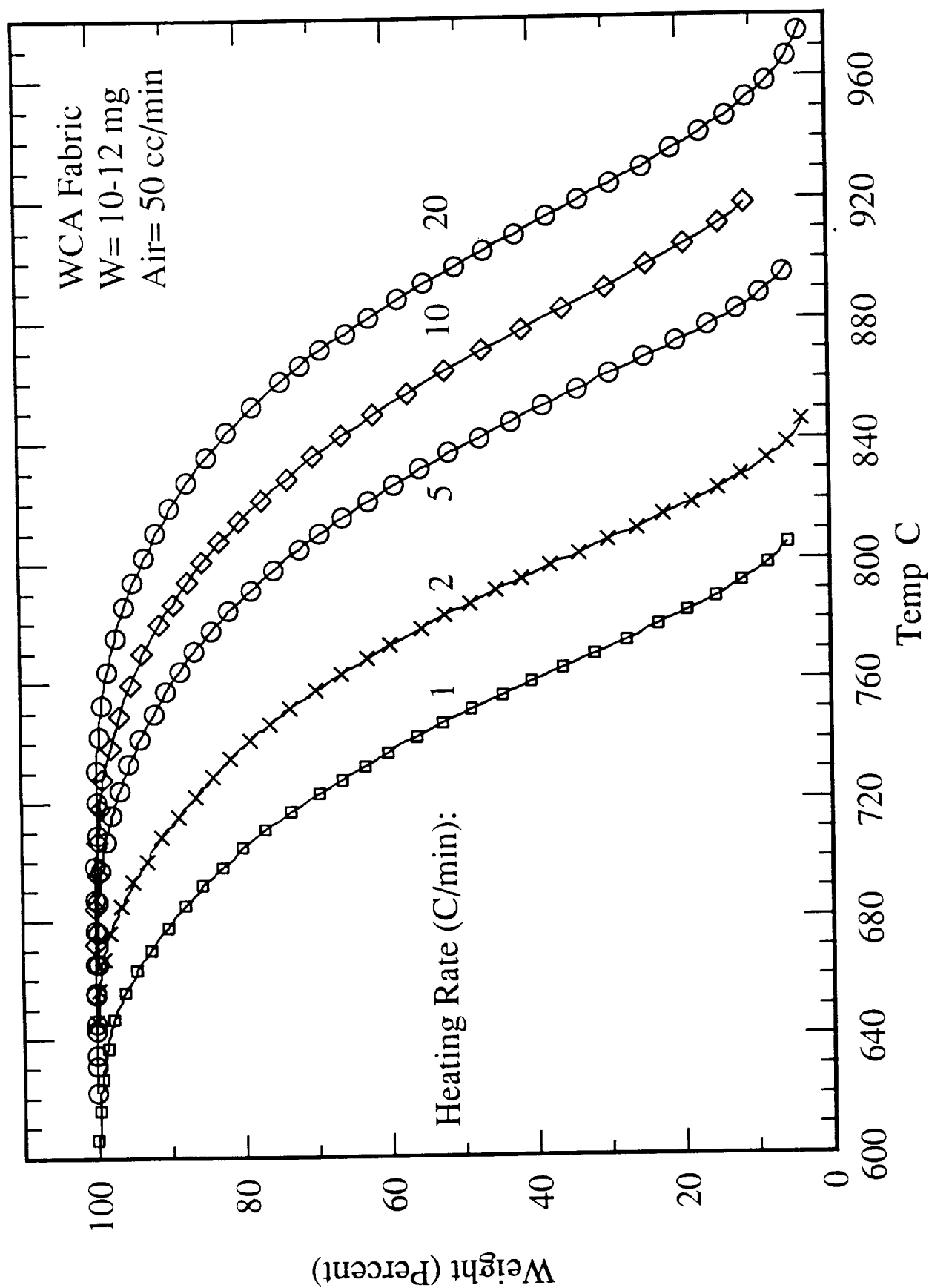


Fig 3: Effect of Heating Rate on Non-Isothermal Oxidation of WCA Fabric

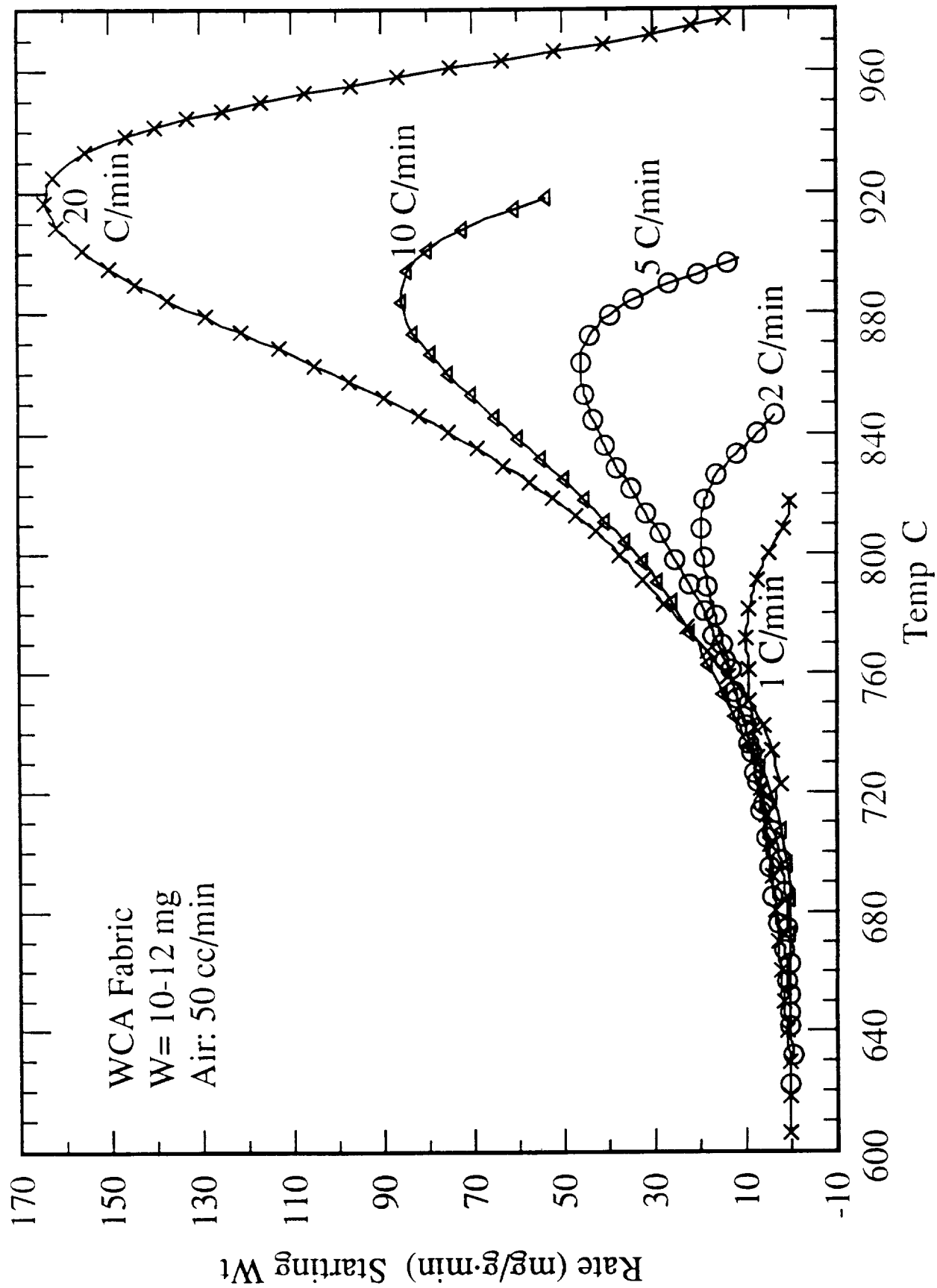


Fig 4: Dependence of Oxidation Rates on Temperature and Heating Rate



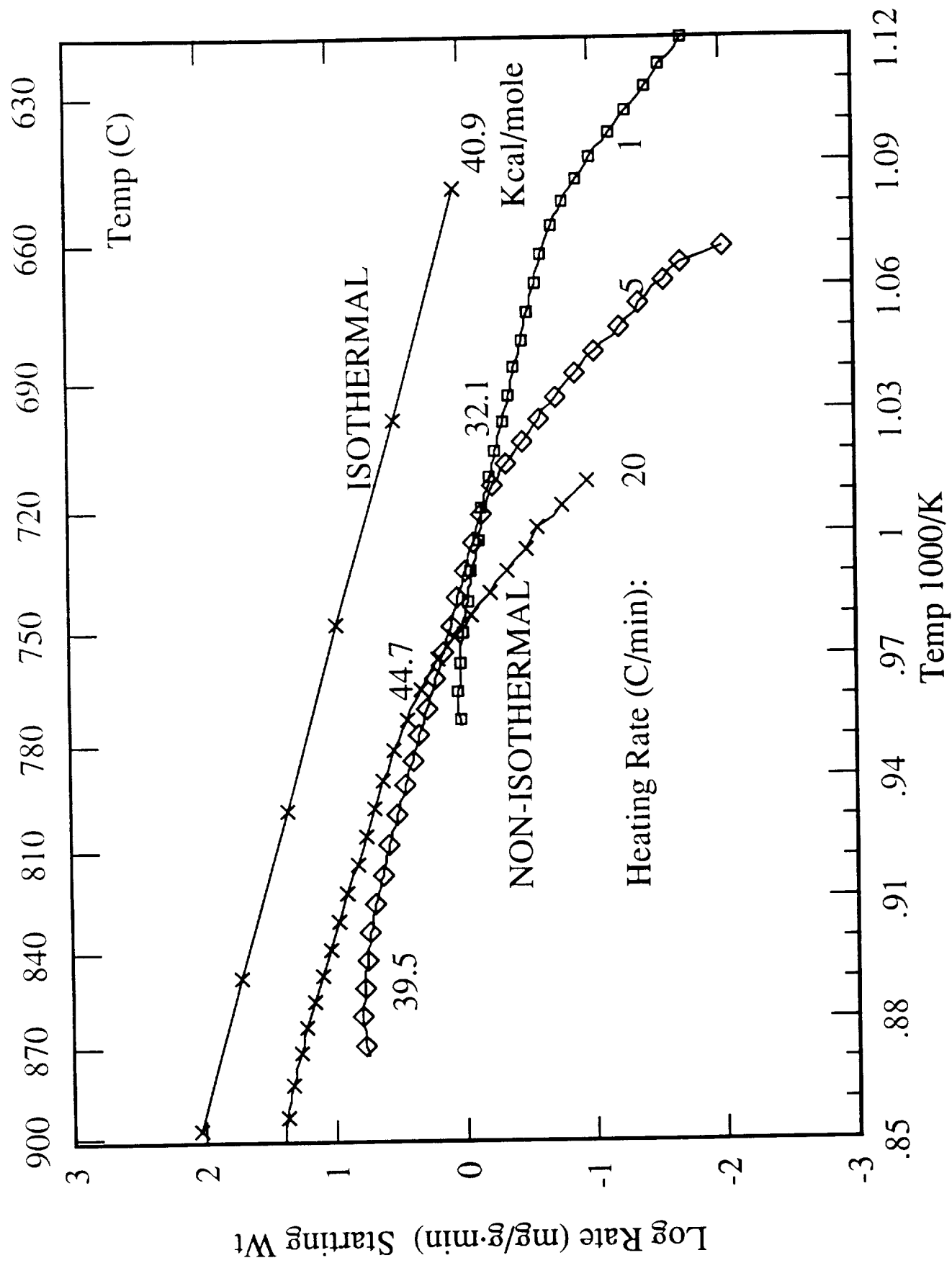


Fig 5: Arrhenius Plots of WCA under Isothermal and Non-Isothermal Oxidation.

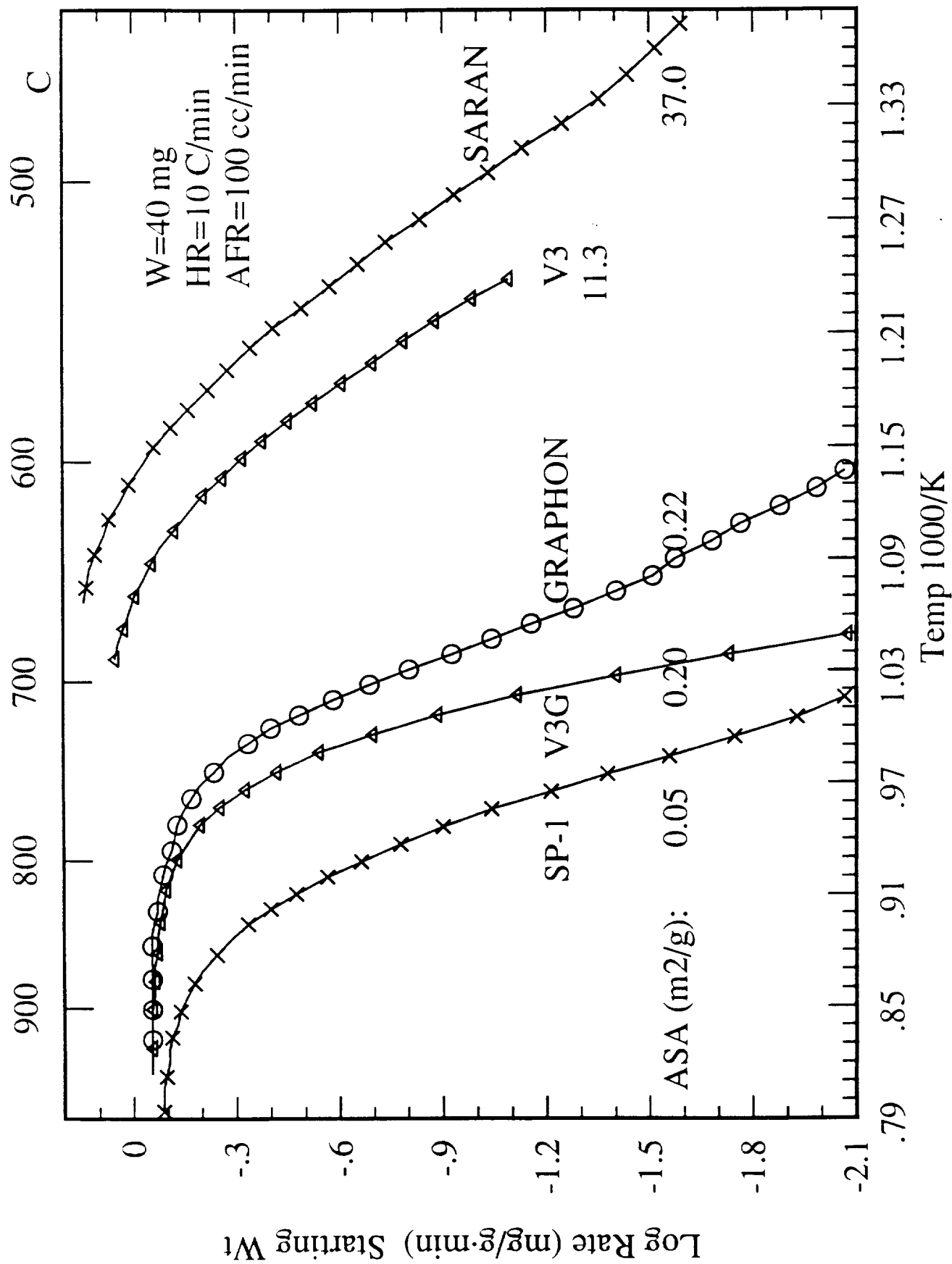


Fig 6: Arrhenius Plots for Non-Isothermal Oxidation of Carbons.

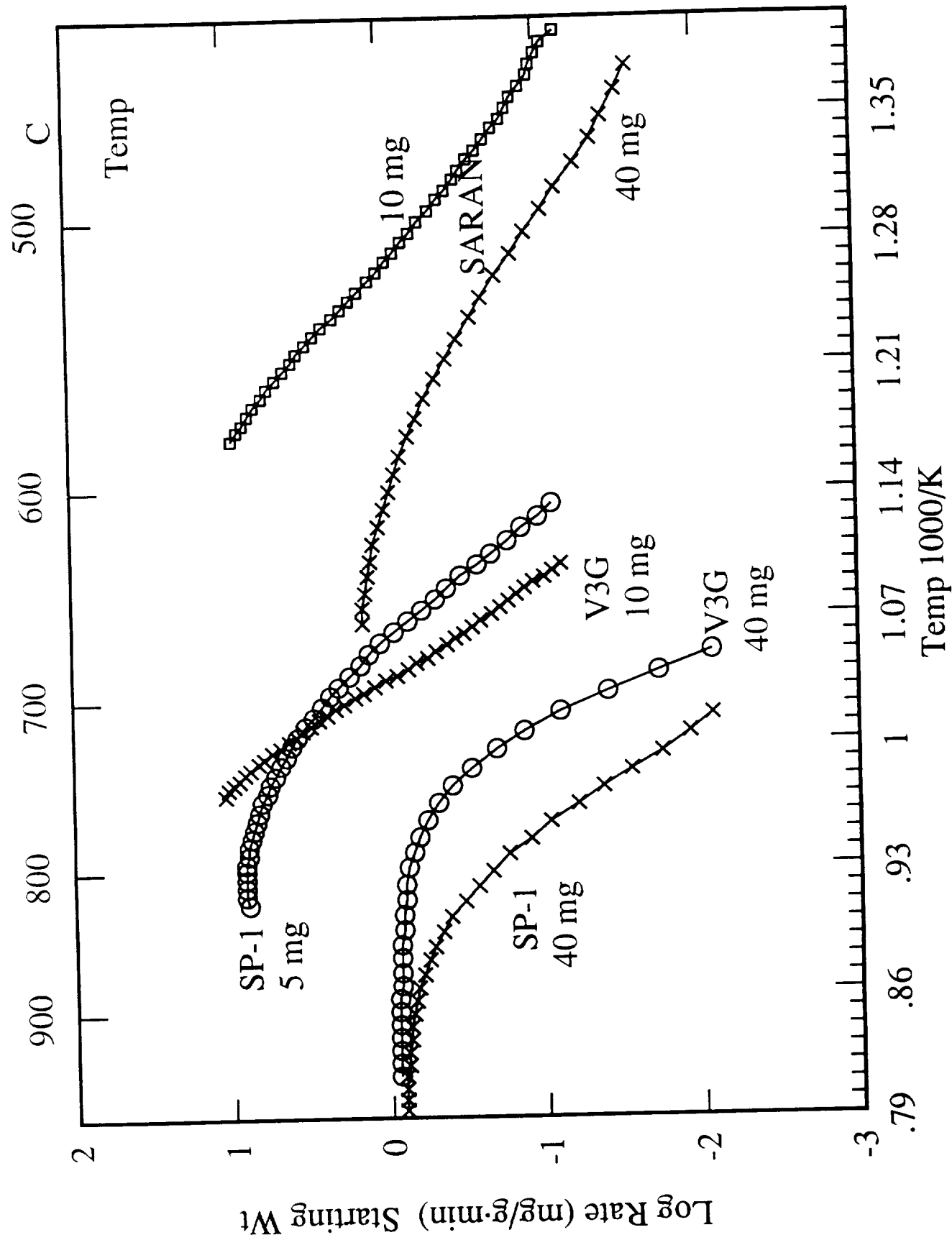


Fig 7: Effect of Sample Size on Non-Isothermal Oxidation Rates.

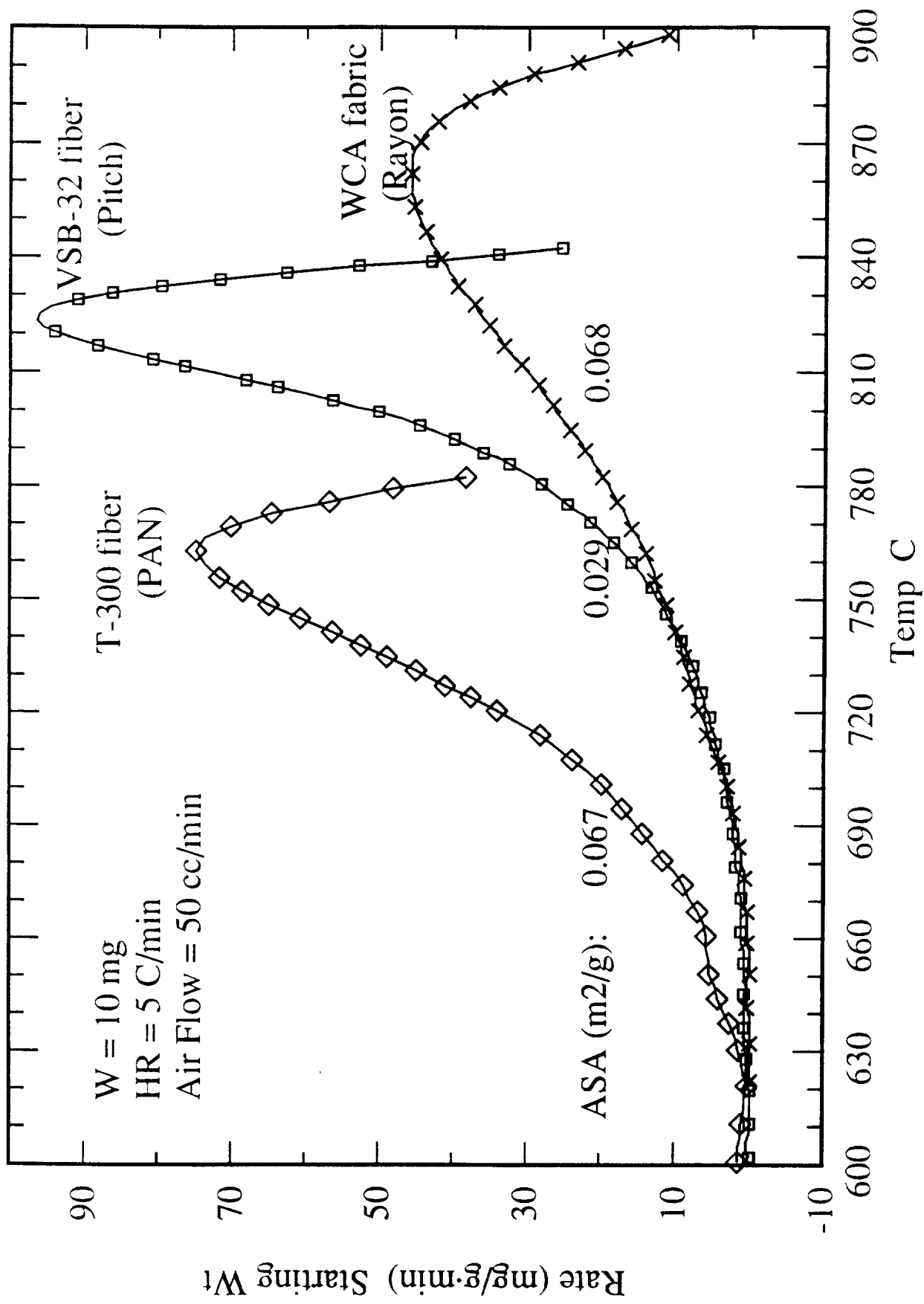


Fig 8: Oxidation Rate Profiles for PAN, Pitch and Rayon CF.

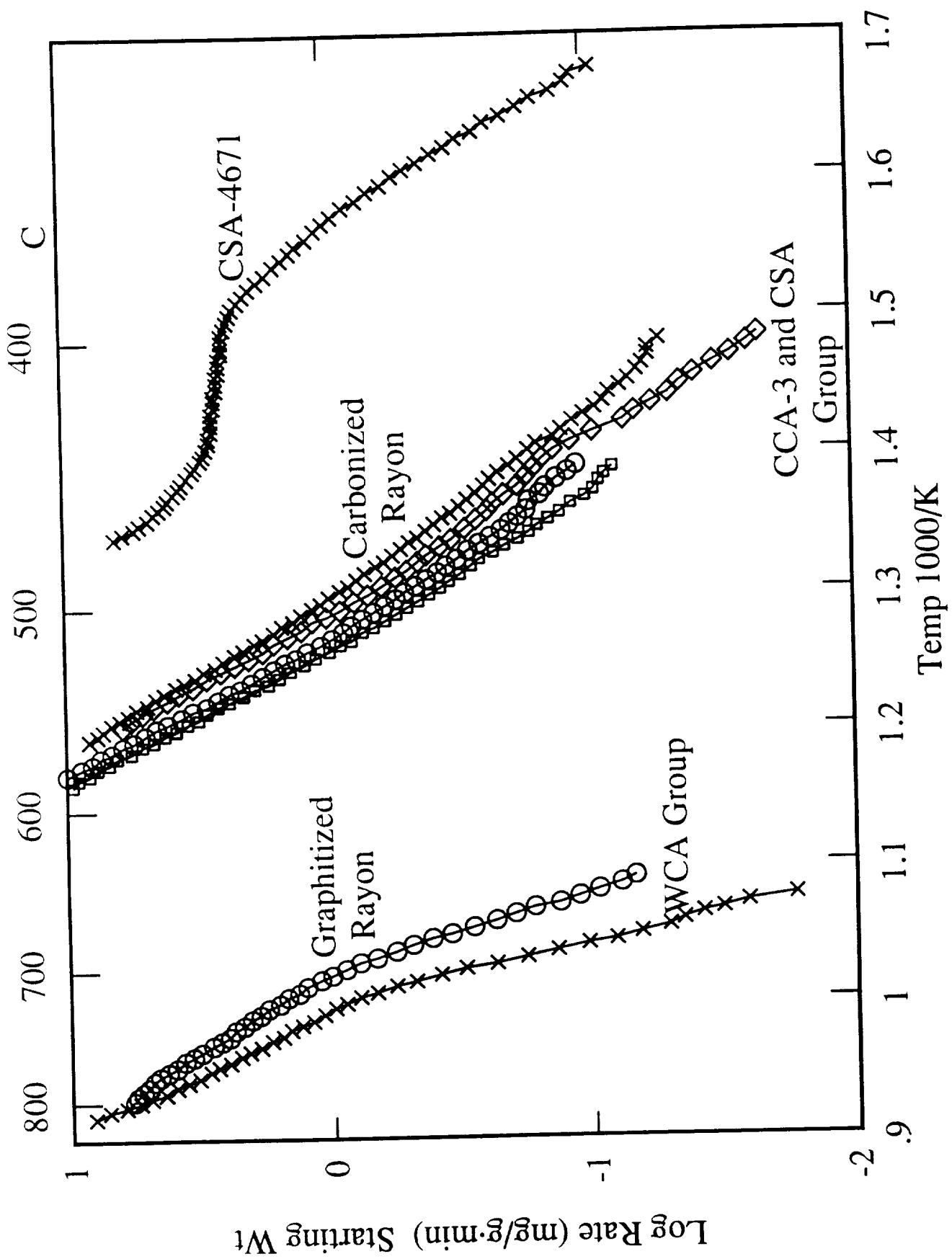


Fig 9: Comprison between NIO Rates of Different Rayon Fabrics.

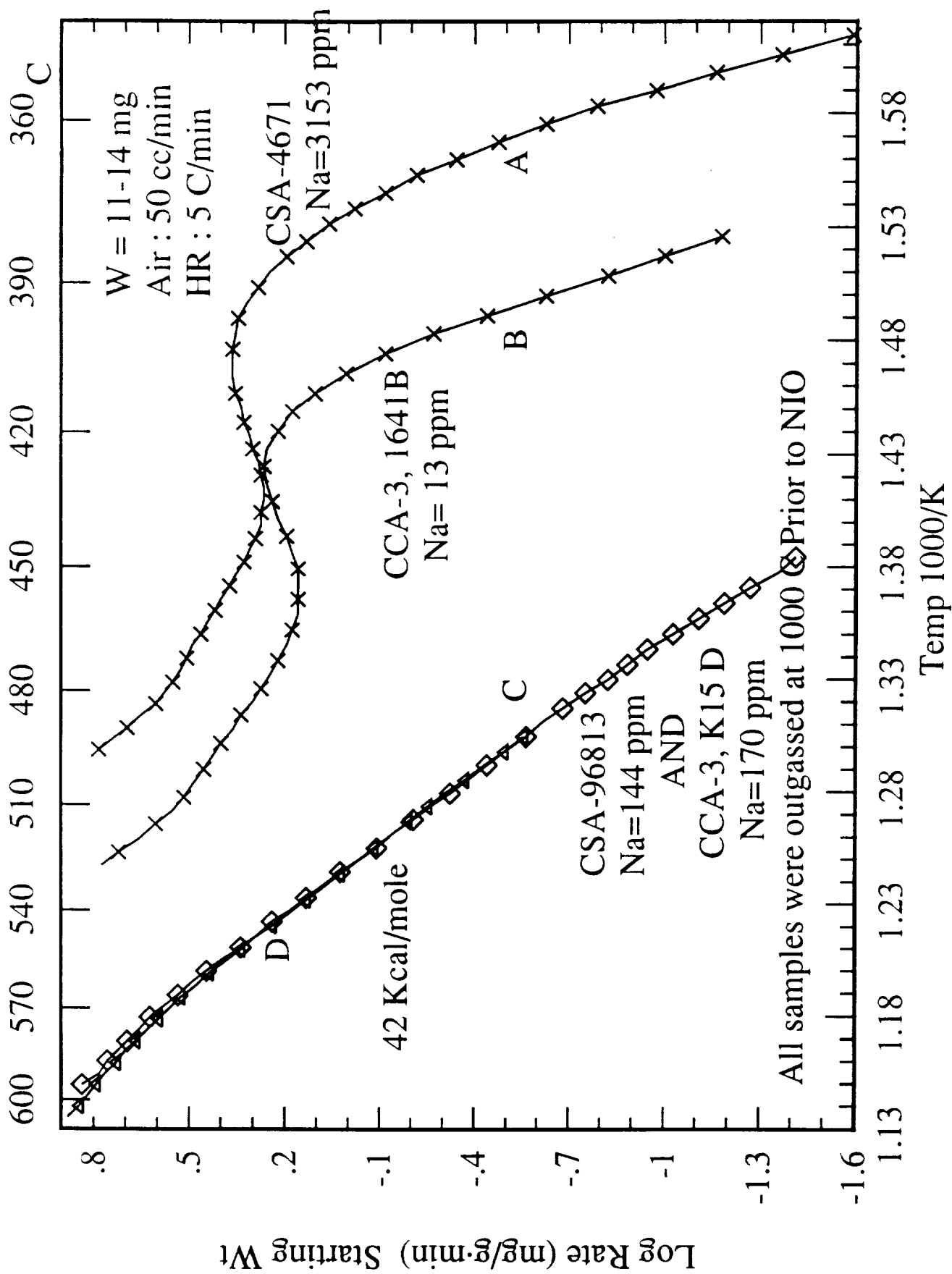


Fig 10: Arrhenius Plots for NIO of Rayon fabrics in Air.

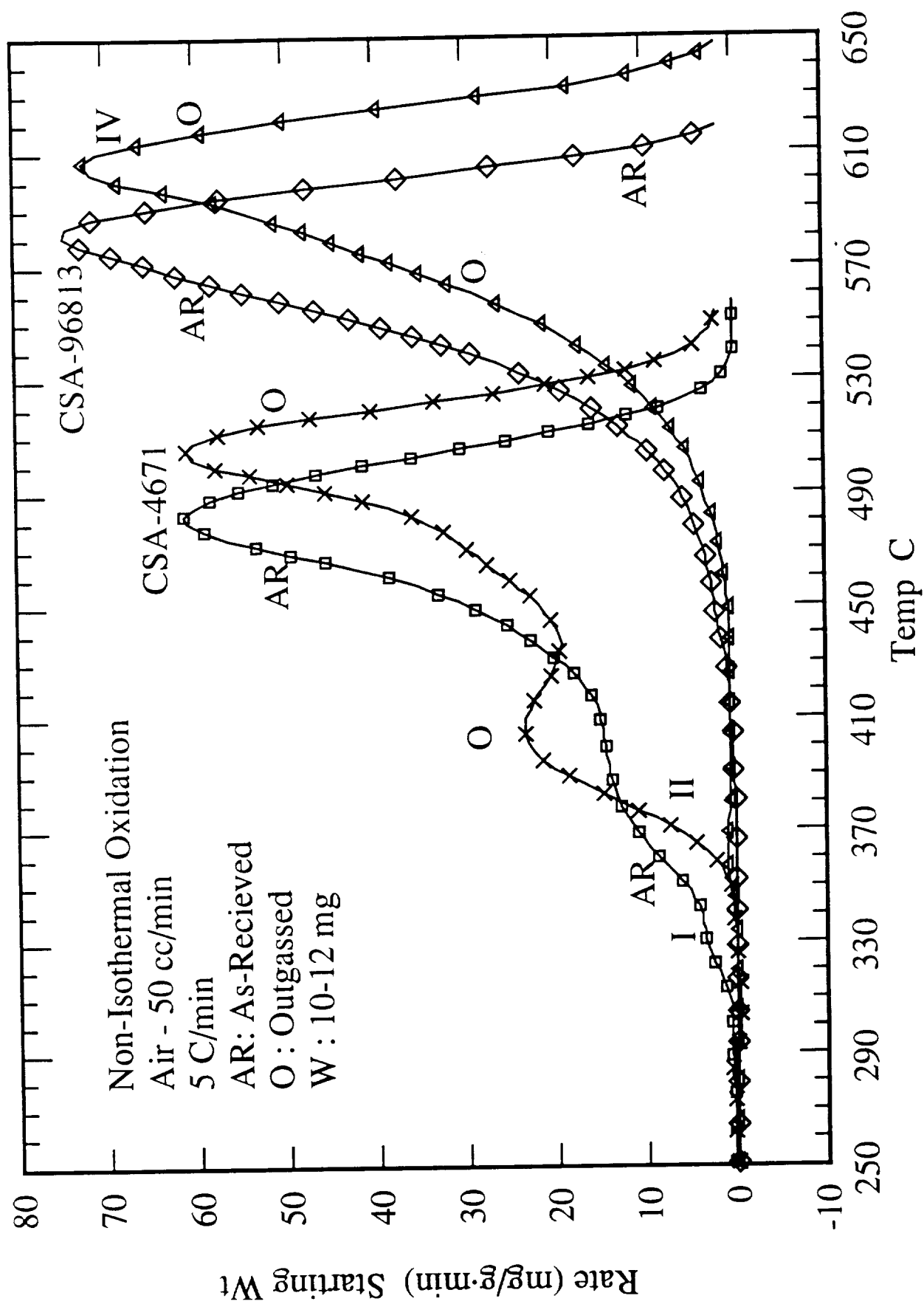


Fig 11: Effect of Outgassing on Kinetics of NiO.

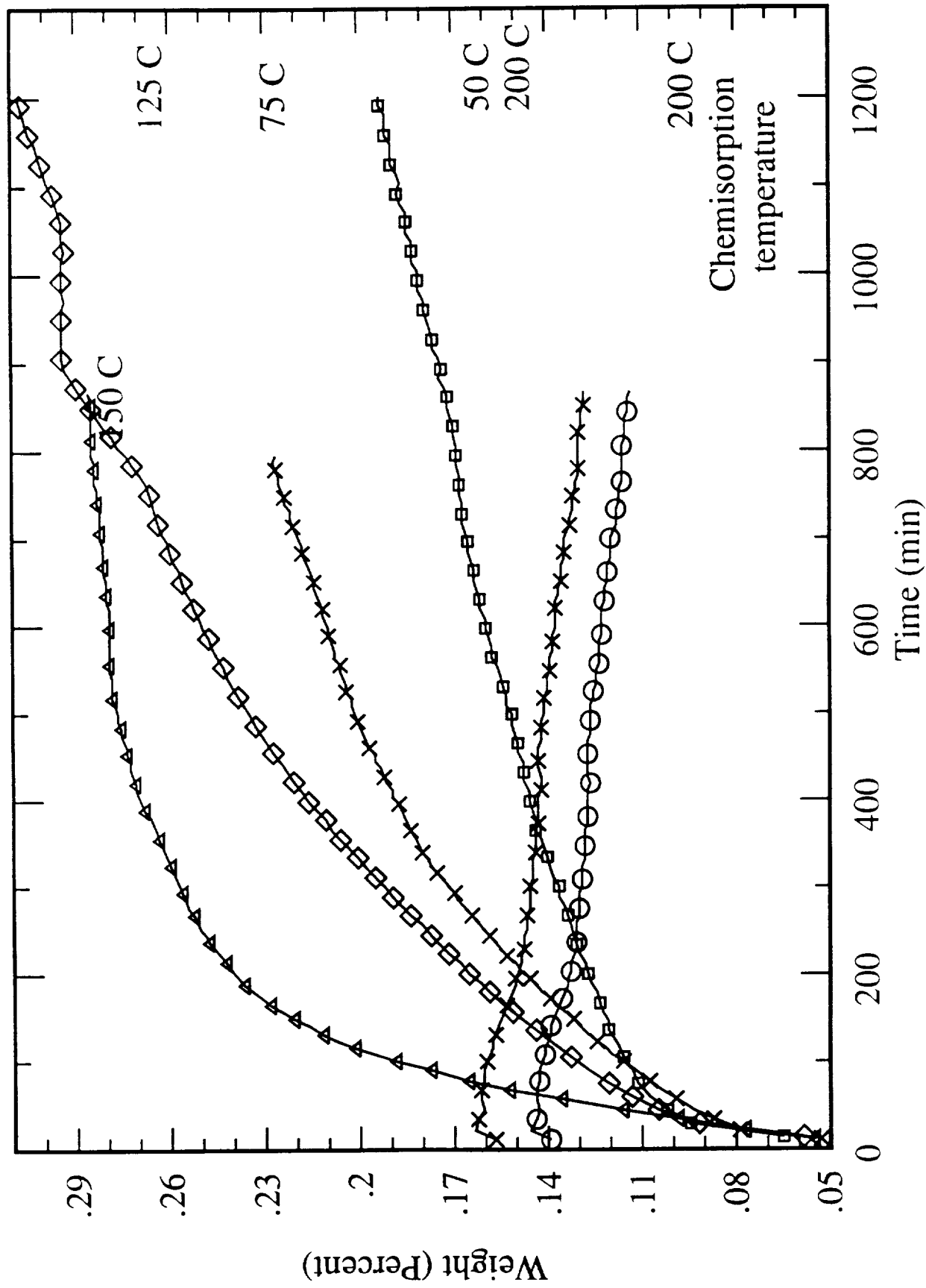


Fig 12: Oxygen Chemisorption on CSA-4671 Rayon Fabric.



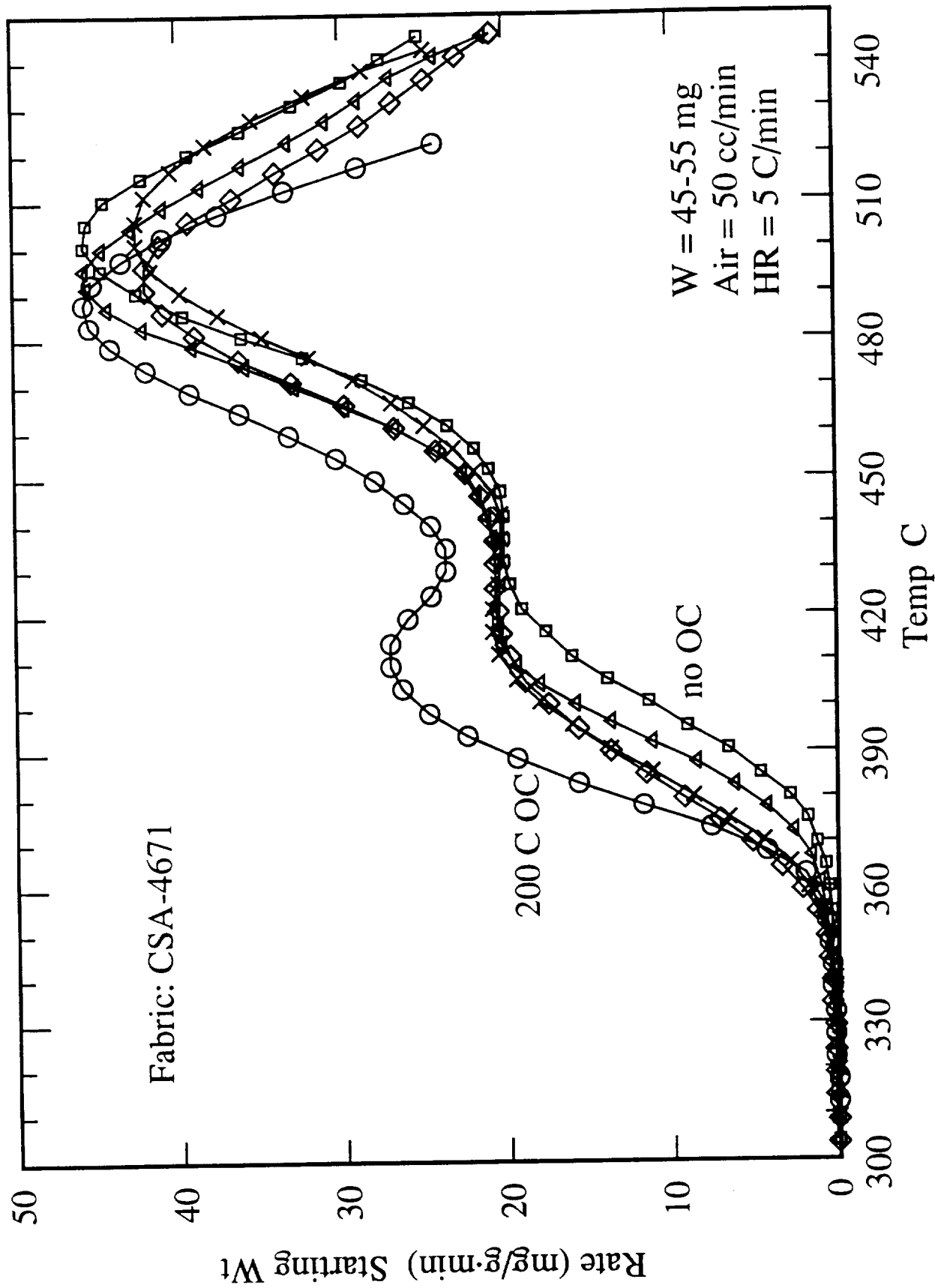


Fig 13: Effect of Oxygen Chemisorption (OC) on Fabric Oxidation.

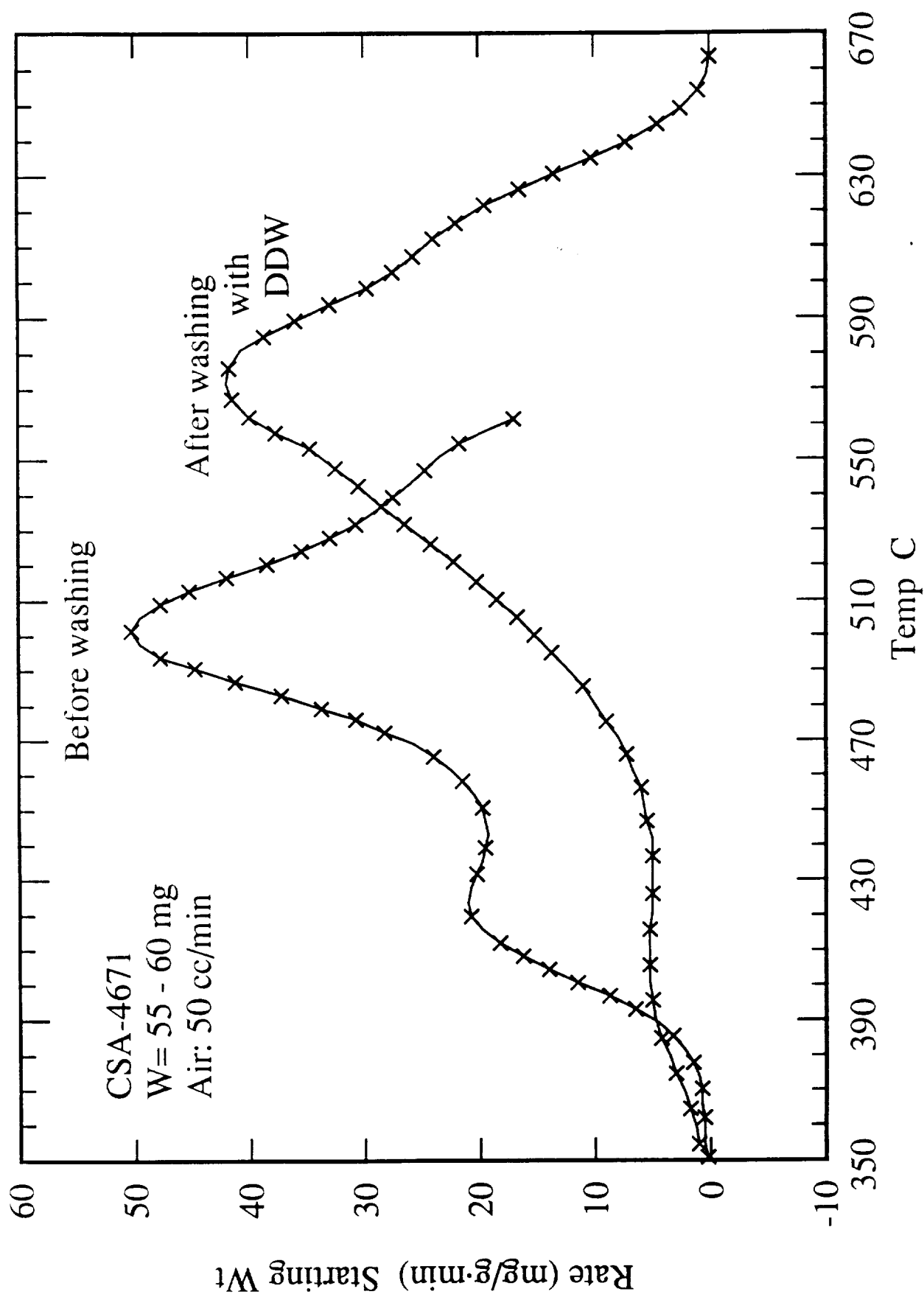


Fig 14: Effect of Sodium Removal on Oxidation Rate Profiles.

**APPENDIX B**

**PAT PINOLI**



**SPIP ACTIVITY**

**CARBON ASSAY TESTING**

**Presented to**

**The Industry Advisory Committee for  
Carbon Phenolic Constituent Test Methodology**

**Amoco R&D Center  
Alpharetta, Georgia  
May 16, 1991**

**Pat C. Pinoli  
Lockheed Research and Development Division**



## CARBON ASSAY TESTING



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### BACKGROUND:

Carbon assay testing is under advisement for test accuracy and precision.

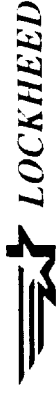
### CONCERNS:

Acceptance test procedures are vague on the following issues:

- Leco CR12 or CHN-600 useage
- Specimen Preparation Procedure
- Calibration Carbon and Frequency
- Definitive Leco operation parameters



## CARBON ASSAY TESTING

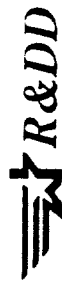


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### AGENDA

This meeting will assess operational issues and data for Leco CR-12 and CHN-600 analyzers

- Leco representatives to review how apparatus functions and procedures employed for round robin testing.
- Pat Pinoli will review test results with input from BP/Hitco, Polycarbon and Amoco.
- Committee recommendations for calibration and operational procedures.



## CARBON ASSAY TESTING



### SPIP - CARBON ASSAY TESTING CALIBRATION ROUND ROBIN TEST RESULTS (502-099/191-A-L)<sup>(1)</sup>

#### LABORATORY

RUN	A	B	C
1	95.2	97.05	95.98
2	95.2	97.22	96.12
3	95.2	97.08	96.42
4	95.3		96.18
5	95.6		96.89
X	95.3	97.12	96.32
S	0.17	0.09	0.36

(1) NBS Carbon Assay 96.81 = 0.38





## CARBON ASSAY TESTING



### ROUND ROBIN TESTING FOR CARBON ASSAY OF FABRIC per VENDOR PROCEDURE

<u>Fabric Identification</u>	<u>Vendor Certification<sup>1</sup></u>	Blind Testing Laboratory					
		"A" <sup>2</sup>		"B" <sup>3</sup>		"C" <sup>4</sup>	
		$\bar{x}$	(s)	$\bar{x}$	(s)	$\bar{x}$	(s)
1. CSA/0534	99.7/98.9	96.9	(0.19)	98.1	(0.65)	96.5	(0.09)
2. CSA/0539	99.5/98.3	96.6	(0.05)	95.8	(0.23)	96.9	(0.07)
3. CSA/0567	97.8/97.9	<u>96.6</u>	(0.26)	<u>96.5</u>	(0.24)	<u>96.7</u>	(0.06)
	98.7	96.7		96.8		<u>96.7</u>	
4. CCA3/42063	97.5/97.6	97.0	(0.08)	96.1	(0.37)	96.8	(0.18)
5. CCA3/42099	97.6/97.2	96.2	(0.77)	96.4	(0.27)	96.8	(0.08)
6. CCA3/42352	97.3/96.0	<u>96.1</u>	(0.14)	<u>96.6</u>	(0.23)	<u>96.5</u>	(0.15)
	97.2	96.4		96.4		96.7	
7. VCX-13	99.8/99.9	99.25	(0.27)	98.25	(0.72)	99.8	(0.06)
8. 10B	96.2/97.5	89.6	(0.06)	94.8	(0.38)	94.2	(0.18)
9. WCA	99.9	99.5	(0.27)	99.6	(0.27)	100.0	(0.06)

1) Outside/Inside of Roll

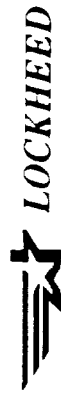
2) n = 3

3) n = 5

4) n = 2



## CARBON ASSAY TESTING



### Round Robin Testing for Carbon Assay Leco Technical Services Laboratory

Fabric Identification	Vendor Certification <sup>(1)</sup>	Leco		Leco CHN-600 (2) x (s)
		CR-12 (2) x (s)		
1. CSA/0534	99.7/98.9	93.84 (0.47)	93.89 (0.27)	
2. CSA/0539	99.5/98.3	93.35 (0.16)	94.28 (0.56)	
3. CSA/0567	97.8/97.9	<u>93.32</u> (0.36)	<u>94.25</u> (0.10)	
	<u>x</u> 98.7	93.50	94.14	
4. CCA3/42063	97.5/97.6	94.27 (0.47)	94.33 (0.35)	
5. CCA3/42099	97.6/97.2	93.18 (0.28)	93.89 (0.19)	
6. CCA3/42352	97.3/96.0	<u>92.67</u> (0.24)	<u>93.13</u> (0.15)	
	<u>x</u> 97.2	93.37	93.78	
7. VCX-13	99.8/99.9	99.00 (0.17)	99.30 (0.15)	
8. 10B	96.2/97.5	89.44 (0.48)	89.34 (0.27)	
9. WCA	99.9	99.77 (0.42)	99.94 (0.14)	

(1) Outside/Inside of Roll

(2) n = 3, Calibration with WCA Fabric



## CARBON ASSAY TESTING



### Round Robin Testing

Identification	Leco (1) (CR-12)	Leco (1) (CHN-600)	Polycarbon (CR-12)	Polycarbon (2) (CHN-600)
----------------	---------------------	-----------------------	-----------------------	-----------------------------

#### ASRM Task 1

Run 1	Run 2
-------	-------

#### Polycarbon, C-5 Yarn

NSC "M"	High Temp.	99.89 (0.21)	99.68 (0.14)	99.1	98.8	99.3 (0.35)
NSC "M"	Std. Temp.	98.82 (0.59)	99.11 (0.19)	98.0	98.6	99.2 (0.15)
NSC "M"	Low Temp.	97.20 (0.16)	96.70 (0.15)	97.7	97.5	98.6 (0.10)

#### BP/Hitco

H-4175-2A	High Temp.	100.0 (0.80)	100.04 (0.12)	98.5	98.8	99.6 (0.31)
S-4175-4A	Std Temp.	98.30 (0.41)	98.34 (0.35)	97.1	97.5	98.7 (0.10)
L-4178-5B	Low Temp.	96.36 (0.53)	97.03 (0.14)	97.0	96.1	97.9 (0.20)

(1) Calibration with WCA Fiber

(2) Calibration with NBS Coke, WCA measured 99.1 & 99.2

## **SPIP ACTIVITY**

### **TESTING CARBON FIBER FOR OXIDATION MASS LOSS**

**Presented to**

**The Industry Advisory Committee for  
Carbon Phenolic Constituent Test Methodology**

**Amoco R&D Center  
Alpharetta, Georgia  
May 16, 1991**

**Pat C. Pinoli  
Lockheed Research and Development Division**

## Procedures for Oxidation Mass Loss, Carbon Fibers

### Equipment

Weighing Bottles: Kimax 151464080 - outside fitting cover

Air circulating oven: Capable of holding 375+/- 3°C

Vacuum oven: Capable of holding 29" or better vacuum and  
-110°C

Balance: Digital Mettler capable of weighing 100gr to four  
decimals

### Sample Size

Approx. 3" x 4", 1.5-2.0 grams - not over 3" in one  
dimension

### Procedures

Weigh identified weighing bottles with matching covers at room temperature,  $W_1$ . Coil samples with 3" or less dimension in axial direction and place in weighing bottle. Place weighing bottles plus samples in vacuum oven at 110°C and full vacuum for minimum of one hour. Remove, immediately cover with matching cover, and let cool to room temperature. Weigh,  $W_2$ , to obtain sample weight,  $W_2 - W_1$ .

Remove covers and place bottles with samples in air circulating oven at 375°C. After four hours, remove bottles, immediately cover with matching covers and cool to room temperature. Weigh bottles with samples.  $W_3$ .

Calculate percent weight loss as follows:

$$\% \text{ wt loss} = \frac{(W_2 - W_1) - (W_3 - W_1)}{(W_2 - W_1)} \times 100$$

Run in triplicate.



# TESTING CARBON FIBER FOR OXIDATION MASS LOSS



## Carbon Fiber Mass Loss Testing at LPARL SPIP-4 Procedure (Amoco) (1)

### Identification

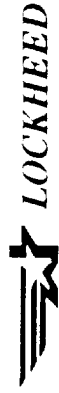
Polycarbon Parametric Study  
(Lot 64065)

Roll 3A (+200°F)	2.04	0.42	21%
Roll 2B (+100°F)	2.55	0.34	13%
Roll 1B Control	2.27	0.33	15%
Roll 4B (-100°F)	6.36	0.83	13%
Roll 5A (-200°F)	4.66	0.19	4%
Roll 10B	14.50	4.80	33%

(1) Weight Loss in Air - 4 Hours at 375°C



# TESTING CARBON FIBER FOR OXIDATION MASS LOSS



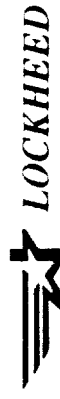
## Carbon Fiber Mass Loss Testing at LPARL SPIP-4 Procedure (Amoco) (1)

<u>Identification</u>	<u>Na, PPM</u>	<u>Mass Loss, W%</u>		<u>c.v.</u>
		<u>x</u>	<u>s</u>	
Polycarbon Parametric Study (Lot 64065)				
Roll 3A (+200°F)	360	2.04	0.42	21%
Roll 2B (+100°F)	360	2.55	0.34	13%
Roll 1B Control	320	2.27	0.33	15%
Roll 4B (-100°F)	950	6.36	0.83	13%
Roll 5A (-200°F)	910	4.66	0.19	4%
Roll 10B	2,240	14.50	4.80	33%

(1) Weight Loss in Air - 4 Hours at 375°C



# TESTING CARBON FIBER FOR OXIDATION MASS LOSS



## Carbon Fiber Mass Loss Testing at LPARL SPIP-4 Procedure (Amoco) (1)

Identification		Mass Loss, W%	
ASRM Task I		$\bar{x}$	C.V.
Polycarbon, C-5 Yarn			
NSC-"M"	High Temperature	+0.66	12%
NSC-"M"	Standard Temperature	0.22	150%
NSC-"M"	Low Temperature	5.98	4%
BP/Hitco, Prewoven Fabric			
H-4175-1A	High Temperature	+0.04	350%
H-4175-2A	High Temperature	+0.22	50%
S-4175-3A	Standard Temperature	1.55	28%
S-4175-4A	Standard Temperature	1.43	27%
L-4178-5A	Low Temperature	1.25	14%
L-4178-5B	Low Temperature	1.25	34%

(1) Weight Loss in Air - 4 Hours at 375°C





# TESTING CARBON FIBER FOR OXIDATION MASS LOSS



## Round Robin Carbon Fabric Mass Loss Testing SPIP-4 Procedure (Amoco)

Identification	LPARL		x	Amoco		
	s	c.v		s	c.v	
VCL, Sample 2A	1.55	0.64	54%	2.71	0.20	7.4%
VCL, Sample 3B	1.62	0.24	15%	2.43	0.27	11.1%
CSA, 1983	18.2	2.3	13%	2.44	1.47	6.0%
WCA (1COWCA-5)	+0.15	0.04	27%	N/A		

**SPIP ACTIVITY**

**CARBON FIBER DENSITY TESTING  
DISPLACEMENT FLUID ASSESSMENT**

**Presented to**

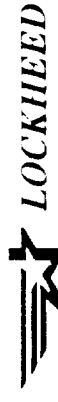
**The Industry Advisory Committee for  
Carbon Phenolic Constituent Test Methodology**

**Amoco R&D Center  
Alpharetta, Georgia  
May 16, 1991**

**Pat C. Pinoli  
Lockheed Research and Development Division**



## CARBON FIBER DENSITY TESTING



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### BACKGROUND

Many rayon based carbon fibers are sensitive to moisture adsorption; therefore water displacement does not provide a value which reflects on effective composite/fiber density.

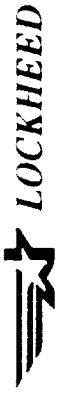
### COMMITTEE RECOMMENDED APPROACH

Evaluate alternate displacement liquids which are environmentally acceptable.



R&DD

## CARBON FIBER DENSITY TESTING



LOCKHEED

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### Preliminary Evaluation at LPARL

- o-Dichlorobenzene
- Hexane
- Cyclohexane

### Test Procedure

- 2 meter length of C-5 yarn, bow tied
- Vacuum dried at 105°C overnight
- 10 minute ultrasonic agitation
- Suspended in fluid to determine volume displacement

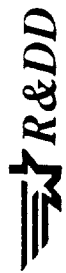


## CARBON FIBER DENSITY TESTING



### Displacement Fluid Assessment

<u>Fiber Identification</u>	<u>Gradient Column</u>	<u>g/cc-60 minutes</u>	<u>g/cc</u>	<u>o-Dichlorobenzene</u>
C-5 Experimental Yarn (NAR Precursor)				
Low-1				
	1.4311		1.413	
	1.4324		1.443	
	1.4334		1.451	
$\bar{x}$	1.432 (0.0009)		1.436 (0.020)	
C.V.	0.06%		0.39%	
Low-2				
	1.4334		1.429	
	1.4350		1.443	
	1.4361		1.466	
$\bar{x}$	1.435 (0.0014)		1.446 (0.019)	
C.V.	0.10%		0.31%	
Medium				
	1.4105		1.427	
	1.4125		1.420	
	1.4137		1.407	
$\bar{x}$	1.412 (0.0016)		1.418 (0.010)	
C.V.	0.11%		0.71%	
High				
	1.4015		1.410	
	1.4022		1.373	
	1.4056		1.407	
$\bar{x}$	1.403 (0.0022)		1.397 (0.021)	
C.V.	0.16%		1.50%	



## CARBON FIBER DENSITY TESTING



### Displacement Fluid Assessment

<u>Fiber Identification</u> C-5 Experimental Yarn (NAR Precursor)	<u>Gradient Column.</u> g/cc-60 minutes	<u>Hexane.</u> g/cc
Low-1	1.4311	1.448
	1.4324	1.451
	1.4334	1.464
$\bar{x}$	1.432 (0.0009)	1.454 (0.085)
c.v.	0.06%	0.58%
Low-2	1.4334	1.539
	1.4350	1.439
	1.4361	1.424
$\bar{x}$	1.435 (0.0014)	1.467 (0.063)
c.v.	0.10%	4.29%
Medium	1.4105	1.390
	1.4125	1.727
	1.4137	1.435
$\bar{x}$	1.412 (0.0016)	1.517 (0.183)
c.v.	0.11%	12.1%
High	1.4015	1.333
	1.4022	1.328
	1.4056	1.412
$\bar{x}$	1.403 (0.0022)	1.358 (0.047)
c.v.	0.16%	3.46%



## CARBON FIBER DENSITY TESTING



### Displacement Fluid Assessment

<u>Fiber Identification</u> C-5 Experimental Yarn (NAR Precursor)	<u>Gradient Column,</u> g/cc-60 minutes	<u>Cyclohexane,</u> g/cc
Low-1	1.4311 1.4324 <u>1.4334</u> 1.432 (0.0009) 0.06%	1.434 1.442 <u>1.443</u> 1.441 (0.007) 0.49%
Low-2	1.4334 1.4350 <u>1.4361</u> 1.435 (0.0014) 0.10%	1.435 1.442 <u>1.442</u> 1.440 (0.004) 0.28%
Medium	1.4105 1.4125 <u>1.4137</u> 1.412 (0.0016) 0.11%	1.421 1.427 1.411 1.420 (0.008) 0.56%
High	1.4015 1.4022 <u>1.4056</u> 1.403 (0.0022) 0.16%	1.413 1.453 <u>1.381</u> 1.416 (0.036) 2.54%
	$\bar{x}$ c.v.	

## **SPIP ACTIVITY**

### **CARBON FIBER DENSITY TESTING DISPLACEMENT FLUID ASSESSMENT**

**Presented to**

**The Industry Advisory Committee for  
Carbon Phenolic Constituent Test Methodology**

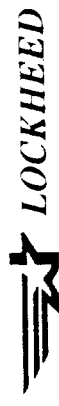
**Amoco R&D Center  
Alpharetta, Georgia  
May 16, 1991**

**Pat C. Pinoli  
Lockheed Research and Development Division**





## CARBON FIBER DENSITY TESTING



---

### BACKGROUND

Many rayon based carbon fibers are sensitive to moisture adsorption; therefore water displacement does not provide a value which reflects on effective composite/fiber density.

### COMMITTEE RECOMMENDED APPROACH

Evaluate alternate displacement liquids which are environmentally acceptable.



## CARBON FIBER DENSITY TESTING



---

### Preliminary Evaluation at LPARL

- o-Dichlorobenzene
- Hexane
- Cyclohexane

### Test Procedure

- 2 meter length of C-5 yarn, bow tied
- Vacuum dried at 105°C overnight
- 10 minute ultrasonic agitation
- Suspended in fluid to determine volume displacement



## CARBON FIBER DENSITY TESTING



### Displacement Fluid Assessment

<u>Fiber Identification</u>	<u>Gradient Column</u>	<u>g/cc-60 minutes</u>	<u>g/cc</u>	<u>o-Dichlorobenzene</u>
C-5 Experimental Yarn (NAR Precursor)				
Low-1				
	1.4311		1.413	
	1.4324		1.443	
	<u>1.4334</u>		<u>1.451</u>	
$\bar{x}$	1.432 (0.0009)		1.436 (0.020)	
C.V.	0.06%		0.39%	
Low-2				
	1.4334		1.429	
	1.4350		1.443	
	<u>1.4361</u>		<u>1.466</u>	
$\bar{x}$	1.435 (0.0014)		1.446 (0.019)	
C.V.	0.10%		0.31%	
Medium				
	1.4105		1.427	
	1.4125		1.420	
	<u>1.4137</u>		1.407	
$\bar{x}$	1.412 (0.0016)		1.418 (0.010)	
C.V.	0.11%		0.71%	
High				
	1.4015		1.410	
	1.4022		1.373	
	<u>1.4056</u>		<u>1.407</u>	
$\bar{x}$	1.403 (0.0022)		1.397 (0.021)	
C.V.	0.16%		1.50%	



## CARBON FIBER DENSITY TESTING



### Displacement Fluid Assessment

<u>Fiber Identification</u> C-5 Experimental Yarn (NAR Precursor)	<u>Gradient Column</u> g/cc-60 minutes	<u>Hexane</u> g/cc
Low-1	1.4311	1.448
	1.4324	1.451
	<u>1.4334</u>	<u>1.464</u>
$\bar{x}$	1.432 (0.0009)	1.454 (0.085)
C.V.	0.06%	0.58%
Low-2	1.4334	1.539
	1.4350	1.439
	<u>1.4361</u>	<u>1.424</u>
$\bar{x}$	1.435 (0.0014)	1.467 (0.063)
C.V.	0.10%	4.29%
Medium	1.4105	1.390
	1.4125	1.727
	<u>1.4137</u>	<u>1.435</u>
$\bar{x}$	1.412 (0.0016)	1.517 (0.183)
C.V.	0.11%	12.1%
High	1.4015	1.333
	1.4022	1.328
	<u>1.4056</u>	<u>1.412</u>
$\bar{x}$	1.403 (0.0022)	1.358 (0.047)
C.V.	0.16%	3.46%



## CARBON FIBER DENSITY TESTING



### Displacement Fluid Assessment

<u>Fiber Identification</u> C-5 Experimental Yarn (NAR Precursor)	<u>Gradient Column,</u> g/cc-60 minutes	<u>Cyclohexane,</u> g/cc
Low-1	1.4311 1.4324 <u>1.4334</u>	1.434 1.442 <u>1.443</u>
$\bar{x}$ C.V.	1.432 (0.0009) 0.06%	1.441 (0.007) 0.49%
Low-2	1.4334 1.4350 <u>1.4361</u>	1.435 1.442 <u>1.442</u>
$\bar{x}$ C.V.	1.435 (0.0014) 0.10%	1.440 (0.004) 0.28%
Medium	1.4105 1.4125 <u>1.4137</u>	1.421 1.427 1.411
$\bar{x}$ C.V.	1.412 (0.0016) 0.11%	1.420 (0.008) 0.56%
High	1.4015 1.4022 <u>1.4056</u>	1.413 1.453 <u>1.381</u>
$\bar{x}$ C.V.	1.403 (0.0022) 0.16%	1.416 (0.036) 2.54%

# METHODOLOGY DEVELOPMENT FOR CHARACTERIZATION OF ABLATIVE CONSTITUENT MATERIALS

Pat C. Pinoli

Lockheed Research & Development Division

3251 Hanover Street

Palo Alto, CA 94304

## INTRODUCTION

This report documents advisory tasks, under SPIP Subtask 3.2.1.1-1, which were closed out during FY-91 and prior years. A more comprehensive review of total progress for FY-91 is presented in the final annual report and two independent reports which document proceedings of the two biannual meetings held in FY-91. This report was prepared by the author, however the Industry Advisory Committee on Ablative Constituent Test Methodology is directed by an executive committee of 2 other members; Chairman, Dr. W. C. Hall, Mississippi and C. G. Upton, COTR, NASA/MSFC. This closure report represents a consensus of the executive committee to close out 4 advisement tasks.

## DISCUSSION

### Advisement Task 1

DMF Substitution      Initiation Date 11/88  
                                 Closure Date 5/89

### Background - RSRM Relevant

This effort was given high priority to insure an alternate solvent for dimethylformamide (DMF) was available for pre-preg resin quantitative analysis. DMF is extremely toxic and replacement is necessary to alleviate the implementation of stringent EPA requirements on laboratory personnel exposure. The two major pre-preg vendors (Fiberite and U.S. Polymeric) are allowed to perform different analytical techniques for measuring resin/filler/fiber content. Reference STW5-3279. A common test procedure is desirable but historical vendor preference was incorporated into the original specification. The USP procedure employs acetone/soxlet extraction to measure resin content. The Fiberite procedure employs DMF solvent for extraction; which is much faster and is used by the vendor for in-process control. Substitution of DMF therefore was a problem only with the Fiberite procedure. Adaption of the USP procedure by Fiberite was unacceptable to the vendor primarily due to the long soxlet extraction time. The long time required to run acetone/soxlet extraction provides good values but data cannot be used for in process control.

### Closure Summary

In February 1989, a recommendation to resolve this issue was transmitted to the RSRM chief engineer. This recommendation was made through R. I. Schwinghamer, Director of the MSFC/M&P laboratory and was based on the SPIP Executive Committee consensus. The recommendation to the RSRM chief engineer included the current test procedure (enclosure 1) and recommended test procedure (enclosure 2). Support documentation for closure of advisory task 1 is included in Appendix A. More comprehensive documentation of activity on advisement task 1 is found in reference document 2.

## Advisement Task 2

Carbon Fabric Oxidation Mass Loss, Initiation Date 11/88  
Closure Date 6/91

### Background - RSRM Relevant

This task was initiated to support a concern identified during the STS-8A pocket erosion investigation. Thermal Gravimetric Analysis (TGA) data on some carbon fabric, employed in HPM motors, was found to be very sensitive of air oxidation. More specifically, some fabric, produced by Polycarbon, Inc. at North Hollywood, would support combustion when exposed to a lighted match. This observation and supporting TGA data was followed by the implementation of an engineering test (for information only) within STW4-3184B acceptance test procedure. This engineering data accumulated at MTI until reviewed by Ben Powers, Deputy Chief Engineer on RSRM, in late 1988. This data suggests low oxidation resistance fabric was entering the RSRM program and SPIP Subtask 3.2.1.1 support was solicited. Within two weeks a document was submitted to Clinton of NASA/M&P and Powers which identified (1) numerous testing procedural problems and (2) analysis of current production carbon fabric entering the RSRM program was normal. Reference Appendix B.

The test procedure for measuring oxidation mass loss of carbon fabric was subsequently taken under advisement.

### Closure Summary

Two distinctly different test procedures were developed and employed in round robin testing. These test procedures are identified SPIP-3 and SPIP-4 in Appendix A. Both procedures have merit but are designed for different goals.

#### SPIP-3 Procedure

This procedure uses a select TGA apparatus (Perkin-Elmer) and provides fundamental oxidation data on any carbon fiber tested. It has been adopted by the ASRM Advanced Ablative Program to evaluate candidate rayon based yarns and fabrics. This test procedure has generated excellent data on clearly identified high Na candidate yarn. The procedure is highly recommended for use by the ablative industry.

#### SPIP-4 Procedure

This procedure was requested by a consensus of the Industry Advisory Committee. The manufacturers wanted a simple and cheap method that could be adopted as a go-no go screening test. The procedure was developed by Amoco Performance Products, Inc. and meets all of the committee objectives. Oxidation rate data generated by SPIP-4 procedure was found to compare favorably with SPIP-3 data. In addition, round robin testing between Amoco and LPARL produced similar results. This procedure is recommended as the basis for a simple test for screening out low oxidation resistance carbon fiber. More comprehensive documentation of activity on advisement task 2 is found in reference documents 2 thru 12.

## Advisement Task 5

Rayon Fiber Specifications Initiation Date 11/88  
Closure Date 6/91

### Background - RSRM Relevant

This task was initiated to provide support to the RSRM/North American Rayon (NAR) Qualification Program. The Industry Advisory Committee offered the best source of knowledge regarding carbonizable rayon and method to disseminate qualification progress at NAR.

### Closure Summary

All of the domestic carbonizers are represented on the Industry Advisory Committee; BP/Hitco, Polycarbon and Amoco. Al Turbak (consultant to NASA on the NAR Qualification Program) presented a review and recommendations for additional rayon testing to the November 1989 meeting at Tempe, Arizona. As an invited speaker, Al made a strong recommendation for inclusion of wet fiber properties (strength and elongation) to complement the standard tests conducted at Avtex. The Industry Advisory Committee supported the rationale for additional testing with no dissent from the carbonizers. In November 1990, the entire Industry Advisory Committee met at the NAR Elizabethton, Tennessee facility. During the meeting, the current specifications were again reviewed and a facility tour made. A complete set of 1650 denier Rayon Yarn Specifications was presented to each committee member for reference. The NASA/NAR qualification effort has proceeded well, with no clearly definable problems. All of the initial objectives for this advisory tasks have been met and the executive committee recommends closure. Appendix C includes a letter from NAR regarding successful conclusion of the NASA qualification program and a list of specifications. More comprehensive documentation of activity on advisement task 5 is found in reference documents 2, 3, 4, 6, 7, 8 and 10.

### Advisement Task 6

Alkali Metal Content Test      Initiation Date 5/90  
Closure Date 6/91

### Background - RSRM and ASRM Relevant

Measurement of alkali metal, predominantly Na, in ablative carbon fiber is preceded by an ashing procedure. The ash is subsequently put into water solution and concentration of alkali metal determined by atomic absorption. Studies conducted by Dr. Ismail M.K. Ismail, for NASA/MSFC, suggested the ashing temperature employed for ashing could strongly influence the ashing yield. Reference 1 (page 2-104). This particular study exhibited a 76% increase of Na when ashing temperature was reduced from 625°C to 500°C. As an invited consultant to our meetings, Dr. Ismail was asked to pursue this issue. A full review of this effort is presented in reference 10.

## Closure Summary

Dr. Ismail presented the results of independent experiments conducted at the Astronautics Laboratory, Edwards AFB, California. As a contracted research scientist for the Air Force, Dr. Ismail performed his work as part of fundamental research on carbon behavior. Particular emphasis was placed on carbon fabrics under redesign activity study and production RSRM fabrics. Significant data from this study (including conclusions and recommendation) are included in Appendix A. The RSRM program employs an ashing temperature of 600°C in STW4-3184. This study recommended a lower range, 500-550°C for ashing. A review of the test data by the executive committee recommended the current 600°C temperature should be maintained for two reasons:

- The effect of reducing ashing temperature from 600 to 550°C would not have a major impact on measured values for current RSRM fabric.
- The extensive HPM and RSRM data base would be placed in question if a new temperature was adopted. With regards to advanced ablatives for the ASRM problem, the higher 600°C temperature remains acceptable since the baseline fiber firing temperature should be significantly higher than employed by the RSRM program. Recommendation for closure on 6/91 was unanimous by the executive committee. More comprehensive documentation of activity on advisement task 6 is found in reference documents 1, 7 and 12.



## REFERENCES

1. P. C. Pinoli, J. A. Freeman and D. M. Berry, High Performance Solid Rocket Motor (HPM) Nozzle Erosion, LMSC-HEC TRDO65599, Mar. 1987
2. W. B. Hall, Proceedings of the Industry Committee Meeting on Standardization of Carbon Phenolic Constituent Test Methods and Specifications, Palo Alto, CA, Nov. 1988
3. W. B. Hall, Proceedings of the Industry Committee Meeting on Standardization of Carbon Phenolic Constituent Test Methods and Specifications, Santa Ana, CA, May 1989
4. P. C. Pinoli, Annual Report on SPIP Subtask 3.2.1.1-1 Activity, June 1989
5. W. B. Hall, L. A. Fikes and P. C. Pinoli, Testing Carbon Fabric for Oxidation Mass Loss, JANNAF/RNTS Meeting, Silver Springs, MD, Oct. 1989
6. W. B. Hall, Proceedings of the Industry Committee Meeting on Standardization of Carbon Phenolic Constituent Test Methods and Specifications, Tempe, AZ, Nov. 1989
7. W. B. Hall, Proceedings of the Industry Committee Meeting on Standardization of Carbon Phenolic Constituent Test Methods and Specifications, Valencia, CA, May 1990
8. P. C. Pinoli, Annual Report on SPIP Subtask 3.2.1.1-1 Activity, July 1990
9. R. G. Clinton, P. C. Pinoli, and A. R. Canfield, Development of Low-Thermal-Conductivity PAN-Based Fibers for Solid Rocket Nozzle Application, JANNAF/RNTS Meeting, Pasadena, CA, Oct. 1990.
10. W. B. Hall, Proceedings of the Industry Committee Meeting on Standardization of Carbon Phenolic Constituent Test Methods and Specifications, Elizabethton, Tenn., Nov. 1990
11. L. A. Fikes, W. B. Hall, P. C. Pinoli and C. G. Upton, Measuring Carbon Fiber Oxidation Rate, SAMPE/ICCM/8 Conference, Honolulu, HA, July 1991
12. W. B. Hall, Proceedings of the Industry Committee Meeting on Standardization of Carbon Phenolic Constituent Test Methods and Specifications, Alpharetta, GA, May 1991 (Publication in Progress)

APPENDIX A  
CLOSURE REFERENCE DOCUMENTS FOR  
ADVISEMENT TASK 1

George C. Marshall Space Flight Center  
Marshall Space Flight Center, Alabama  
35812

Reply to Attn of EH34(89-9)

FEB 17 1989

TO: SA42/Mr. Mitchell  
THRU: EE51/Mr. Coates *MSC*  
FROM: EH01/Mr. Schwinghamer

SUBJECT: Recommended Change to the Procedure for the Determination of Resin  
Solids Content, Filler Content, and Cloth Content Test Methodology  
for Evaluation of Carbon Cloth Phenolic Prepreg

We would like to recommend a change in the technique for the determination of resin solids, filler content, and cloth content testing in MTI/W specification STW5-3279A for Preimpregnated Carbon Cloth Phenolic. Current testing procedures listed in the specification have come under scrutiny of safety, health, and environmental groups due to the safety hazards of N,N-dimethyl formamide (DMF) use. The proposed test method consists of using ultrasonic acetone extraction to directly measure filler content and cloth content. For acceptance criteria, the resin solids content will then be used to back calculate filler and cloth content from formulation data. No changes will be made in the accept/reject range presently being utilized. (See enclosure 1 for a copy of the current test method found in STW5-3279A dated May 8, 1987, and see enclosure 2 for a copy of the proposed test method.) This recommendation has also been agreed upon by the Advisory Committee for Standardization of Carbon Phenolic Tests Methods and Specifications which is a part of the SPIP program. Therefore, for the time being, the MSFC M&P Laboratory recommends that this change be utilized by all parties involved in carbon cloth phenolic prepreg testing for the Shuttle SRM program, which includes U. S. Polymeric, Fiberite, and MTI/W. A more direct measurement approach would be preferable; we are in the process of trying to develop such a test procedure, and as it comes to fruition we will present it for consideration.

*R. J. Schwinghamer*

R. J. Schwinghamer  
Acting Director  
Materials and Processes Laboratory

2 Enclosures

cc:  
EH01/Mr. Schuerer  
EH02/Mr. Key  
EH31/Mr. McIntosh  
EH34/Mr. Nichols/Ms. Fikes

Enclosure 1: Resin Solids, Filler Content, and Cloth Content Test Methodology Found in STW5-3279A. Section 4.6.2.2 Dated May 8, 1987.

Resin Solids, Filler Content, and Cloth Content. Resin solids, filler content, and cloth content shall be determined for each sample in accordance with the following:

- a. Place an approximately 5.0-square-inch sample of material, weighed to the nearest 0.01 g (specimen weight), into a 250-milliliter (ml) beaker (A).
- b. Calculate devolatilized specimen weight (W) as follows:

W = specimen wt -

$$\frac{(\text{percent volatiles}) (\text{specimen wt})}{100}$$

100

Where: percent volatiles is the value determined from the volatiles content (see 4.6.2.1)

- c. Add 50 ml of N,N-dimethylformamide (DMF) and bring to a boil. Occasionally gently stir the boiling DMF and prepreg cloth for a minimum of 5 minutes. Remove beaker from heat source and cool for a minimum of 5 minutes while occasionally gently stirring.
- d. Decant and transfer the liquid solution to a second 250-ml beaker (B).
- e. Rinse the remaining fabric with DMF several times to ensure complete extraction of resin and filler from fabric and add the rinses to a second 250-ml beaker (B).
- f. Finally rinse the fabric with acetone to remove all traces of DMF.
- g. Add all rinses to the second 250-ml beaker (B).
- h. Dry a filter and a crucible or filtering crucible at 350 degrees F minimum for a minimum of 30 minutes. Weight filter and crucible or filtering crucible to the nearest 0.01 g (W2).
- i. Dry the fabric in an oven for minimum of 20 minutes at 325 degrees F minimum, cool in a desiccator to room temperature and reweigh to the nearest 0.01 g (W1).

- j. Using an aspirator or vacuum pump, filter the contents of the second 250-ml beaker (B) through a filter and crucible, or a filtering crucible, into a vacuum flask.
- K. Rinse the crucible and filter or filtering crucible several times with acetone to remove all resin.
- l. Dry the crucible and contents at 350 + 10 degrees F for minimum of 20 minutes, cool in a desiccator to room temperature and reweigh to the nearest 0.01 g (W3).
- m. Calculate the resin solids content, filler content, and cloth content as follows:

Resin solids content (percent) =

$$\frac{W - (W1 + W4)}{W} (100)$$

$$\text{Filler content (percent)} = \frac{W4}{W} 100$$

$$\text{Cloth content (percent)} = \frac{W1}{W} 100$$

Where: W = calculated devolatilized weight of prepreg specimen, g

W1= weight of fabric after resin and filler removal, g

W2= crucible and filter or filtering crucible weight, g

W3= filler + crucible and filter or filtering crucible weight, g

W4= W3 - W2 = filler weight

NOTE: The soxhlet extraction method specified in ASTM C 613 may be used as an alternate test procedure.

Enclosure 2: Proposed Test Methodology for Resin Solids, Filler Content, and Cloth Content of Carbon Cloth Phenolic Prepreg taken from Preliminary STW5-3279A dated January 26, 1987

Resin Solids, Filler Content, and Cloth Content. Resin solids, filler content, and cloth content shall be determined for each sample in accordance with the following:

- a. Assemble several pairs of filters with a Whatman EPM 2000, or equivalent, on the bottom and a Whatman GF/F, or equivalent, on the top and precondition by filtering approximately 25 ml of acetone through the paired filters. Place the filters in an aluminum weighing pan and dry at  $163 \pm 3$  degrees centigrade (C) for 20 minutes or until dry. Store preconditioned filters in a desiccator.
- b. Weight a  $2\frac{1}{4} \times 1\frac{1}{4}$  square inch bias cut specimen to the nearest 0.0001 g into a clean 250 ml beaker.
- c. Under a fume hood, ultrasonically extract the specimen twice, for three minutes minimum each time, in 50 to 75 ml of acetone. Use fresh acetone for each extraction. Stir the specimens several times during extraction.  
  
NOTE: Samples may be extracted for 5 minutes using 50 to 75 ml of boiling N,N-dimethylformamide (DMF).  
  
NOTE: Use approximately 150 ml of solvent for prepreg weights over 6 g.
- d. Weight a preconditioned pair of filters and pan (from Step 1) to the nearest 0.0001 g and place the pair of filters, with the smaller filter on top, in the membrane filtration apparatus (W2).  
  
NOTE: If the filter sticks to the funnel base, a polytetrafluoroethylene gasket may be placed between the bottom filter and the stainless steel screen.
- e. Hold the specimen in the beaker with a glass stirring rod while decanting the liquid solution through a 200- to 230-mesh filtering sieve placed on top of the filtering funnel.
- f. Rinse the remaining fabric twice with acetone to ensure complete extraction of the resin and filler. Complete rinsing is indicated by a clear acetone solution.
- g. Add all rinses to the filtering funnel as in Step e.

- h. Remove the fabric and place into a preweighed aluminum drying dish. Any fiber remaining on the filtering sieve is to be transferred to the aluminum weighing pan using a rubber policeman. Dry the fabric in an air circulating oven at  $163 \pm 3$  degrees C for 20 minutes or until dry. Cool in a desiccator to room temperature and weight to the nearest 0.0001 g (W1).
- i. Filter the contents of the filtering funnel through the pair of filters. Rinse the sides of the filtering funnel with acetone to insure that all the filler is entrapped in the filters.
- j. Remove the filters from the filtering funnel and place back into the original weighing pan (the top filter should be placed into the pan first and covered by the larger, bottom filter). Transfer any filler remaining on the bottom rim of the filtering funnel to the weighing pan with a small metal spatula. Close loosely around the edges and dry in an air circulating oven at  $163 \pm 3$  degrees C for 20 minutes or until dry. Cool to room temperature in a desiccator and reweigh to the nearest 0.0001 g (W3).
- k. Calculations:

Devolatilized weight (W) = specimen weight - ((percent volatiles) x (specimen weight))/100  
 Resin solids content (percent) =

$$\frac{W - (W1 + W4)}{W} (100)$$

$$\text{Filler content (percent)} = \frac{W4}{W} 100$$

$$\text{Cloth Content (percent)} = \frac{W1}{W} 100$$

Where: W = calculated devolatilized weight of prepreg specimen, g

percent Volatiles = value determined in 4.6.2.1

W1 = weight of fabric after resin and filler removal, g

W2 = crucible and filter or filtering crucible weight, g

W3 = filler + crucible and filter or filtering crucible weight, g

W4 = W3 - W2 = filler weight

APPENDIX B

CLOSURE REFERENCE DOCUMENTS FOR

ADVISEMENT TASK 2



INTERDEPARTMENTAL COMMUNICATION

TO: C. Clinton/B. Powers

14 Oct 88

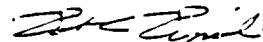
FROM: Pat C. Pinoli O/93-30 B/204 Fac. 2 X42253

SUBJECT: ASSESSMENT OF CARBON FABRIC OXIDATION RATE DATA PER STW4-3184B  
PROCEDURE, RSRM/SPIP ACTIVITY

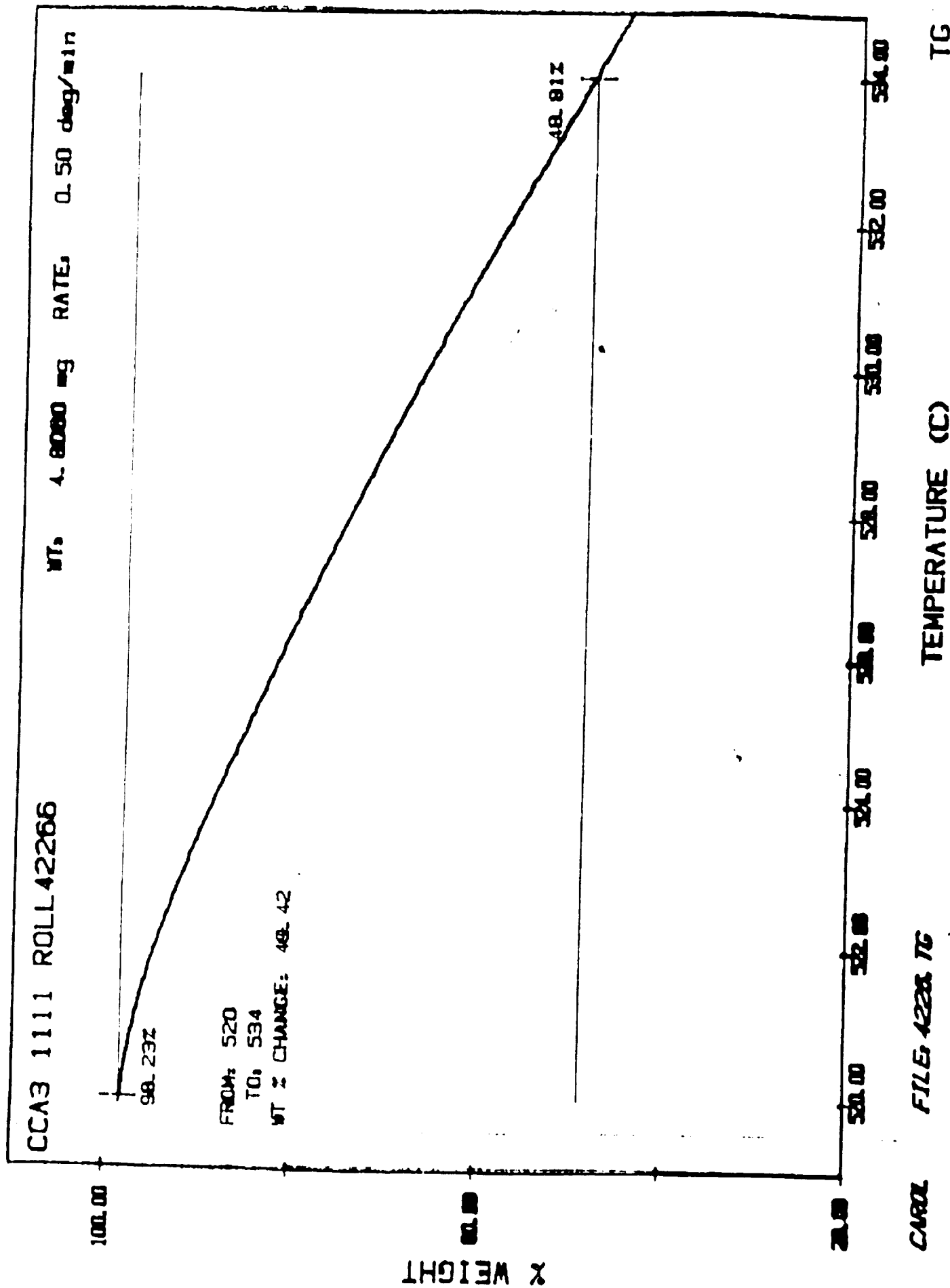
Enclosed are TGA curves, data summary and an independent assessment of 6 carbon fabrics roll samples submitted by M&P. Additional TGA runs were performed on VCX-13, WCA and CSA/N. Hollywood fabrics to provide reference information. This assessment was coordinated with Patricia Pyles (MSFC/M&P), Tony Day (MTI/W), and Robb Youst (Fiberite/Tempe).

The data indicates:

- The oxidation rate of CSA and CCA3 fabric at 525°C is strongly catalyzed by Pt.
- All of the investigation laboratories employ a conventional Pt pan to hold the TGA specimen.
- High oxidation rate values may also be incurred by air sweep gas blowing filaments out of the specimen pan. This is the Tony Day (MTI/W) conclusion and appears reasonable with respect to the short fiber lengths employed.
- The RSRM data generated at Fiberite/Winona, which reflects high oxidation rates, is not valid due to test procedure problems.
- With proper test procedure changes, the LPARL reference runs, with a tall Alumina pan, confirm the ability of this test to discriminate a low quality fabric (CSA/N. Hollywood) and a higher fired fabric such as VCX-13/WCA.
- Independent assessment of the 3 ea. CSA and 3 ea. CCA3 rolls for density and moisture adsorption capacity indicate these critical fabric properties fall within the LPARL data base for these commercial fabrics.

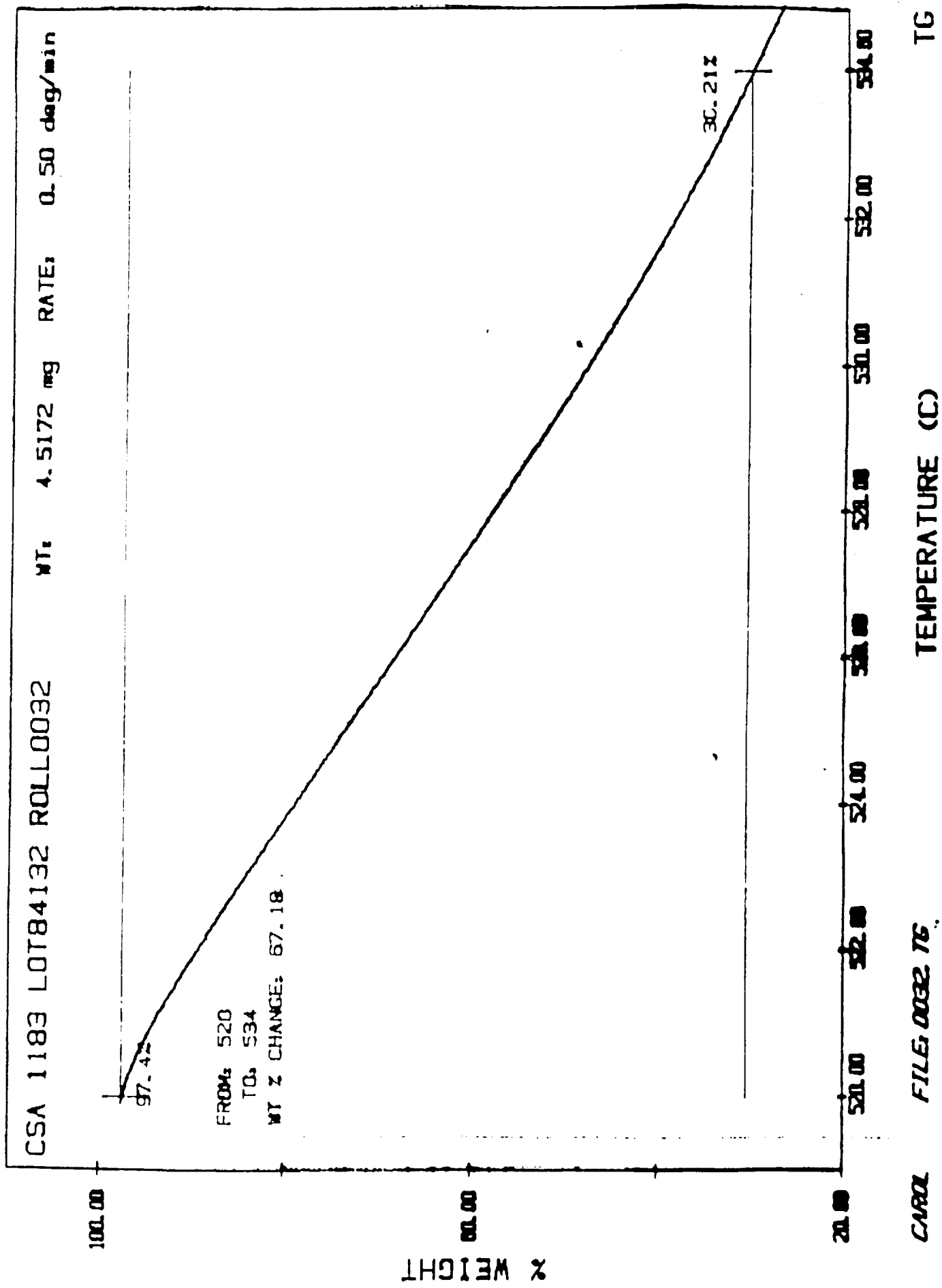


Pat C. Pinoli  
SPIP Subtask 3.2.1.1 Task Leader



CAROL FILE: 42266 TG

DATE: 08/08/20 TIME: 21.48



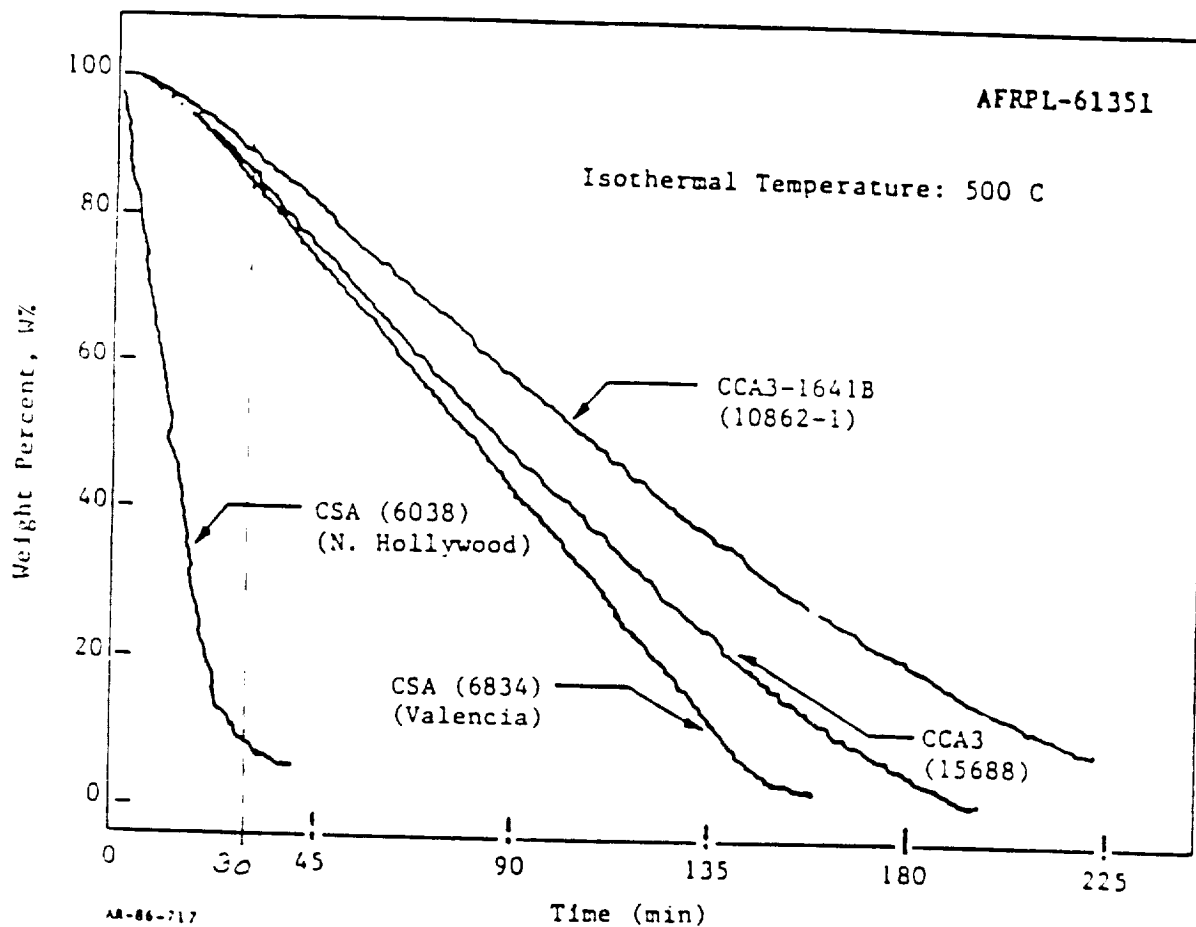
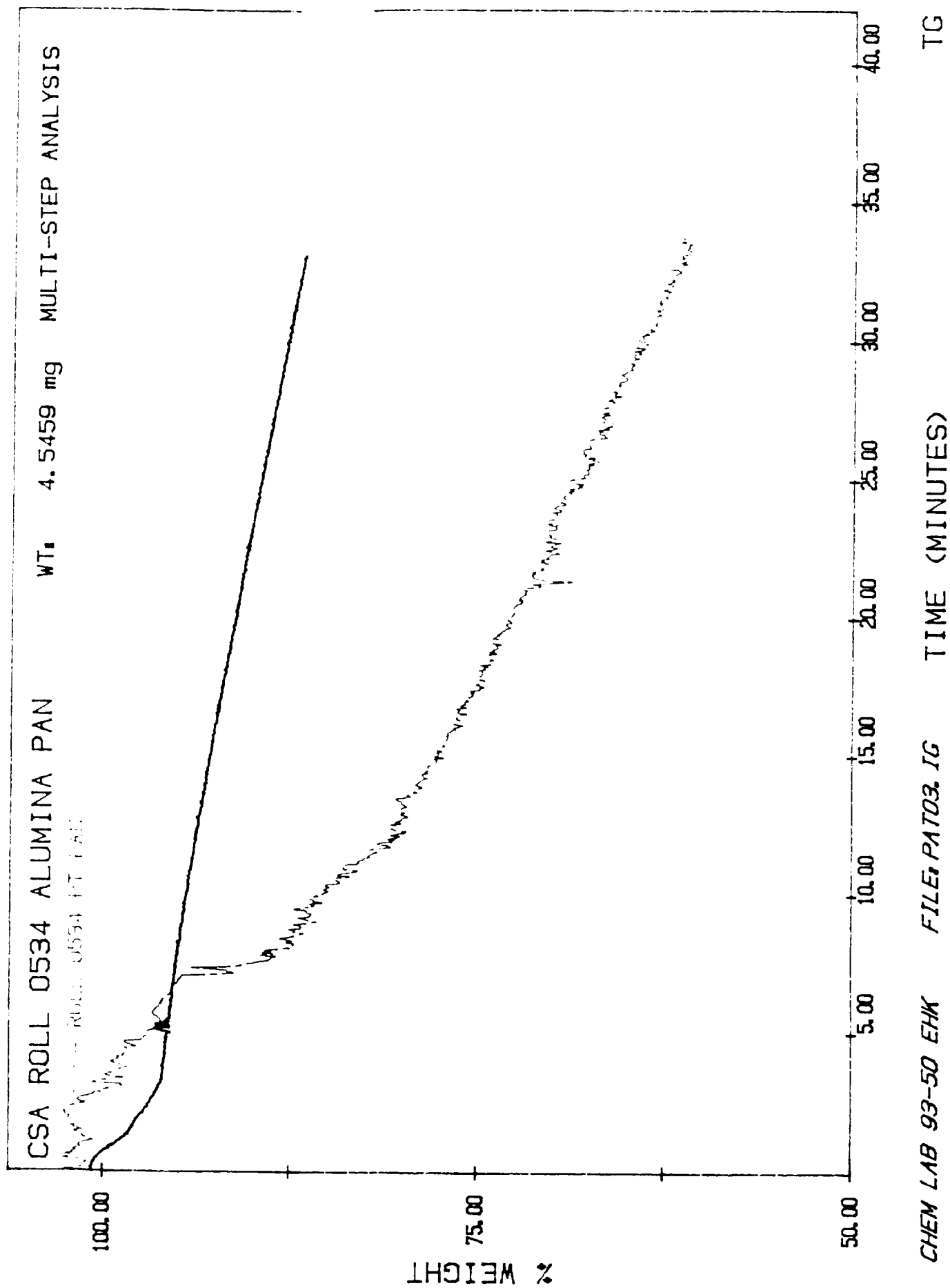


Fig. 2-51 Air Oxidation Weight Loss of CSA and CCA3 Carbon Fabrics

# LPARL TGA OXIDATION DATA SUMMARY

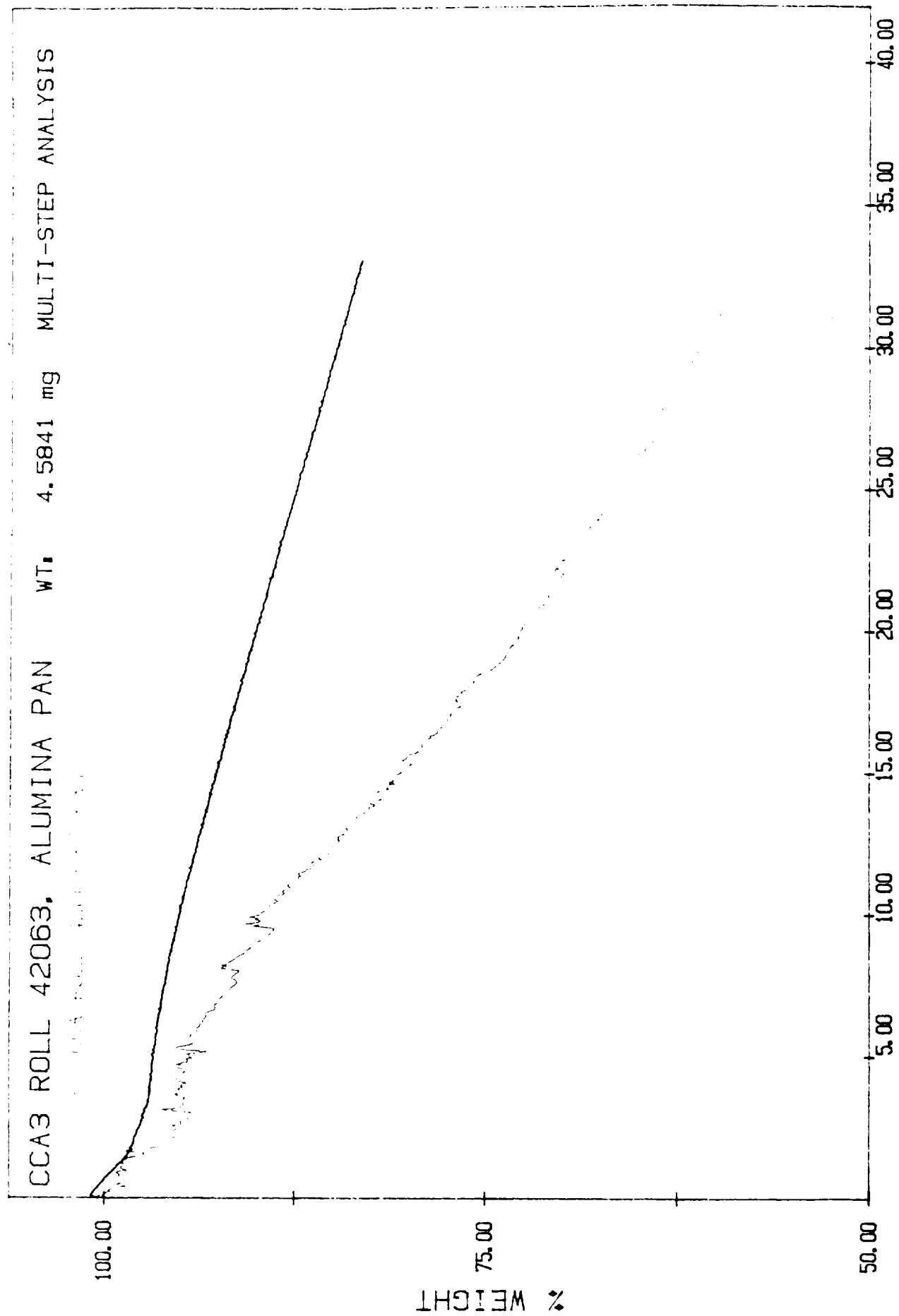
		30 Minute Weight Loss <sup>1</sup> , wt %	
<u>Mfg/Roll</u>	<u>Run</u>	<u>Alumina</u> <sup>2</sup>	<u>Pt</u> <sup>3</sup>
<u>CSA</u>			
0534	1	10.71	37.38
	2	<u>9.52</u>	
	x	10.12	
0539	1	14.43	
	2	<u>15.26</u>	
	x	14.845	
0567	1	14.29	
	2	<u>14.99</u>	
	x	14.64	
<u>CCA3</u>			
42063	1	14.21	37.25
	2	<u>12.94</u>	
	x	13.525	
42099	1	15.47	
	2	<u>16.55</u>	
	x	16.01	
42352	1	13.78	
	2	<u>14.19</u>	
	x	13.985	
Reference Fabrics			
CSA/N. Hollywood, 10B		88.42	97.6
Amoco/VCX-13		9.76	25.08
Amoco/WCA		0.51	3.71

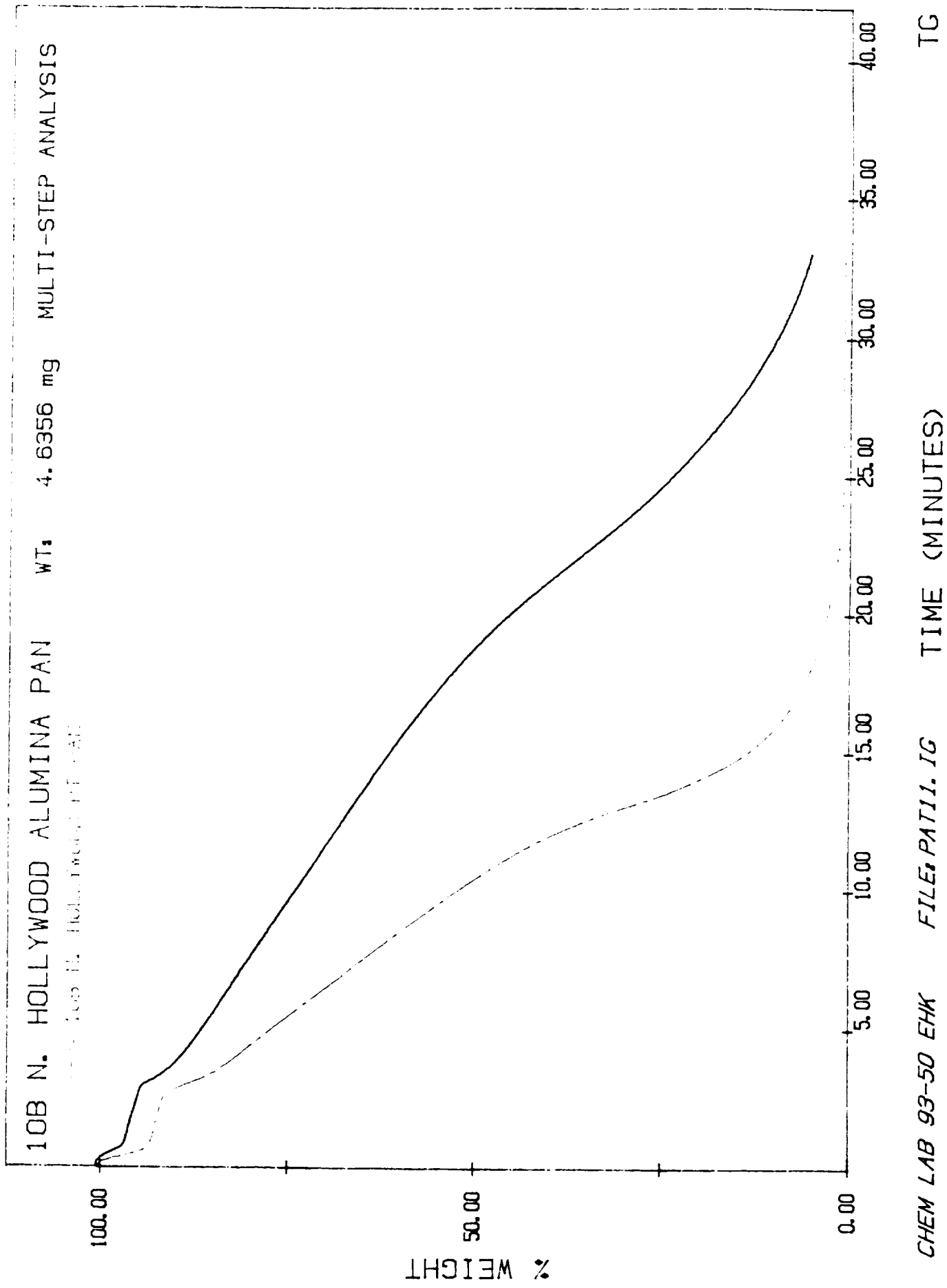
1. Isothermal 525°C per STW4-3184B procedure.
2. Pan Size, 4.5 mm deep.
3. Pan Size, 1.5 mm deep.



CHEM LAB 93-50 EHK      FILE: PA103.1G

DATE: 88/10/02      TIME: 14:53

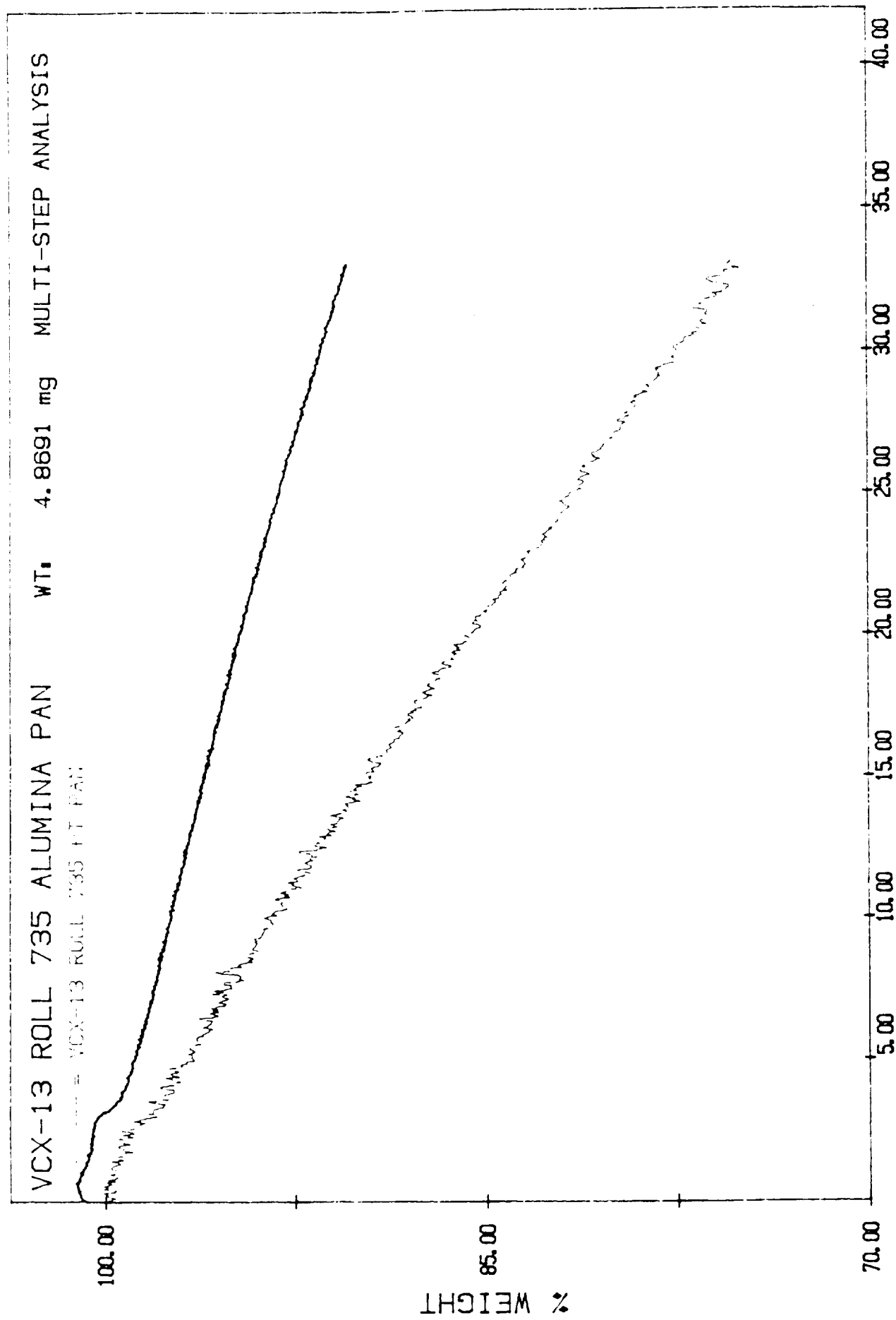




CHEM LAB 93-50 EHK    FILE: PAT11.IG

DATE: 88/10/04    TIME: 13.25





WCA ALUMINA PAN

WT. 4.6153 mg MULTI-STEP ANALYSIS

WCA PT PAN

103.00

% WEIGHT

93.00

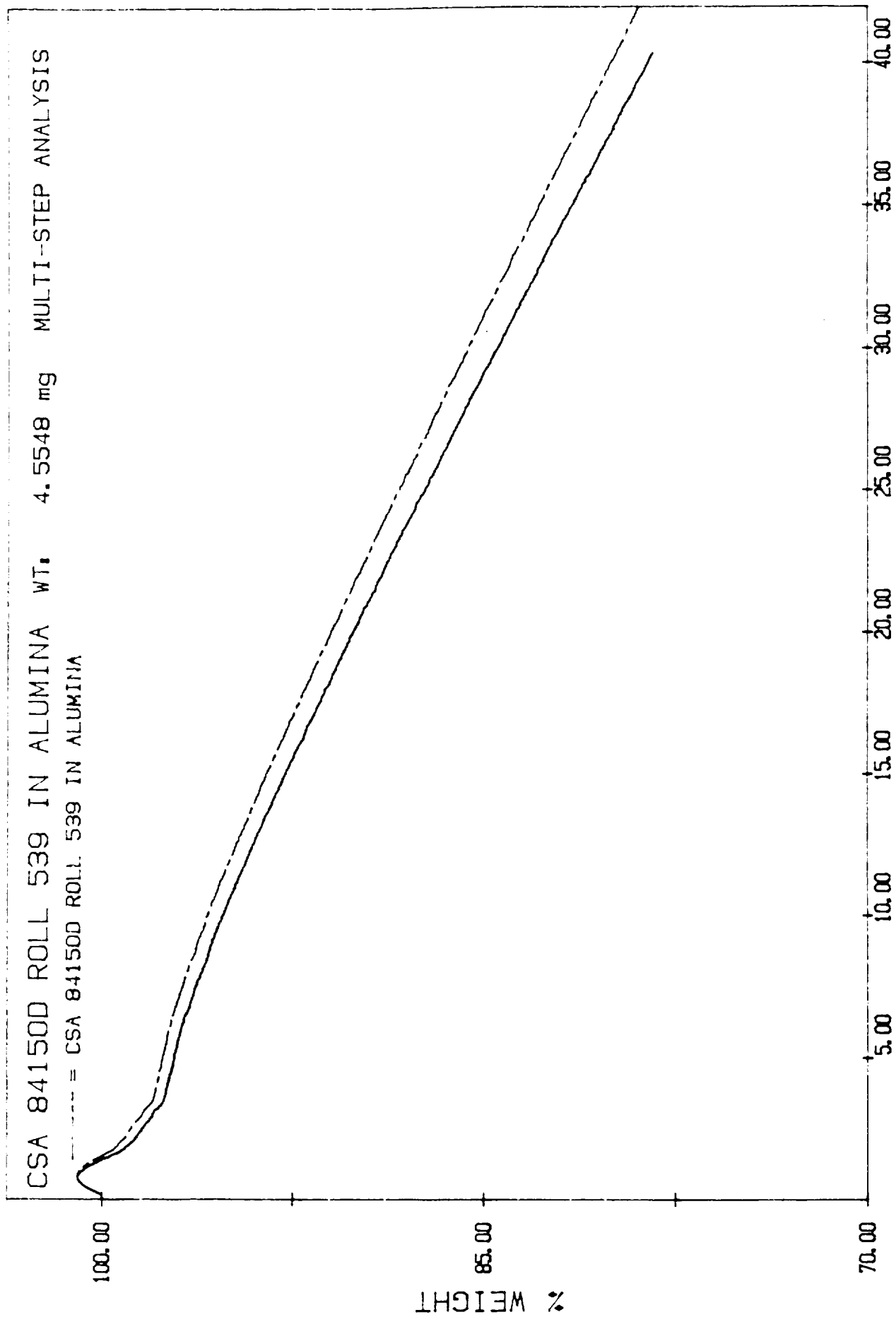
5.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00

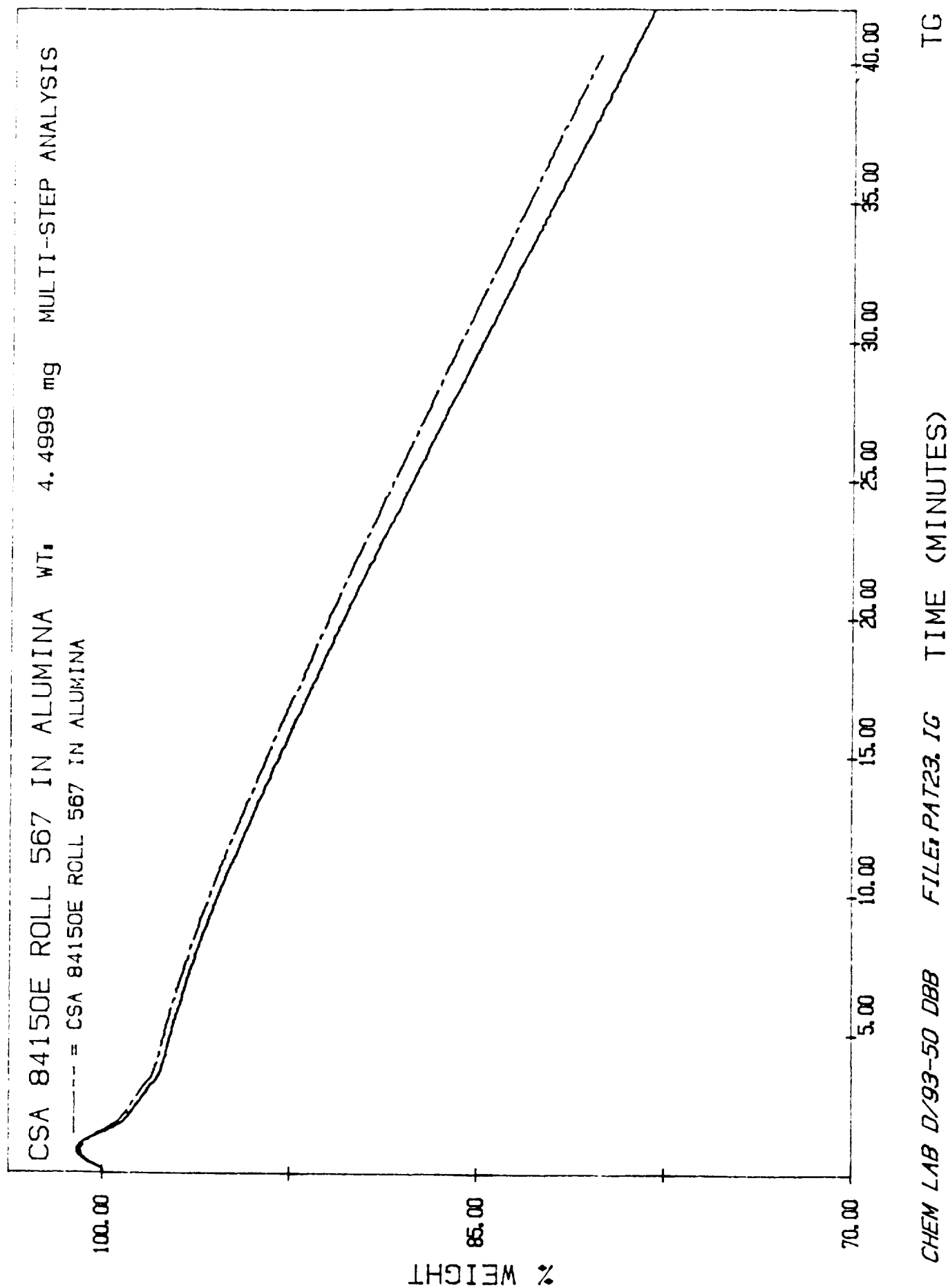
CHEM LAB 93-50 EHK FILE: PAT10.IG

TIME (MINUTES)

TG

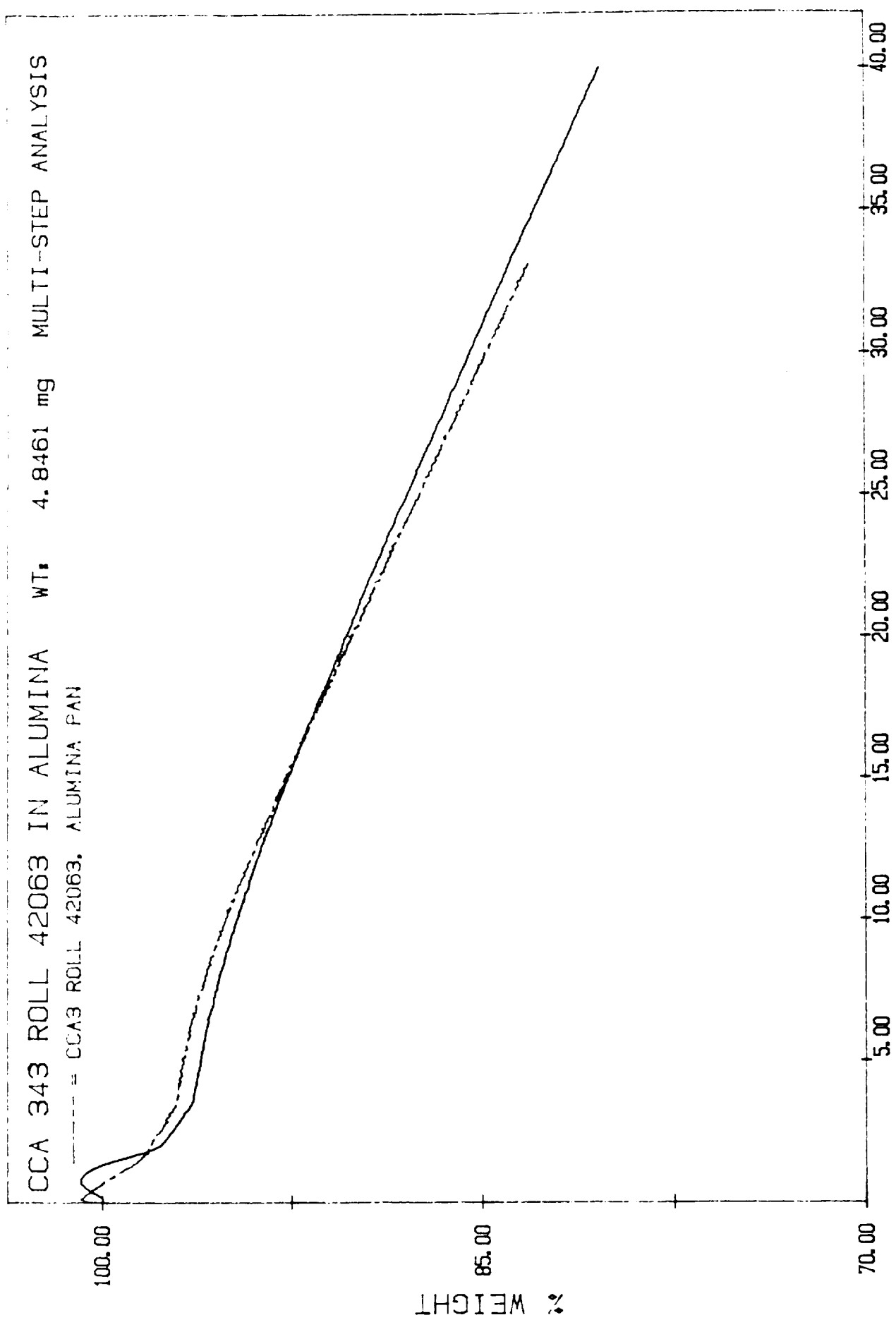
DATE: 88/10/04 TIME: 11.54



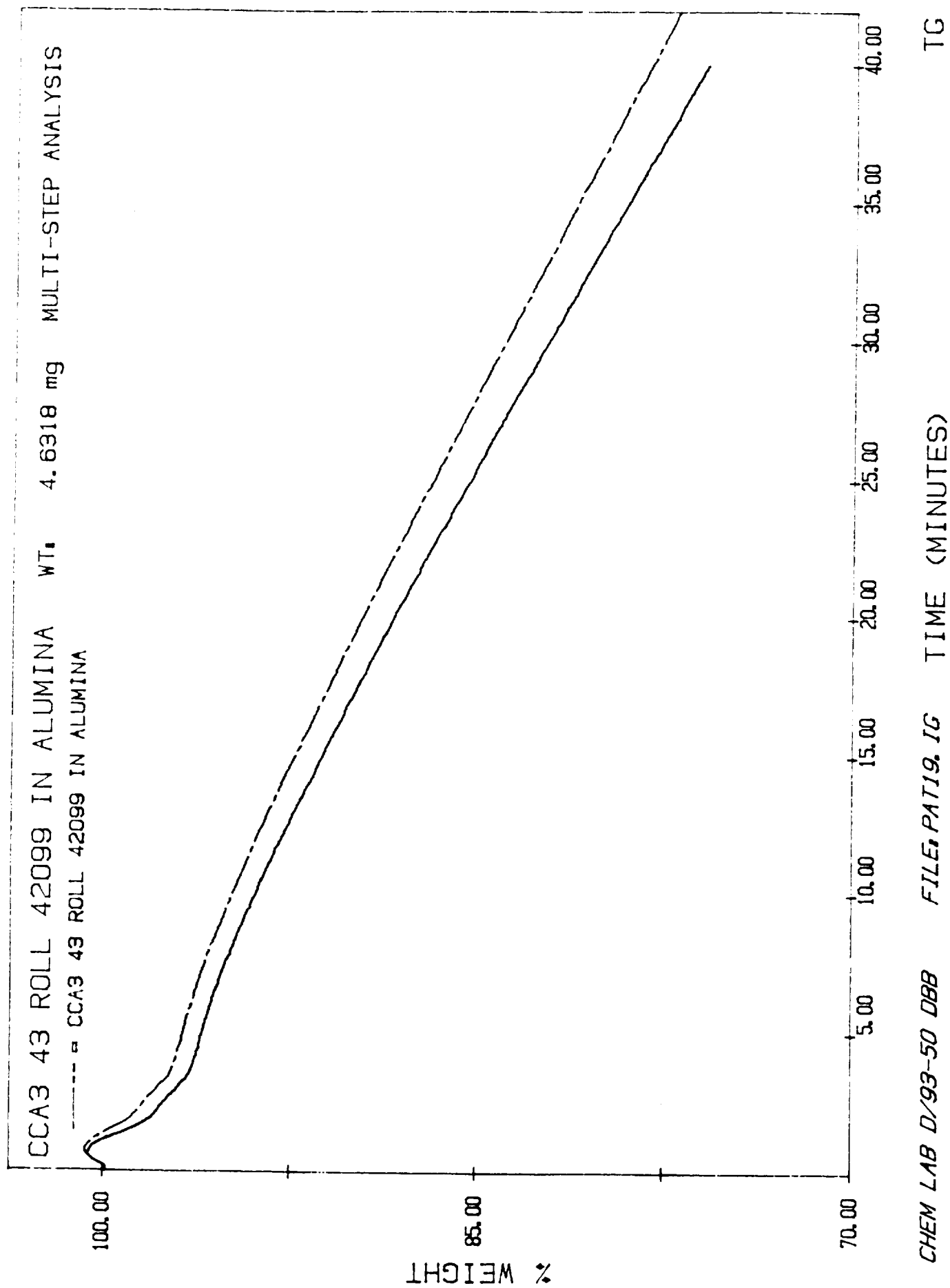


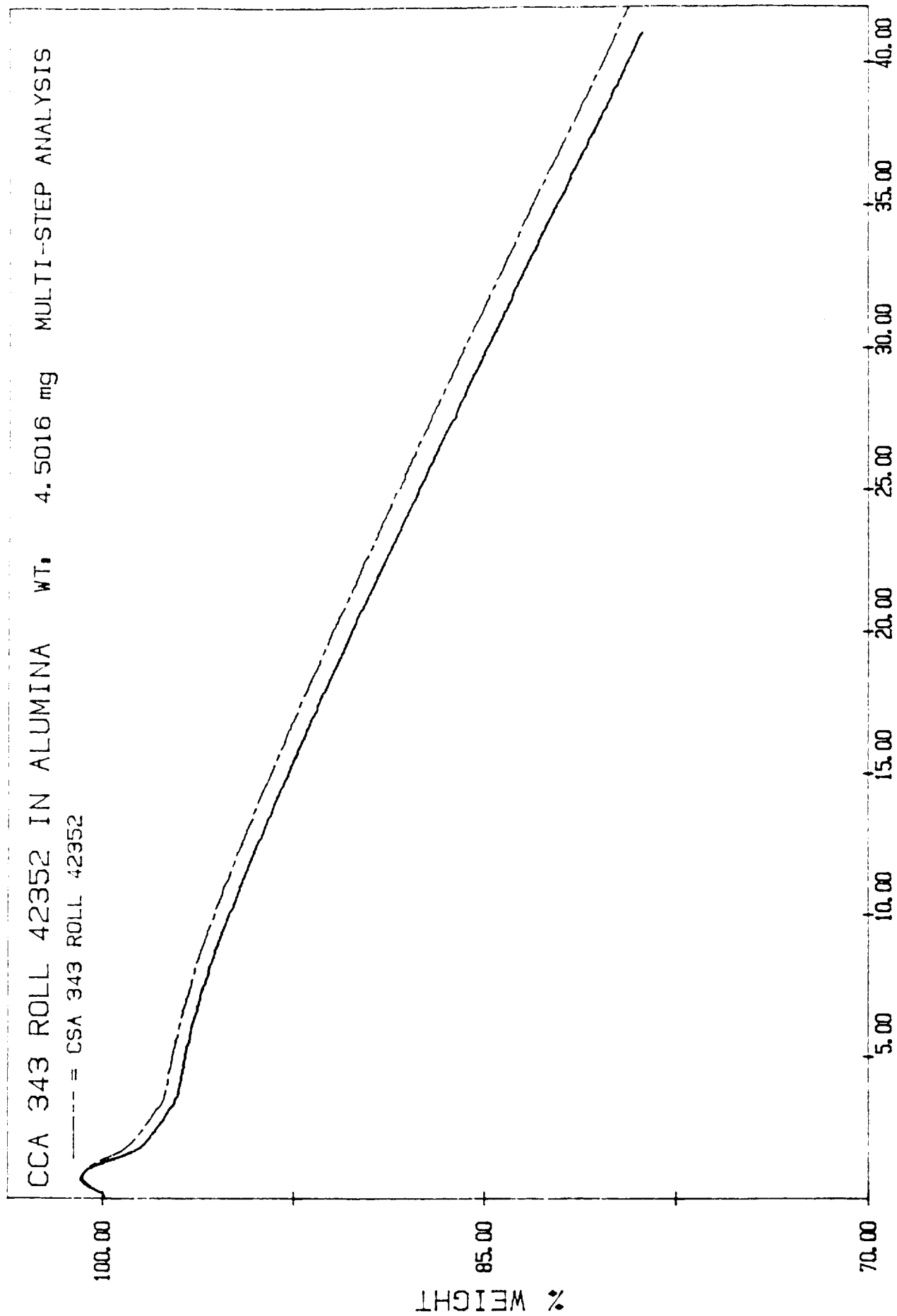
CHEM LAB D/93-50 DBB FILE: PAT23.1G

DATE: 88/10/14 TIME: 11:38



% WEIGHT





# LPARL TGA OXIDATION PAN STUDY

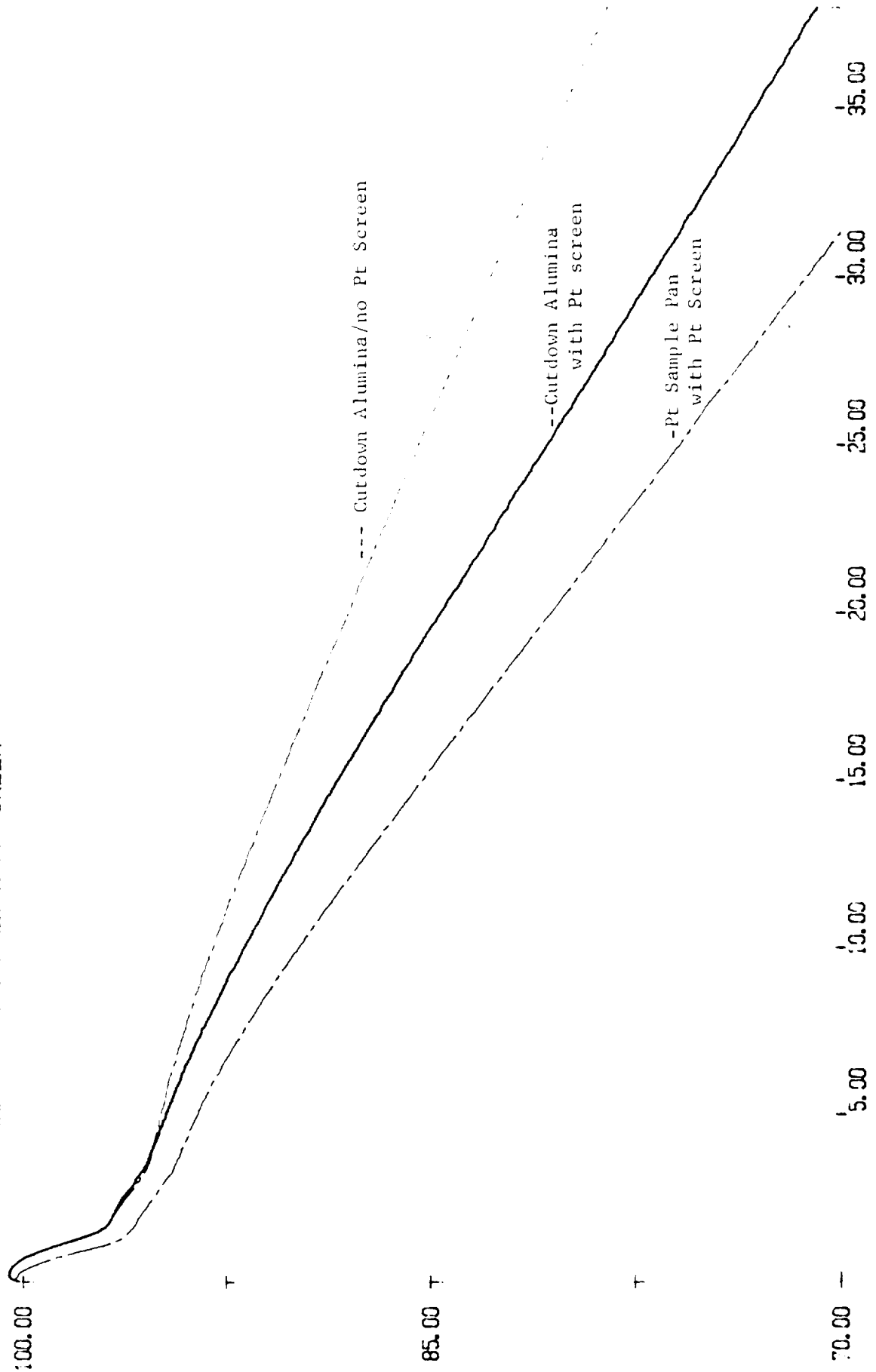
Mfg/Roll	30 Minute Weight Loss*, w/%
CSA Roll 0534	
1.5 mm deep alumina pan	14.57
1.5 mm deep alumina pan w/Pt. screen	21.33
1.5 mm deep Pt pan w/Pt screen	26.38

\*Isothermal 525°C per STW4-3184B procedure.

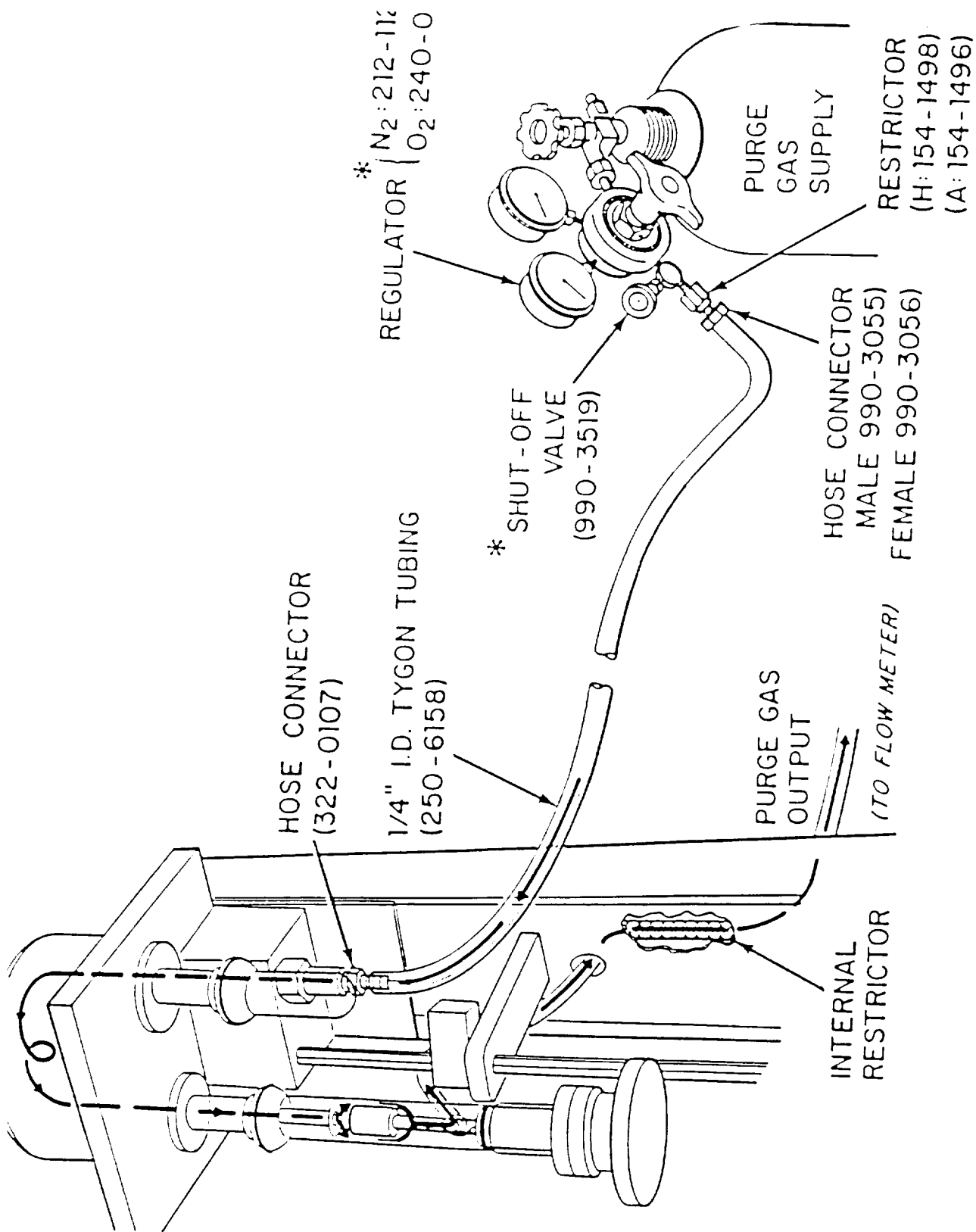


CSA 534 CTDM ALUMINA W. PT WT. 4.5603 mg MULTI-STEP ANALYSIS

----- CSA 534 CTDM ALUMINA SCREEN



WEIGHT %



*\* NOT INCLUDED WITH ANALYZER*

Fig. 4-2 Purge Gas Connections

# CARBON FABRIC PROPERTY TEST SUMMARY

<u>Mfg/Lot</u>	<u>Acceptance Data</u>						<u>LPARL DATA</u>	
	<u>Carbon Assay, w%</u>		<u>Na, ppm</u>		<u>Ash, w%</u>		<sup>*</sup> <u>Density</u> <u>g/cc</u>	<u>Adsorption</u> <u>Capacity,</u> <u>w%</u>
<u>CSA</u>	<u>Start</u>	<u>End</u>	<u>Start</u>	<u>End</u>	<u>Start</u>	<u>End</u>		
0534	99.7	98.9	290	230	0.05	0.12	1.460	14.80
0539	99.5	98.3	200	200	0.11	0.06	1.467	15.04
0567	97.8	97.9	490	190	0.25	0.15	1.458	15.01
<u>=</u> x	98.7		267		0.12		1.462	14.95
 <u>CSA3</u>								
42063	97.5	97.6	140	170	0.2	0.2	1.482	13.65
42099	97.6	97.2	260	460	0.1	0.2	1.473	15.13
42352	97.3	96.0	190	220	0.2	0.2	1.485	14.37
<u>=</u> x	97.2		240		0.2		1.480	14.38

\*60 minutes, center of fabric

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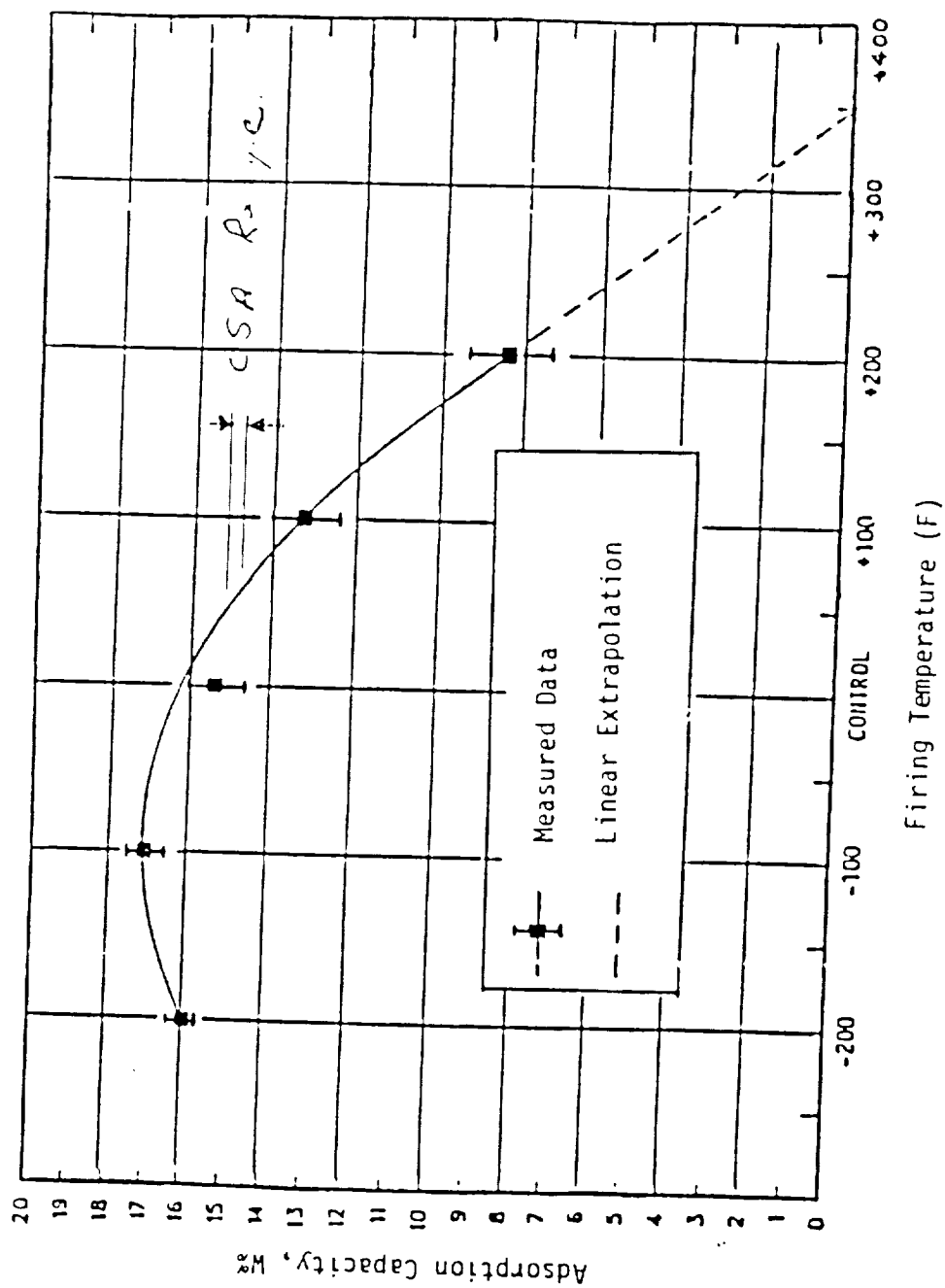


Fig. 2-25 Effect of Firing Temperature on Fabric Moisture Adsorption Capacity

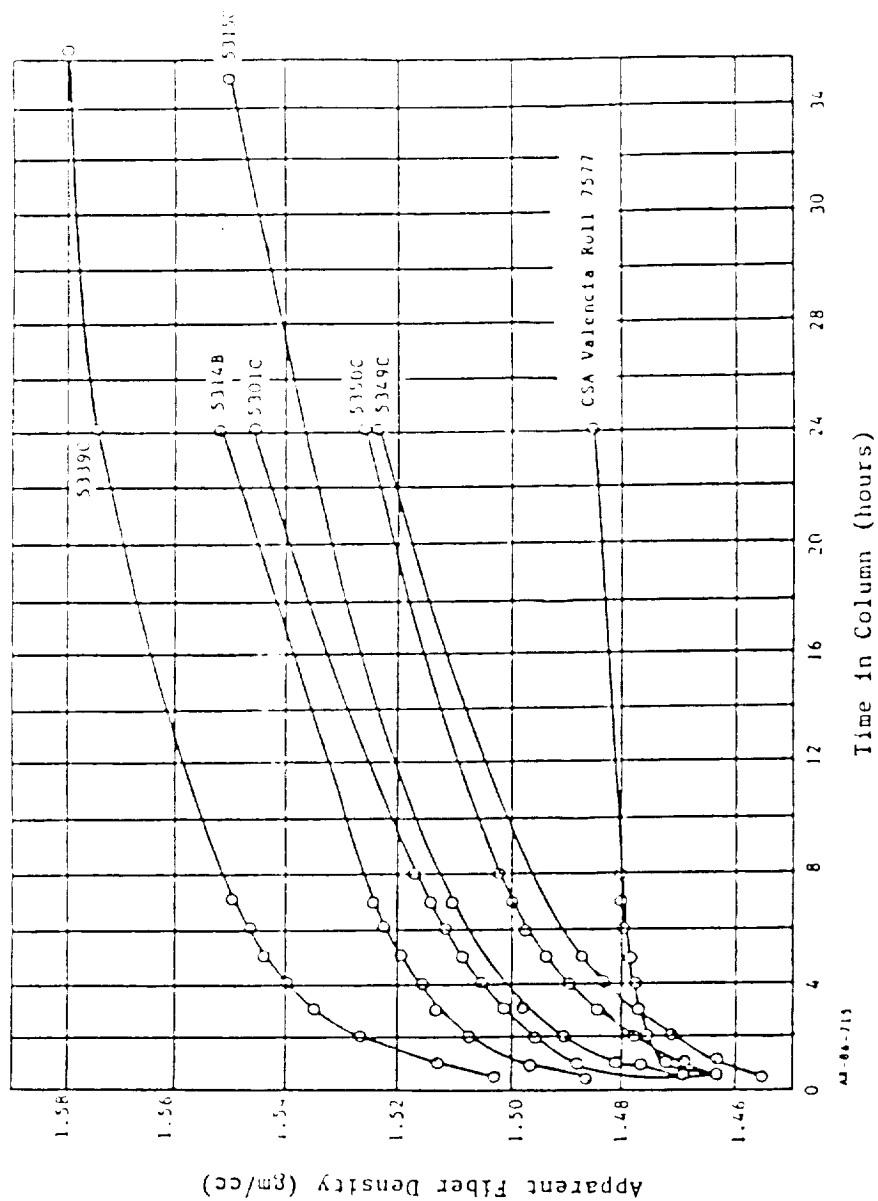
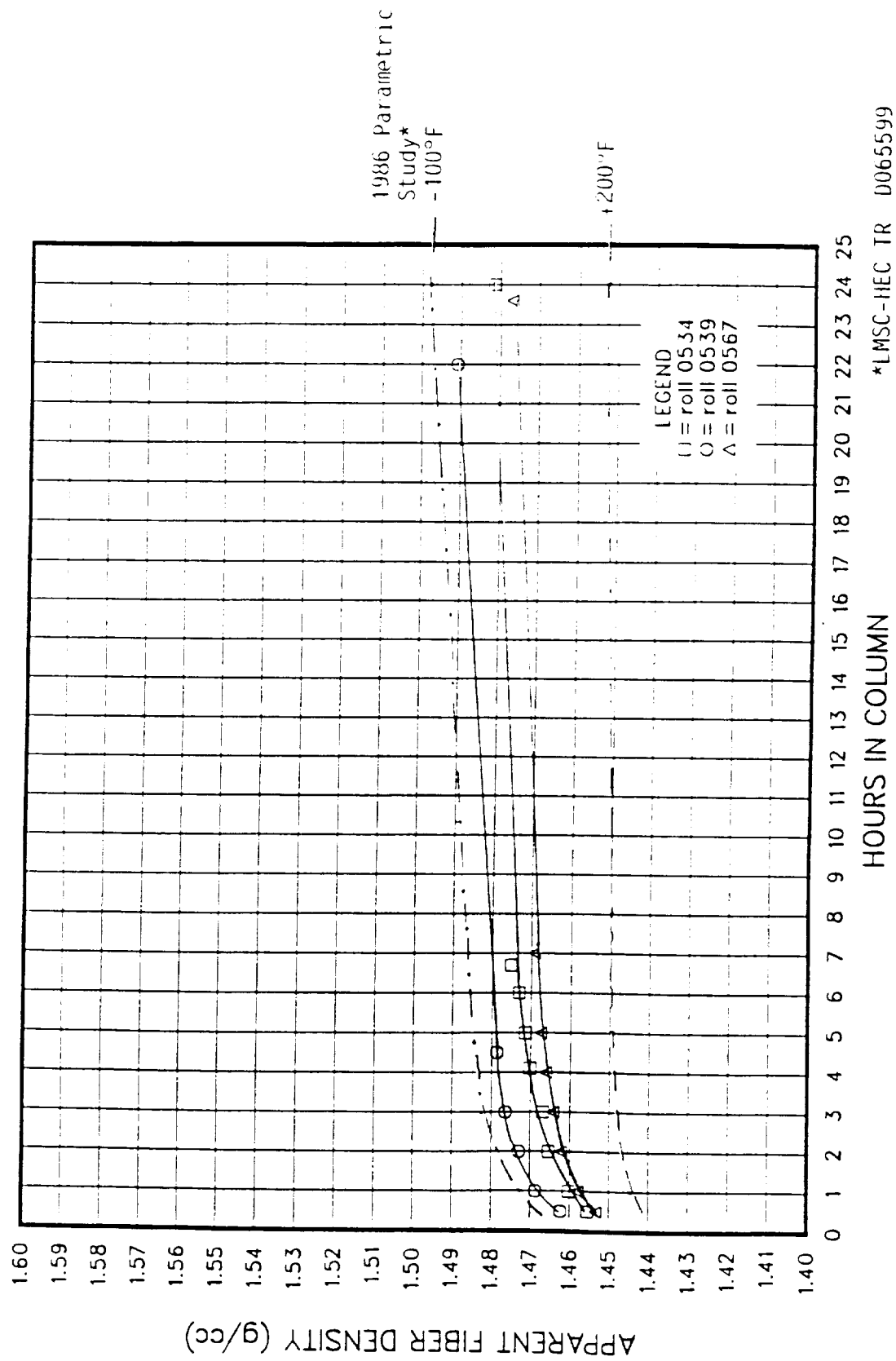


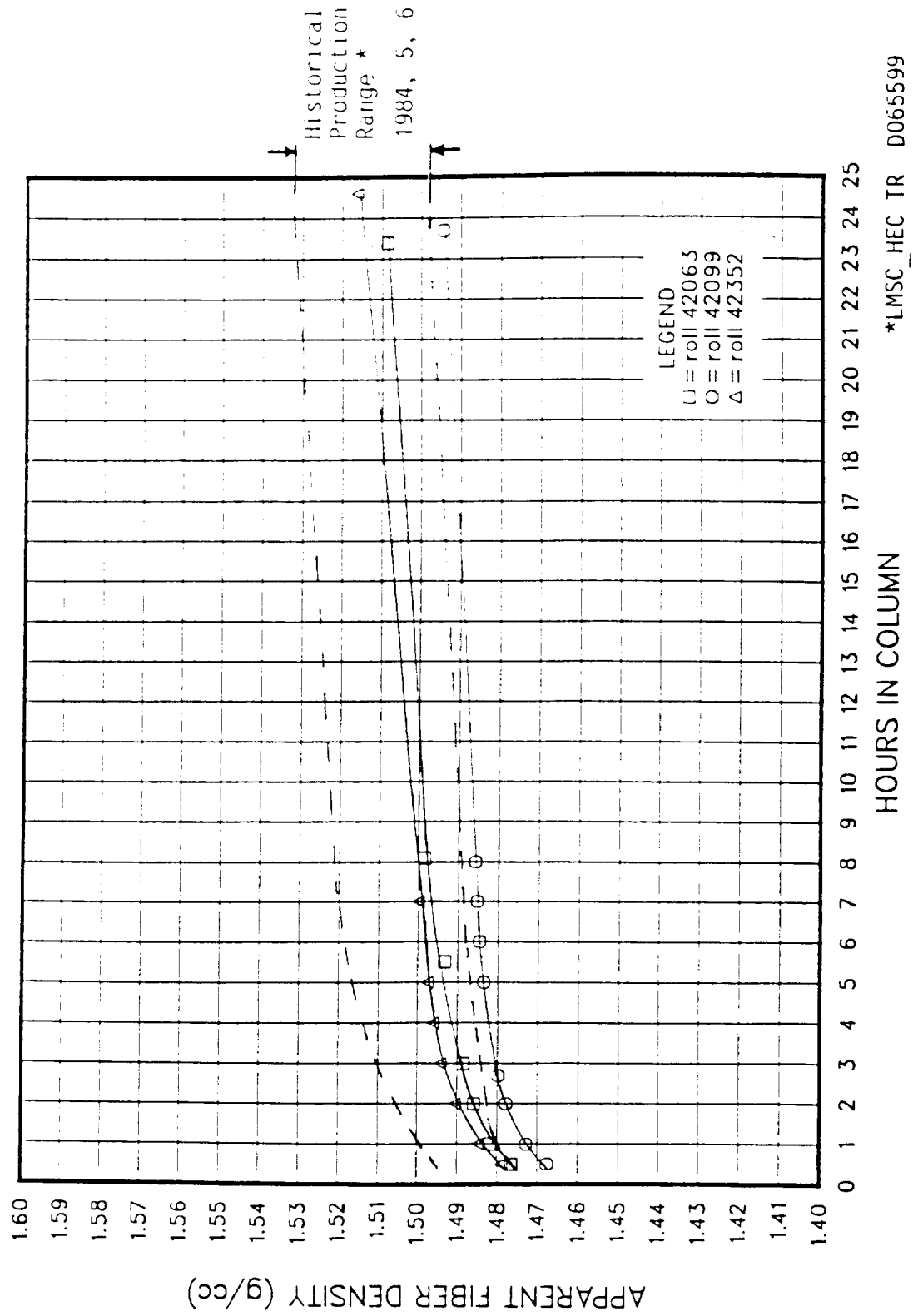
Fig. 2-16 Density Gradient Column Response of Polycarbon  
High Na Rayon Processed at N. Hollywood;  
Conventional N. Hollywood and Valencia Fabrics

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# DENSITY GRADIENT COLUMN RESPONSE OF POLYCARBON CSA FABRIC

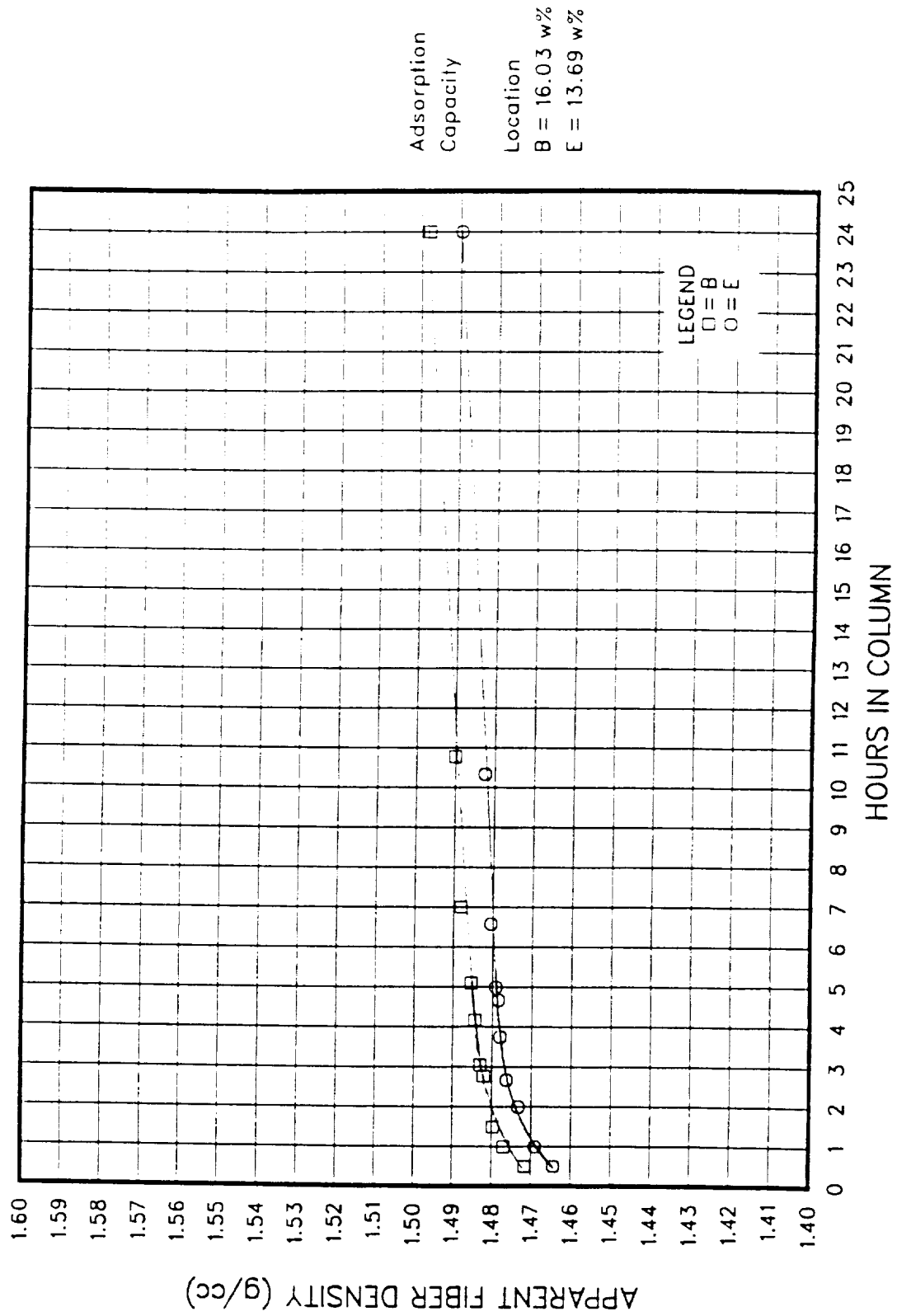


# DENSITY GRADIENT COLUMN RESPONSE OF HITCO CCA3 FABRIC



# DENSITY GRADIENT COLUMN RESPONSE OF POLYCARBON CSA FABRIC

Roll 0539 Survey





# TGA COMPARISON BETWEEN CCA AND CSA

SYSTEM	OPERATOR	PAN TYPE	AVE. %WT. LOSS/ STD. DEV.	
			CSA	CCA
DuPONT	MTL/H	PLATINUM	30.68/ 1.37	30.81/ 3.57
DuPONT	MTL/H	ALUMINA	26.61/ 3.39	25.69/ 5.66
PERKIN ELMER	P. PINOLI	ALUMINA	13.20/ 2.45	14.51/ 1.31
PERKIN ELMER	T. DAY	PLATINUM	20.06/ 1.56	22.00/ 2.95
PERKIN ELMER	MTL/H	PLATINUM	10.32/ .72	10.25/ 2.83

## TESTING CARBON FABRIC FOR OXIDATION MASS LOSS\*

Dr. W. B. Hall†, L. A. Fikes‡, and P. C. Pinoli¶

†Mississippi State University, Mississippi State, Mississippi

‡NASA-Marshall Space Flight Center, MSFC, Alabama

¶Lockheed Research and Development Division, Palo Alto, California

### ABSTRACT

Rayon based carbon fabric has been studied to assess reactivity to air oxidation/gasification. Excessive laboratory to laboratory variability of mass loss data by conventional thermal gravimetric analysis mandated a more fundamental approach to determine the sensitivity factors which influence the gasification process. Reaction activation energy and pre-exponential factor derived from the Arrhenius equation was used to assess the role of fabric firing temperature and Na catalytic action. Low temperature oxidation (400-500°C) was found to be most strongly influenced by Na catalytic action. At 400°C the oxidation rate was increased 681% by 2,240 ppm Na. The presence of water soluble Na anion significantly reduced the reaction activation energy from 34 to 21 Kcal/mole. The effect of firing temperature shifted the pre-exponential factors progressively from  $2.49 \times 10^6$  to  $2.63 \times 10^3$  g/g-sec after 2,500°C heat treatment. The Arrhenius temperature dependency was also used to assess laboratory to laboratory variance. Reaction rate data generated at ICI Fiberite, Tempe, Arizona, and Lockheed Research was found to deviate by 13°C, when compared at 525°C isothermal temperature.

### INTRODUCTION

Rayon based carbon fabric is employed exclusively in the current ablative nozzle employed on the shuttle redesigned solid rocket motor (RSRM). The shuttle qualified commercial fabrics (VCL, TGA and CCA3) represent a class of "activated carbon" fabrics which exhibit properties not typical of other commercial carbon fiber used for structural composite applications. This paper addresses the bare fabric properties which influence air oxidation sensitivity and assess test methodology issues. The work was performed under the auspices of the NASA sponsored Solid Propulsion Integrity Program (SPIP), Nozzle Initiative Subtask 3.2.1.1 on constituent materials test methodology.

### EXPERIMENTAL

A Perkin Elmer Model TGS-2 was used to measure mass loss of carbon fabrics when heated to temperature in 5 minutes and held isothermal for 30 minutes. Perkalloy magnetic transition at 596°C was used to calibrate furnace temperature. Fabric samples were prepared by cutting equal quantities of warp and fill yarns, 2-4 mm in length. Each TGA sample was pre-weighed to  $4 \pm 0.4$  mg and packed into a 4 mm ID glass tube prior to being transferred a quartz TGA pan. Pre-packing of each sample provided a consistent preform for transfer to the quartz pan. Bottled dry air, Linde UN-1002 with <3 ppm water, was employed with a constant purge rate of  $25 \pm 3$  cc/minute. The programmed heating cycle employed a heating rate from 25°C to temperature of 100°C/minute, followed by an isothermal hold for 30 minutes.

### DISCUSSION

The classic method to study the oxidation/gasification of carbon materials is compliance to the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

where:  $k$  = specific reaction rate,  $\text{sec}^{-1}$   
 $A$  = pre-exponential factor,  $\text{sec}^{-1}$   
 $E_a$  = activation energy, cal/mole carbon  
 $R$  = gas constant, cal/mole  $^\circ\text{K}$   
 $T$  = absolute temperature,  $^\circ\text{K}$

Specific reaction rates can be normalized to initial specimen weight or surface area. In this study we chose to use the specimen weight at the onset of reaching the isothermal temperature.

\*This work was performed under NASA contract NASA8-37801, Solid Propulsion Integrity Program - Nozzle Initiative SUBTASK 3.2.1.1 at Lockheed R&DD, Palo Alto, California. Paper presented to JANNAF Rocket Nozzle Technology Subcommittee Meeting, NSWC, Silver Spring, MD - October 17, 1989.

The heterogeneous carbon-oxygen reaction rate of carbon fiber can be predominantly influenced by one of three zones.<sup>1,2,3</sup>

Zone I relates to surface chemisorption of oxygen and concurrent desorption of CO or CO<sub>2</sub>. Activated carbon, such as the qualified shuttle fabrics, respond strongly to this process. Zone I influence is generally predominant at low temperature (<500°C).

Zone II involves the diffusion of oxygen into the fiber micropore structure and diffusion of CO or CO<sub>2</sub> out of the pores. Zone II is generally predominant at moderate temperature (500-650°C).

Zone III involves the diffusion of oxygen through a stagnant gas stream of CO and CO<sub>2</sub> at the carbon surface. This is commonly referred to as the "reaction controlling factor", i.e., reaction products must be removed to allow carbon access to oxygen. This zone is generally most influential at higher temperature - (>650°C).

The issue of Zone III influence on TGA assessment of fiber oxidation rates at lower temperature was highly suspect due to the pan shape and variability of fiber packing. The TGA quartz pan employed in this study was about 4 mm in diameter x 1 mm deep. In order to minimize packing variability, a preform of 4±0.5 mg fibers was compacted prior to being introduced into the quartz pan. Reaction products (CO and CO<sub>2</sub>) were not allowed to stagnate by using a high flow rate of air, 25 cc/min, directed into the quartz pan. All of the TGA runs conducted for this study were to a linear programmed heating cycle from ambient temperature to temperature in 5 minutes followed by a 30 minute isothermal hold. Isothermal temperatures were chosen to obtain measureable low rates that would preferably fall within Zone I influence.

The influence of fabric firing temperature, Na level and surface area was investigated by evaluating the reaction kinetics of 5 rayon based fabric variations. The properties of these fabrics are summarized in Table I. Experimental 10B fabric represents the effect of low firing temperature (<1300°C), high Na (2,240 ppm) and high surface area (~800 m<sup>2</sup>/g). A water washed 10B fabric was prepared by exposing a sample of as received 10B fabric to 5 sequential soakings in boiling distilled water. This operation significantly reduced Na anion level by about 40%.<sup>4</sup> The CCA3 fabric represents shuttle grade fabric fired to a 1300°C range. VCX-13 fabric is a higher fired version of shuttle grade fabric-fired by Amoco ~100°C above commercial VCK fabric. Unique aspects of VCX-13 vs. shuttle grade fabric is the significant reduction in measured surface area and moisture adsorption capacity; <7 m<sup>2</sup>/g and 0.7 wt% respectively. The effect of very high heat treatment is represented by commercial WCA fabric. This fabric reflects high purity, no moisture adsorption capacity and surface area close to theoretical round/solid filament (1 m<sup>2</sup>/g).

Table I. Carbon Fabric Properties

Fabric Identification	Firing Temp. °C	Fiber Density, g/cc**	Carbon Assay, wt%	Ash wt%	Na ppm	Moisture Adsorption Capacity, wt%***	Surface Area, m <sup>2</sup> /g
1. Experimental 10B	<1300	1.467	97.5	0.89	2,240	24.4	~800
2. Experimental 10B W/W*	<1300	1.467	~97.5	~0.89	~1,000	~16	~800
3. CCA3 - Roll 42063	1300°C Range	1.482	97.6	0.2	140/170	13.6	476-923
4. VCX-13 4C7VCX 13/735	>1400	1.472	>99	0.08	25/125	0.7	<7
5. WCA	>2500	1.448	99.9	0.01	0	0.1	1

\*Water Washed 5 times in distilled water.

\*\*By Gradients Column, 60 minutes

\*\*\*Weight Gain after exposure to 100% R.H. for 24 hours.

A progressive series of oxidation rates at isothermal temperature were measured on each of 5 fabric variations to assess compliance with the Arrhenius equation. Table II presents measured reaction rates with corresponding temperatures for the 5 fabric variations.

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Table II. Air Oxidation Rates of Carbon Fabrics

Temperature, °C	Rates (g/g-sec x 10 <sup>-5</sup> )				
	Exp. 10B As Received	Exp. 10B Water Washed	CCA3 (42063)	VCX-13	WCA
400	3.40	0.70			
425	5.61				
450	9.09	3.00	1.05		
475	16.5		2.37		
500	24.4	12.1	5.30	3.78	
510	32.4	16.3			
525	53.7/51.3/61.7	24.0	11.2	7.47	
535	69.1				
550	120.9	47.3	25.8	15.4	
575				30.1	1.08
600				57.0	2.32
625					3.32
650					4.93
675					9.30
700					13.6

The strong influence of firing temperature on reaction rate is evident by the need to progressively increase isothermal temperature to achieve comparable mass loss rates. The Arrhenius plots in Figure 1 however show 10B W/W, CCA3, VCX-13 and WCA all reflect a common activation energy (line slope).

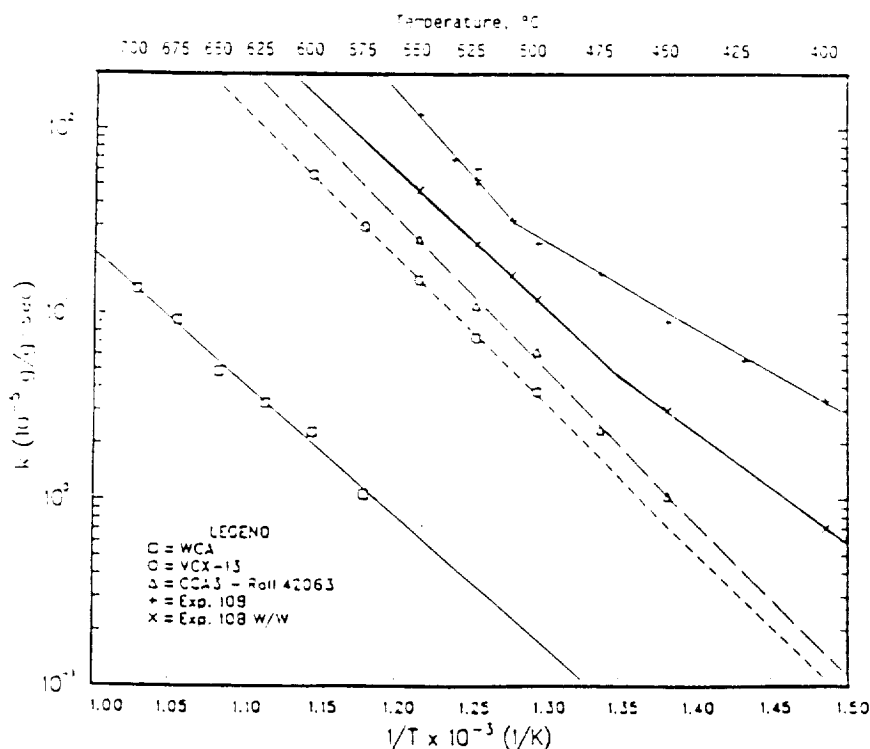


Fig. 1. Arrhenius Plots of Carbon Fabric Oxidation Response

The measured high surface areas of 10B W/W and CCA3 did not influence the oxidation reaction activation energy. Obviously Zone II oxygen diffusion into filament micropores is not an influential factor effecting the reaction activation energy. In particular, the three higher fired samples, WCA, VCX-13 and CCA3 all reflect an excellent agreement with the Arrhenius equation - temperature depending. The effect of Na catalytic action is most pronounced with as received experimental 10B fabric. The rate change at low temperature reflect a significantly lower activation energy extending up to ~500°C and transcending to a much higher energy level. Activation energy and pre-exponential factors related to the fabric samples studied are summarized in Table III.

Table III. Activation Energy and Pre-exponential Factor

Fabric Identification		$E_a$ , Kcal/mole	A, Pre-exponential Factor
1. Experimental 10B	To 500°C	20.8±0.7	1.82 x 10 <sup>2</sup>
	Above 500°C	40.1±2.3	5.29 x 10 <sup>7</sup>
2. Experimental 10B W/W		34.2±0.8*	5.53 x 10 <sup>5</sup>
3. CCA3 Roll 42063		37.6±1.3	2.49 x 10 <sup>6</sup>
4. CCA3 Roll 42063**		36.1±0.6	6.72 x 10 <sup>5</sup>
5. VCX-13 Roll 4C7VCX13/735		36.4±0.5	7.23 x 10 <sup>5</sup>
6. WCA		32.4±1.6	2.62 x 10 <sup>3</sup>

\* 4 Data Points only, 500 to 550°C

\*\* Data generated at ICI, Tempe, Arizona

Figure 2 compares Arrhenius plots of as received experimental 10B with 2,240 ppm Na and 10B after a water wash reduction in Na content to about 1,200 ppm. Reduction of Na level by water washing was demonstrated by previous effort.<sup>4</sup> The strong influence of Na on the reaction rate of 10B as received is clearly evident from 400°C up to about 500°C. This low temperature range reflects a significantly lower activation energy of 20.8 Kcal/mole carbon. Above 500°C the activation energy is less easily defined (40.1 Kcal/mole carbon) but appears to revert to a primary Zone I influence. The water washed version of 10B reflects a small amount of Na influence as indicated by the dotted line below 475°C. The rate differences between this dotted line and the as received 10B value can be interpreted as the influence of Na on the carbon-oxygen reaction. Table IV summarizes reaction rate values and normalizes the reaction rate change to the influence of Na. The effect of Na is most pronounced at the lowest measured temperature of 400°C reflecting a 681% rate increase.

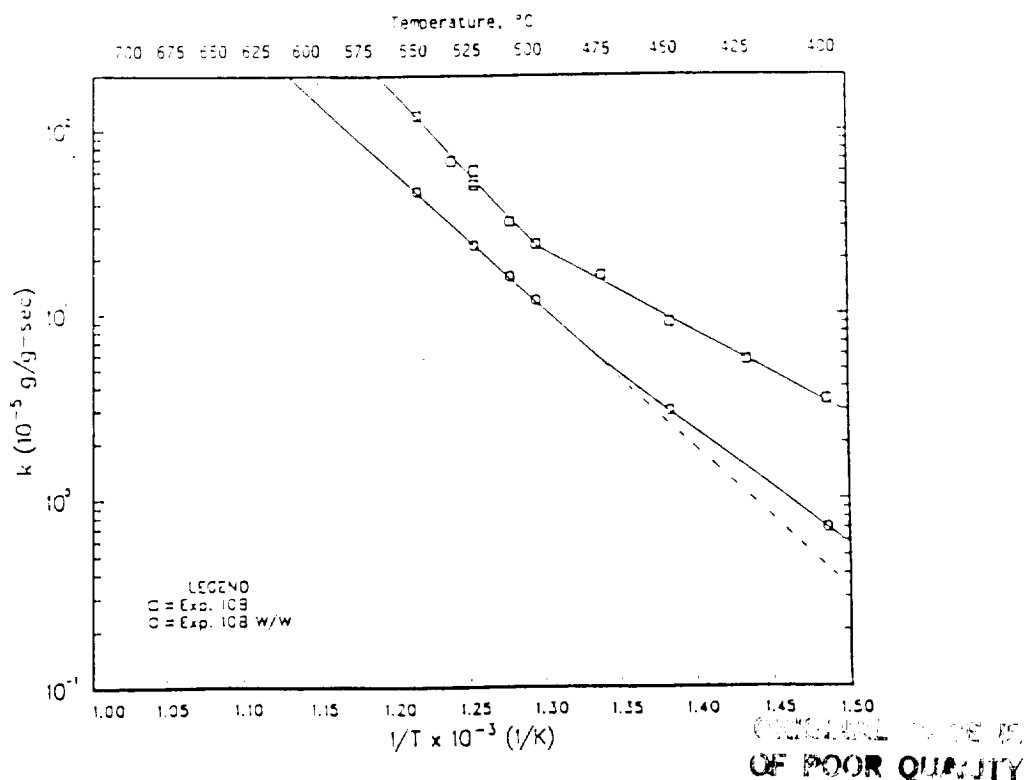


Fig. 2 Arrhenius Plots of 10B As Received vs. 10B Water Washed

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Table IV. Effect of Na on Oxidation Rate of Exp. 10B Fabric

Temperature °C	A.R. Air Oxidation Rate*, g/g - sec	W.W. Air Oxidation Rate**, g/g - sec	Influence of Na, % Rate Increase
500	$24.4 \times 10^{-5}$	$12.1 \times 10^{-5}$	102
475	$16.5 \times 10^{-5}$	$8.61 \times 10^{-5}$	194
450	$9.09 \times 10^{-5}$	$2.54 \times 10^{-5}$	259
425	$5.61 \times 10^{-5}$	$1.09 \times 10^{-5}$	415
400	$3.40 \times 10^{-5}$	$0.435 \times 10^{-5}$	681

\* As Received

\*\* Water Washed, rates up to 475°C are extrapolated to remove Na influence

The effect of firing temperature on the reaction activation energy is minimal as indicated by a 37.6 Kcal/mole carbon value for commercial CCA3 fabric extending to a 32.4 Kcal/mole value for high fired WCA fabric. Equally important is the confirmation by the plots of close agreement with the reaction-temperature dependency of the Arrhenius equation. Lack of data scatter clearly indicates the predominant reaction kinetics in these temperature ranges is the same (Zone I). Excellent agreement of the individual run data (lack of scatter) also suggests the influence of Zone III oxygen diffusion is minimal.

The influence of fiber surface area on the reaction kinetics can be studied by analyzing measured fiber properties, TGA mass loss, and Arrhenius plots. Measured surface area (by CO<sub>2</sub> adsorption) for 10B, 10B W/W and conventional CCA3 reflect "activated carbon" values (476-923 m<sup>2</sup>/gm).<sup>4</sup> The surface area of VCX-13 (<7 m<sup>2</sup>/gm) suggests pore closure has developed a skin/core condition; the filament skin being impermeable to CO<sub>2</sub> molecular intrusion and the inner core reflecting a high surface area. Fiber density analysis by gradient technique has verified the sensitivity of skin/core pore structure to oxidation.<sup>5</sup> The high fired fiber, WCA reflects a surface area of 1 m<sup>2</sup>/gm - no accessible microporosity. In theory, higher fiber surface area should provide proportionally higher isothermal oxidation rates; and activation energy should be independent of surface area.

The high measured surface area fibers (10B, 10B W/W and CCA3) therefore should reflect proportionally higher oxidation rates than VCX-13 or WCA. If we assume WCA as the baseline low surface area fiber (1 m<sup>2</sup>/gm), individual oxidation rates for the other fabrics should be progressively higher in proportion to surface area. Fabric VCX-13 should reflect up to 7 times higher isothermal rates as opposed to commercial CCA3, 476 to 923 times higher. The Arrhenius plots show VCX-13 exhibits a much larger 25X increase; however CCA3 reflects a much smaller (than surface area indicates) 39X increase. This analysis indicates isothermal oxidation rates increase with higher measured fiber surface area but not in direct proportion to the measured surface area. The Arrhenius plots do show the strong influence of firing temperature on oxidation sensitivity. Unresolved however is whether high temperature heat treatment is influencing available surface area during the oxidation process and/or is reducing exposed edge plane atoms of carbon (armchair and zig zag).

The same Arrhenius plotting technique was employed to assess reproducibility of TGA data between different facilities. A series of runs on CCA3 Roll 42063 were performed at Fiberite, Tempe, Arizona, for comparison with Lockheed research data. Figure 3 compares the Arrhenius plots and shows good agreement of line slope (activation energy). Activation energy values of the runs were comparable 36-38 Kcal/mole carbon values, Ref. Table III. The line offsets suggest at 525°C the two runs reflect a potential calibration offset of 13°C. This sensitivity to calibration was further studied by using the Arrhenius equation ( $E_a = 37,600$  Kcal/mole and  $A = 2.49 \times 10^6$ ) to assess reaction rate sensitivity to isothermal temperature. The 525°C oxidation rate of shuttle grade carbon fabric will double at 549°C (Δ24°C) and the 450°C oxidation rate will double at 470°C (Δ20°). This defines the criticality of laboratory to laboratory calibration and indicates reducing the current mass loss test temperature from 525°C to 450°C will not significantly reduce oxidation rate sensitivity to calibration temperature.

The results of this study on cellulosic (rayon) based carbon are consistent with the behavior of other hard polymeric carbons.<sup>6</sup> Similar reactivity studies on glass-like carbons developed activation energy values of 35±5 Kcal/mole carbon and the effect of heat treatment temperature is similar.<sup>7,8,9</sup>

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### CONCLUSIONS

The oxidation behavior of rayon based carbon fabric in air was found to be in compliance with the reaction rate vs. temperature relationship of the Arrhenius equation. The reaction rate of RSRM shuttle grade carbon fabric in air can be expressed by the following equation:

$$k = 2.49 \times 10^6 e^{-37,600/RT}$$

The isothermal oxidation rates of shuttle grade fabric were found to not increase proportionally to fiber surface areas determined by  $CO_2$  adsorption and the Dubinin-Polanyi equation. The oxidation resistance of rayon based carbon fiber was found to be strongly influenced by fabric firing temperature, with oxidation resistance increasing with firing temperature.

The oxidation sensitivity of Experimental 10B fabric is influenced by both firing temperature and Na anion level. The effect of Na catalytic action is most pronounced at low temperature and at 400°C the oxidation rate is increased by 681%. The Na catalytic effect on oxidation rate diminishes with increasing temperature and at 520°C the reaction activation energy changes from 21 to 40 Kcal/mole carbon. Removal of Na by water washing was very effective in reducing the residual Na level and the fabric oxidation rate was correspondingly reduced.

These results indicate the oxidation sensitivity of shuttle grade carbon fabric is influenced by two factors; firing temperature and Na level above ±1200 ppm. Current fabric specifications monitor firing temperature by carbon assay analysis and Na content is determined by measuring the Na level in carbon fabric ash. Accurate assessment of these two factors should preclude the need for an oxidation mass loss test.

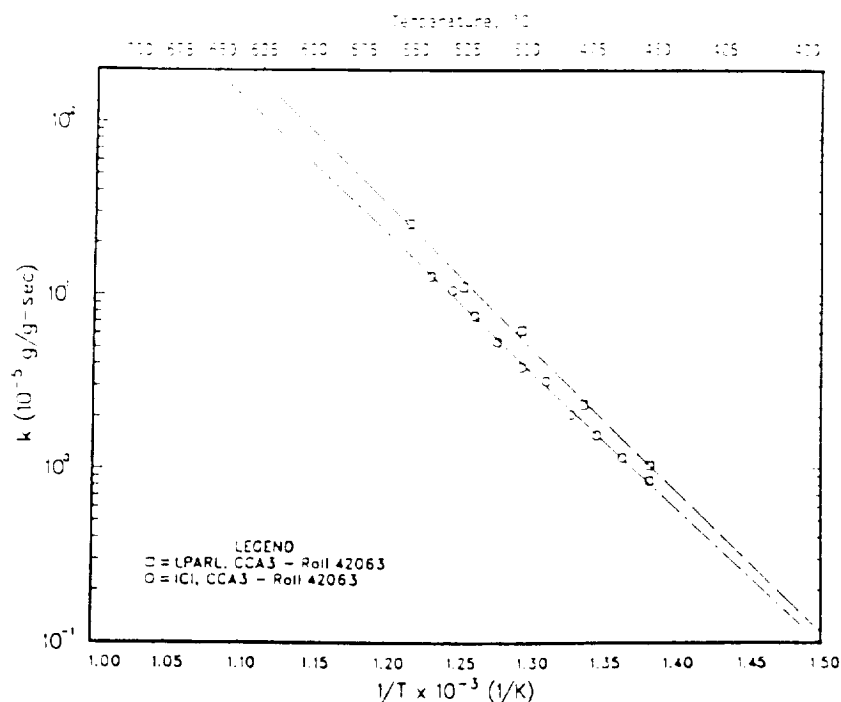


Fig. 3. Arrhenius Plots of LPARL and ICI Fiberite Generated Data

### ACKNOWLEDGEMENTS

The authors thank Mr. Rob Yost of Fiberite, Tempe, Arizona, for his experimental work and technical contribution.

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## **CARBON FIBER OXIDATION** **MASS LOSS TEST**

**Scope:** This test procedure is a proposed technique to measure the air oxidation mass loss rate of carbon fiber employed for ablative application. The procedure is identified as tentative under the auspices of the Solid Propulsion Integrity Program (SPIP) Nozzle Initiative, Subtask 3.2.1.1 Activity. This procedure was submitted by Lockheed Palo Alto Research Laboratory, Palo Alto, California.

**Reference Test Procedure** STW4-3184B

### **Summary**

This procedure is designed to measure the mass loss rate of carbon fiber exposed to isothermal temperatures. For analysis with the Arrhenius equation, 5 isothermal temperature runs are required. For screening or comparative purpose only single isothermal runs at 400°C are required.

### **Test Procedure**

**Calibration - Use Perkalloy magnetic temperature @596°C per P&E standard test procedure.**

1. Cut fiber to specimen lengths, 2-4 mm long. For fabric, cut equal quantity of warp and fill yarn.
2. Record quartz boat tare weight and balance TGA apparatus.
3. Weigh out  $4 \pm 0.4$  mg of filaments on weighing paper. (Equal warp and fill filaments.)
4. With clean tweezers, pack the pre-weighed filaments into a 4 mm ID glass tube. Tap down filaments with appropriate compacting rods using rotation until height is sufficient to fit in crucible.
5. Transfer filament preform directly into tared quartz boat.
6. Introduce boat and specimen into a Perkin-Elmer Model TGS - (2 of higher) Thermogravimetric Analyzer (TGA).
7. Employ bottled dry air, Linde UN-1002 or equivalent <3 ppm water, for a 5 minute purge at a low rate of  $25 \pm 3$  cc/minute. Set initial weight after 5 minute purge.
8. Program heating cycle as follows:
  - 25°C to isothermal temperature in 5 minutes
  - Isothermal hold for 30 minutes (Total program time of 35 minutes)
9. Plot specimen weight during ramp heating and isothermal cycle.
10. Determine residual volatile, w % loss - Loss associated with ramp to temperature.
11. Determine 30 minute isothermal rate as follows:  
Rate, g/g-sec =  $\frac{\text{Mass Loss from 5 minutes to 35 minutes}}{1800 \text{ sec.} \times \text{Initial Spec. wt @ 5 minutes}}$

## **CARBON FIBER OXIDATION** **MASS LOSS TEST**

**Scope:** This test procedure is a proposed technique to measure the air oxidation mass loss of carbon fiber employed for ablative application. The procedure is identified as tentative under the auspices of the Solid Propulsion Integrity Program (SPIP) Nozzle Initiative, Subtask 3.2.1.1 Activity. This procedure was submitted by Amoco Performance Products, Alpharetta, Georgia.

**Reference Test Procedure** None

### **Equipment**

Weighing Bottles: Kimax 151464080 - outside fitting cover

Air circulating oven: Capable of holding  $375 \pm 3^{\circ}\text{C}$

Vacuum oven: Capable of holding 29" in. of Hg or better vacuum and  $110^{\circ}\text{C}$

Balance: Digital Mettler capable of weighing up to 100 grams and to four decimals.

### **Sample Size**

Fabric: 3" x 4", 1.5-2.0 grams - not over 3" in one dimension

Yarn: Coil 1.5-2.0 grams of yarn to fit inside of weighing bottle

### **Test Procedure**

1. Weigh identified weighing bottles with matching covers at room temperature,  $w_1$ .
2. Coil samples with 3" or less dimension in axial direction and place in weighing bottle.
3. Place weighing bottles plus samples in vacuum oven at  $110^{\circ}\text{C}$  and full vacuum for minimum of one hour.
4. Remove, immediately cover with matching cover, and let cool to room temperature.
5. Weigh,  $W_2$ , to obtain sample weight,  $W_2 - W_1$ .
6. Remove covers and place bottles with samples in air circulating oven at  $375^{\circ}\text{C}$ .

**CARBON FIBER OXIDATION**  
**MASS LOSS TEST (Con't)**

7. After four hours, remove bottles, immediately cover with matching covers and cool to room temperature.
8. Weigh bottles with samples.  $W_3$ .
9. Calculate percent weight loss as follows:  
$$\% \text{ wt loss} = \frac{(W_2 - W_1) - (W_3 - W_1)}{(W_2 - W_1)} \times 100$$
10. Run in triplicate and report individual and x values of % mass loss after 4 hour exposure to air at 375°C.

APPENDIX C  
CLOSURE REFERENCE DOCUMENTS FOR  
ADVISEMENT TASK 5



**NORTH AMERICAN RAYON CORPORATION**  
AN EMPLOYEE OWNED COMPANY

**CHARLES K. GREEN**  
PRESIDENT AND  
CHIEF EXECUTIVE OFFICER

June 25, 1991

Aerojet  
Lockheed  
B. P. Chemicals (Gardena & Santa Ana)  
Polycarbon  
Fiberite  
Highland  
Milliken  
Amoco

Gentlemen:

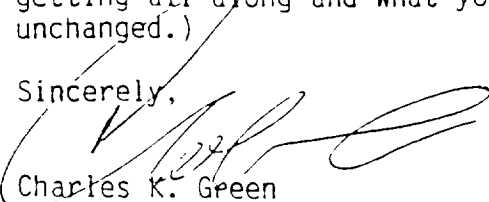
After an enormous amount of testing by NASA, Thiokol and North American Rayon, NASA has reached the decision to modify the specification for the 1650 denier rayon precursor: adding new characteristics for monitoring, and describing more accurately the statistical distribution of the data that represents products that have performed successfully.

North American Rayon will continue to supply the same consistent product to all users that we have for the past one and a half years. Once the new NASA/Thiokol purchase contract is finalized, we will adhere to this new specification for everyone, thereby avoiding confusion and extra cost in having to cope with two inventories and product segregation at the weavers, the carbonizers, the pre-preggers, the fabricators and the prime contractors.

This action reflects the conclusion by NASA after detailed testing, including a full-scale static firing of a solid rocket booster, that NAR rayon performs as well as Avtex rayon. Also, it is our understanding that the Navy's D-5 propulsion testing, including full-scale static firing concludes the same findings that NAR rayon performs as well as the previous rayon. A comparison of the old and new specifications is attached.

Let me strongly emphasize that NAR will not change its manufacturing standards or its process control; the new specification simply reflects what you have been getting all along and what you will continue to get. (1100 denier specification is unchanged.)

Sincerely,




  
Charles K. Green  
President

1650/720 CARBONIZABLE RAYON  
SPECIFICATIONS

<u>PROPERTY</u>	<u>PRESENT</u>	<u>NEW</u>
DENIER	1590-1710	1600-1720
BREAK STRENGTH, LBS. (COND.)	10.3-13.5	11.0-14.0
ELONGATION, % (COND.)	5.5- 9.5	6.5-10.0
TENACITY, g/g (COND.)		2.73-3.80
BREAK STRENGTH LBS. (WET)		5.0- 7.0
ELONGATION % (WET)		10.0-20.0
SHRINKAGE, %	2.9- 4.7	3.0- 5.0
TWIST, t.p.i.	1.6- 2.4	1.6- 2.0
FINISH, %	0.2- 1.0	0.2- 1.0
pH	5.0- 8.0	5.0- 7.0
ASH, %	0.45 MAX	0.45 MA.
SULFUR, %	0.25 MAX	0.20 MA.
ZINC, %	0.07 MAX	0.06 MA.
MOISTURE, %	13.0 MAX	13.0 MA.

APPENDIX D  
CLOSURE REFERENCE DOCUMENTS FOR  
ADVISEMENT TASK 6

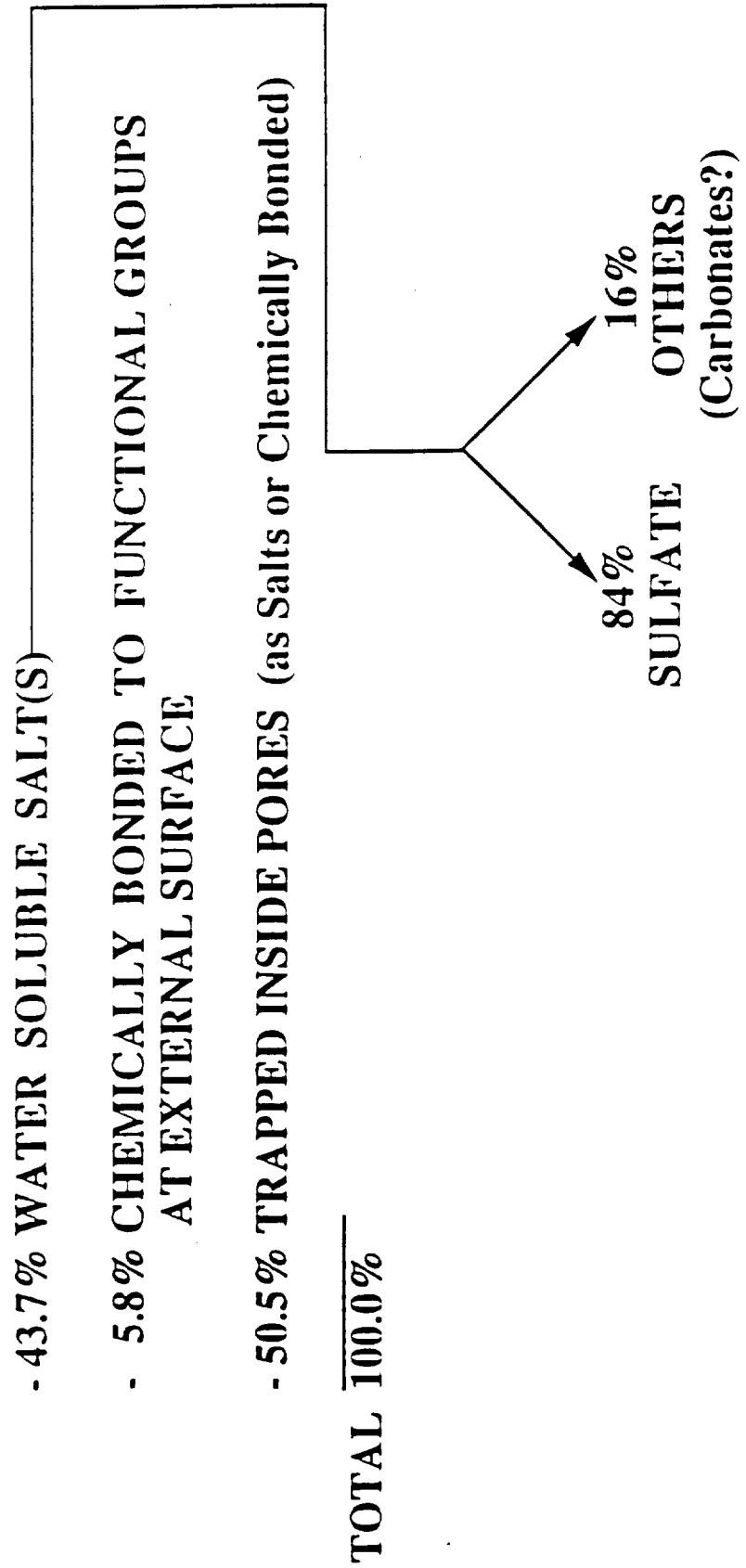
## Summary of ASTM Ashing Tests

Material	ASTM Designation	Sample wt. (g)	Ashing Temp. (C)	Preheated Oven (Y/N)	Ashing Time	Remarks	Repeatability (single Operator)	Reproducibility (Multi Lab)
Carbon Black	D1506-85	2.0 (dry)	550  950	yes yes	16 h 4-5 h	uncovered permissible	20%	23%
Activated Carbon	D2866-83	Sufficient to yield 0.1 ash	650 ± 25	yes	3-16 h	constant weight achieved	being investigated	being investigated
Graphite	C561-69	?	500  750 950 	no	1h 2h 1 h	Platinum dish (250 µm)	being developed	being developed
Coal & Coke	D3174-82	1.0	450-500 700-750	no	1 h 2 h/or more	Capsule/ Porcelain or Platinum cover	0.2-0.3%	0.3-0.5%
Petroleum Coke	D4422-84	10.0*	700-750	no	until constant mass	<75µ	0.02 (%)?	0.06 (%)?
Graphite lubricants	D1553-83	1.0 (dry)	950±25	yes	3 h	Capsule < 1 mg loss in 1/2 h	0.15%	0.22%

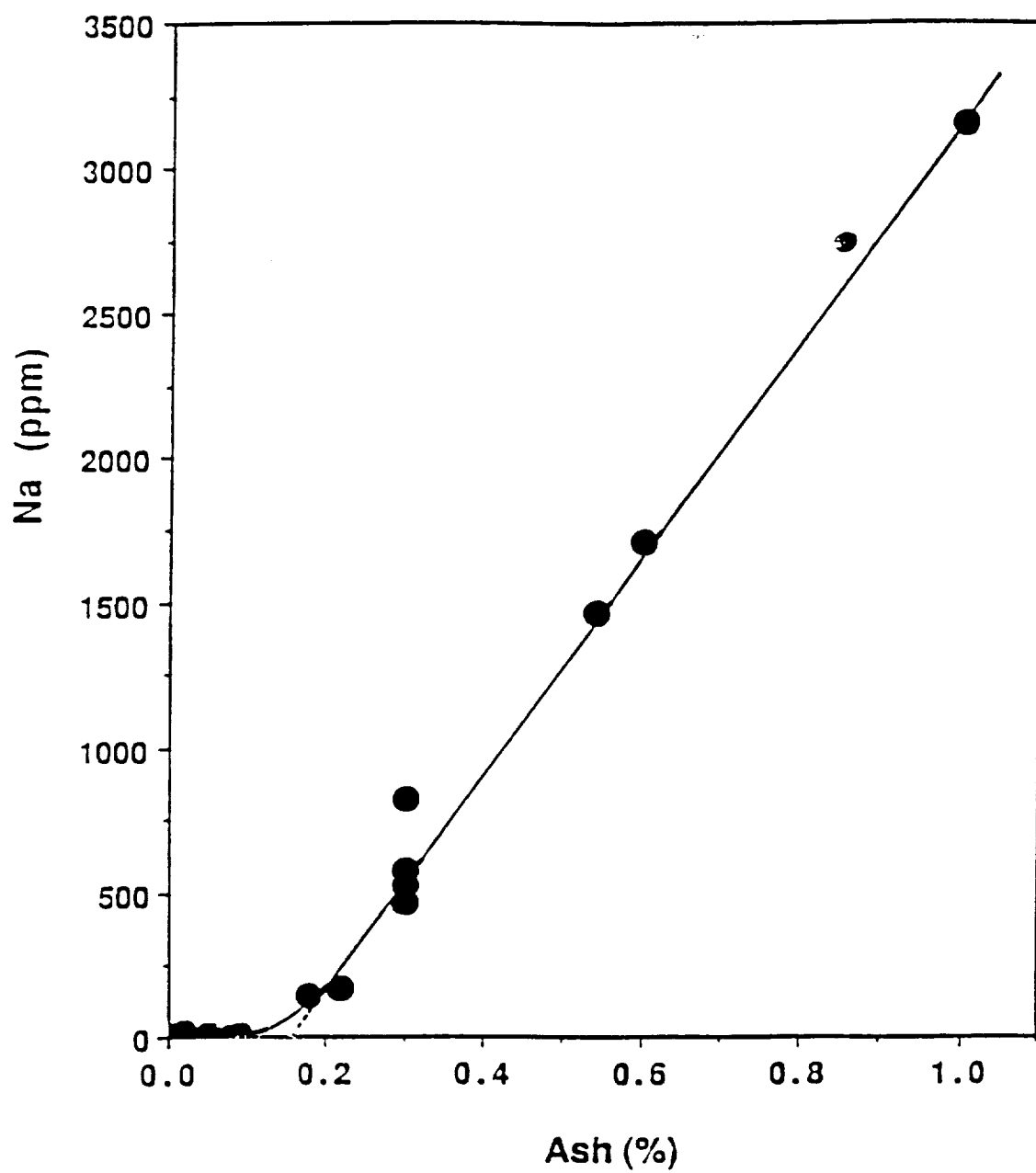
\*ASTM: 10 ± 0.1 mg (Typo?)



## DISTRIBUTION OF SODIUM IN CSA-4671 FABRIC:



## Relation Between Ash and Na Content



## Ashing Temperature (T) and Time (t)

Condition	Result	Ash Content
Low T, short t	Ashing is incomplete	Over estimated
High T, short t	Ashing is complete	May be acceptable or underestimated
Low T, long t	Ashing is probably complete	May be acceptable, underestimated, or over estimated
High T, long t	Ash may evaporate	Underestimated

---

ASTM:	Lowest temperature - 550 C Highest temperature - 950 C	<u>Melting Points:</u> N <sub>2</sub> CO <sub>3</sub> : 851 C Na <sub>2</sub> SO <sub>4</sub> : 884 C
ASTM time:	Shortest time - 1 hour Longest time - until a constant weight is reached	

## CONCLUSIONS

- Ashing Rayon fabrics at 950 C underestimates the ash content; it may yield 0% Ash.
- Ashing of the fabrics at 750 C for longer periods of time, > 3 hours, underestimates the Ash content.
- Ashing temperature of carbon fibers and fabrics should be at 500-600 C; depending on the material.
- Low temperature ashing is an attractive alternative.
- With low fired Rayon fabrics most of the sodium is present as  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$ .

## RECOMMENDATIONS

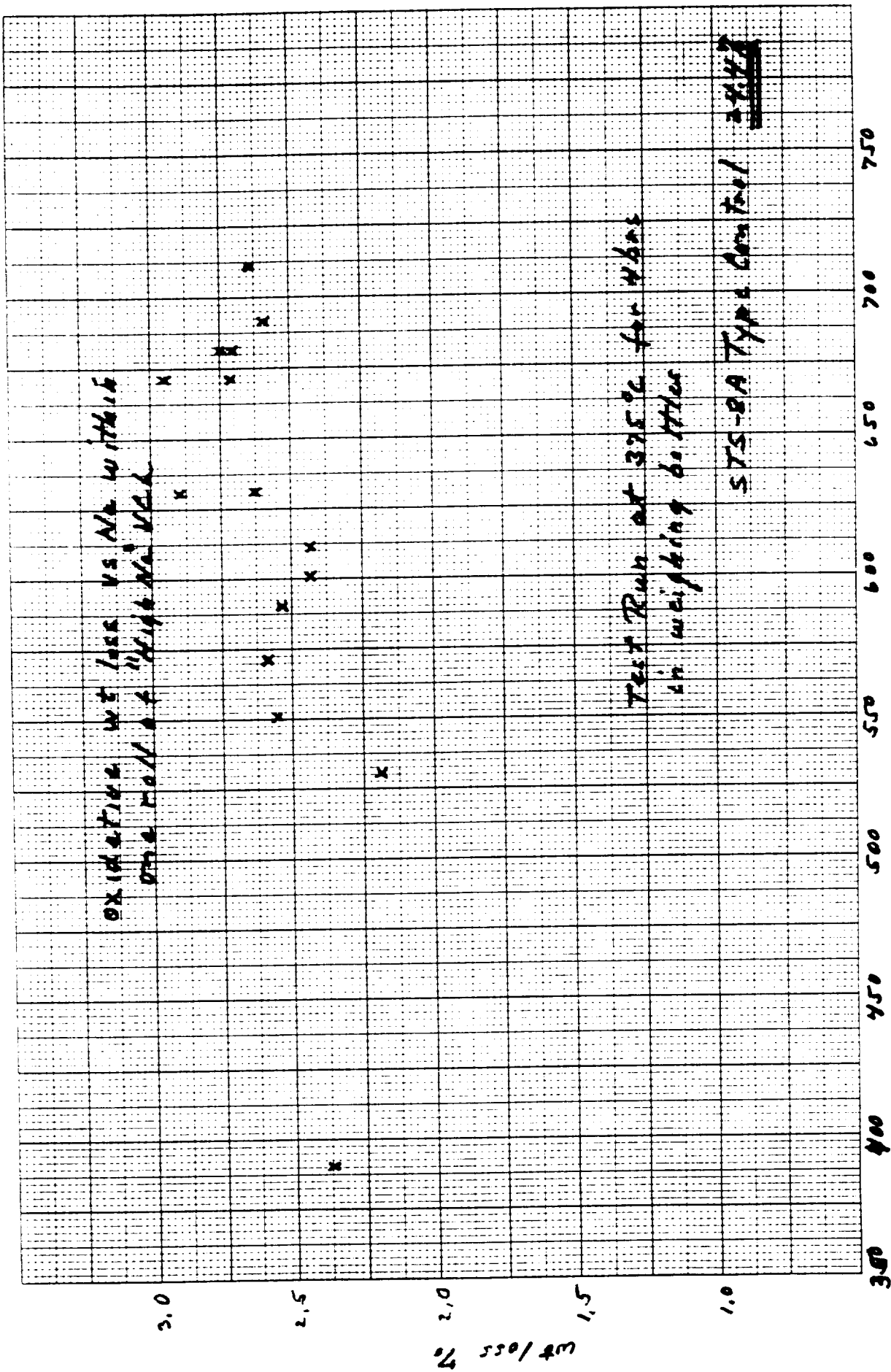
- Proposed Ashing Temperature for low fired Rayon fabrics: 500-550 C.
- Proposed Ashing Temperature for high fired Rayon fabrics (e.g., WCA): 550-600 C.
- Low Temperature Ashing in an oxygen plasma is recommend, if the equipment is available.

**APPENDIX C**

**MYLES TOWNE**



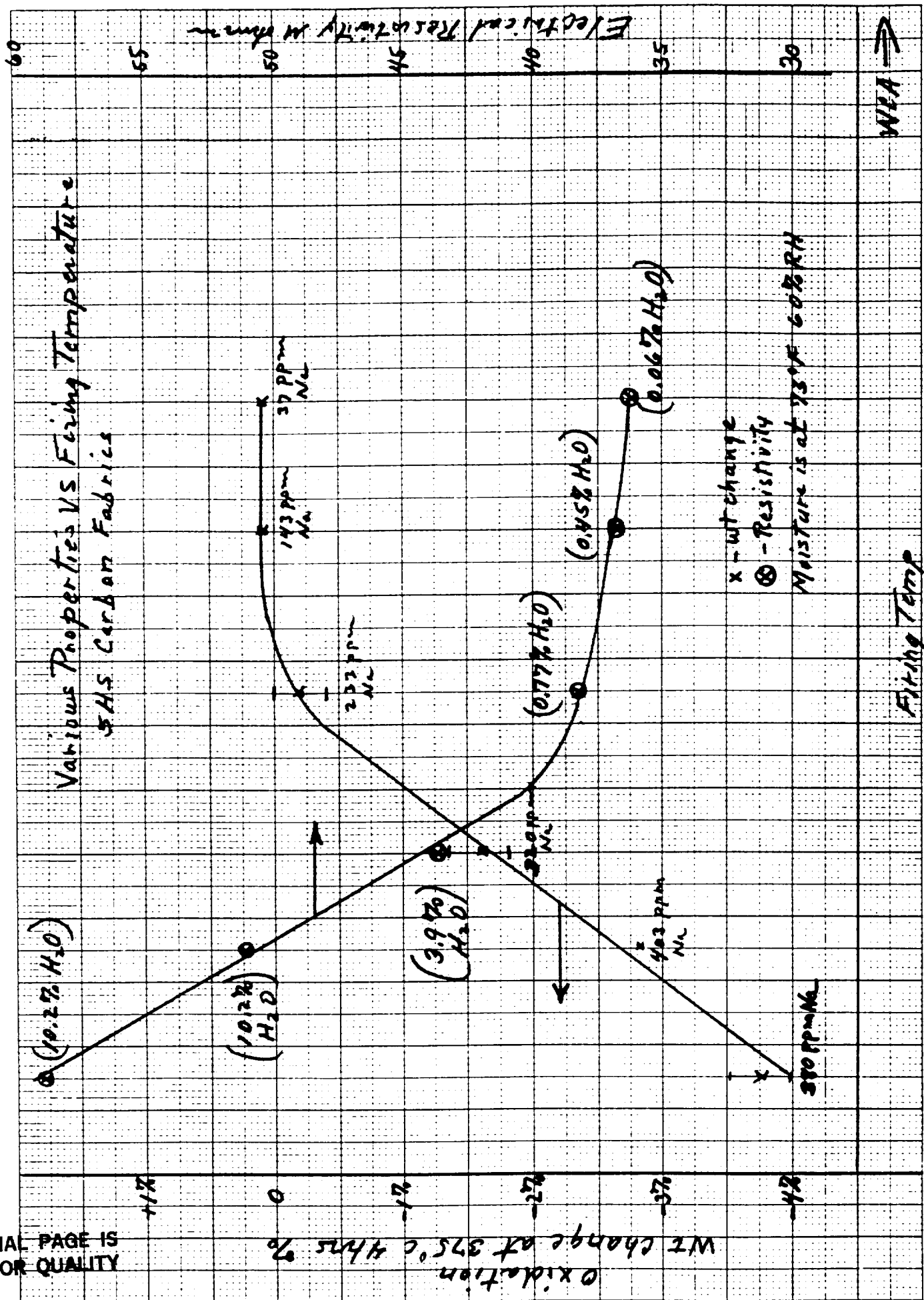




PPM Sodium



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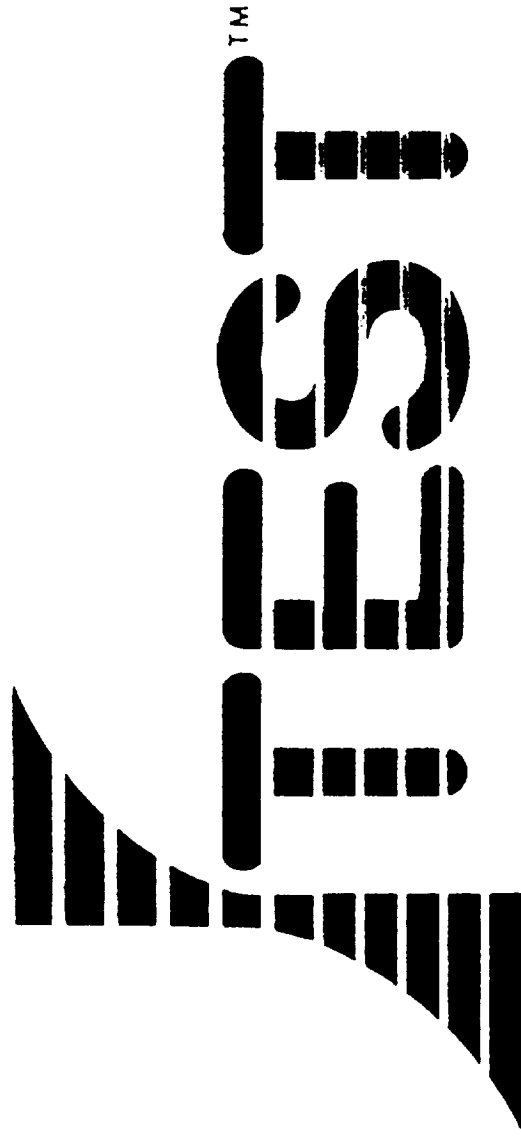




**APPENDIX D**

**GLORIA MA**





The **Expert** System Technologies, Inc.

# URA 2000

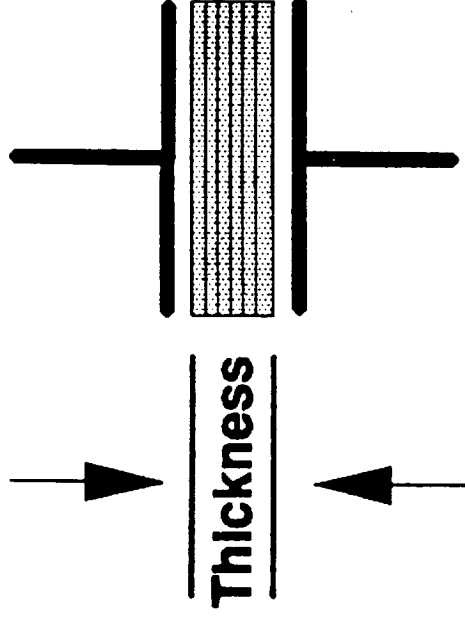
Velocity  
through RESIN



Velocity through FIBER



Velocity through COMPOSITE

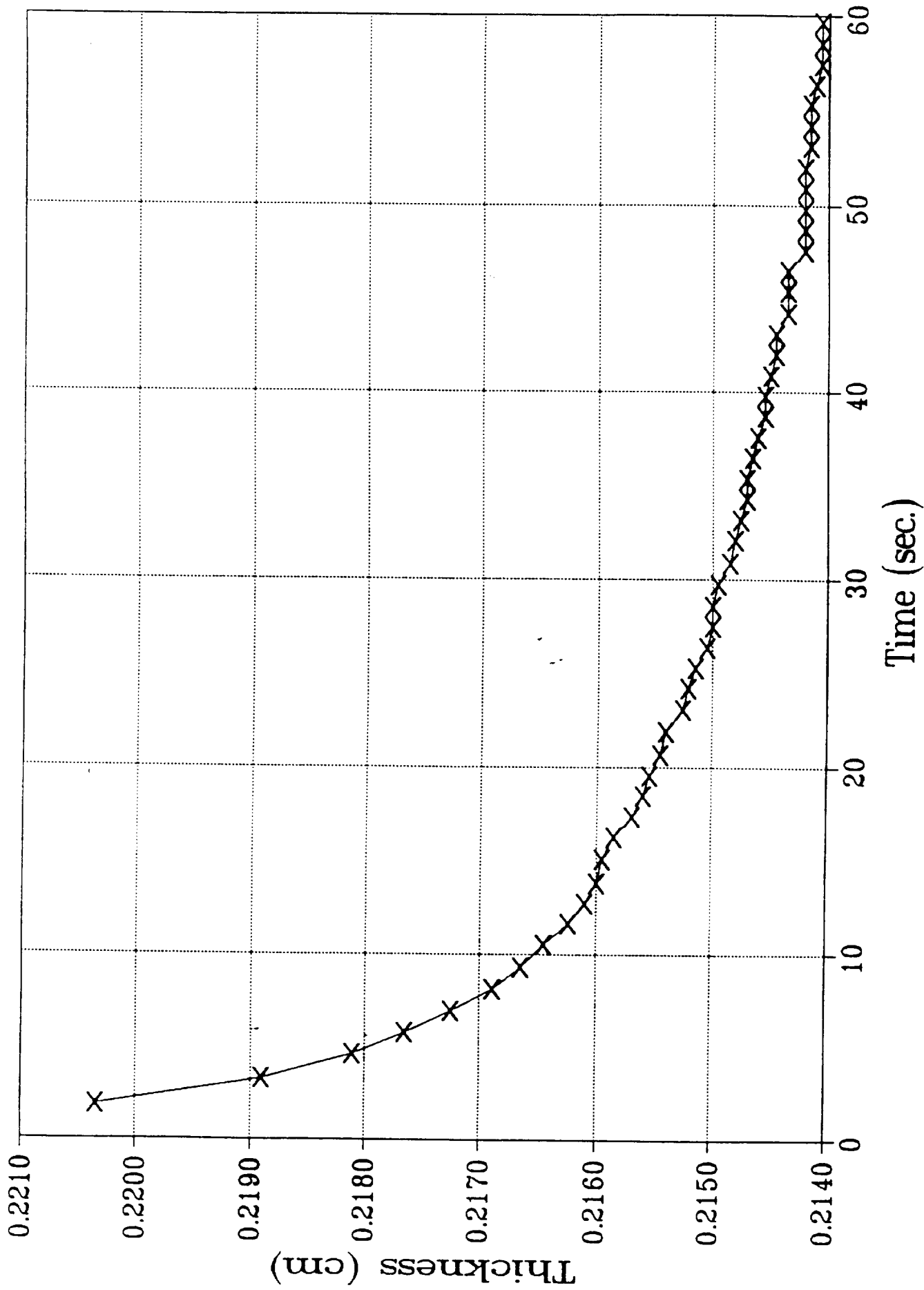


$$\text{SLOWNESS} = 1/\text{Velocity}$$

$$= \frac{\text{Time-of-Flight}}{\text{Thickness}}$$

TEST Inc.

Typical Optimal Consolidation Curve



# URA 2000

Calibration Curve

Destructive Testing

32.4

37.8

.

42.3

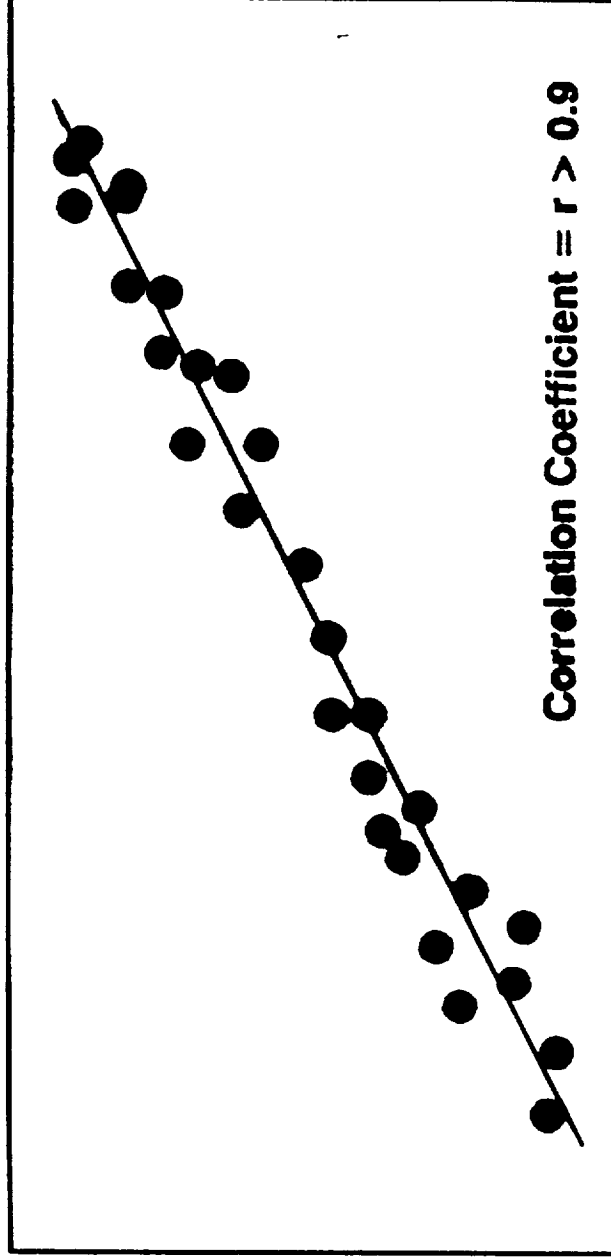
URA 2000 Measurement

3.6788

3.7598

.

3.8273



TEST INC.



-----  
ASTM ROUND ROBIN

Aluminum Reference Block Statistics  
-----

all units in NANOSECONDS

n = 35

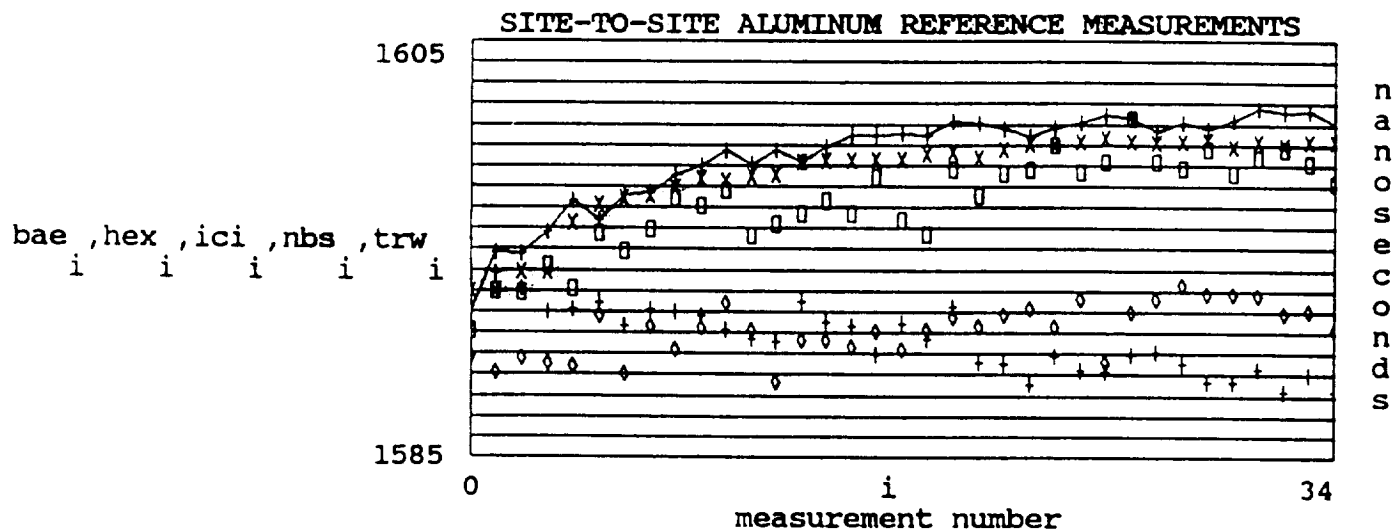
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2 range [REDACTED] = 9.85  
3 range [REDACTED] = 4.59  
4 range [REDACTED] = 7.38  
5 range [REDACTED] = 9.74

mean [REDACTED] = 1597.207  
mean [REDACTED] = 1590.819  
mean [REDACTED] = 1591.128  
mean [REDACTED] = 1598.575  
mean [REDACTED] = 1599.476

1 var [REDACTED] = 5.334  
2 var [REDACTED] = 3.707  
3 var [REDACTED] = 1.522  
4 var [REDACTED] = 4.412  
5 var [REDACTED] = 5.283

stdev [REDACTED] = 2.31  
stdev [REDACTED] = 1.925  
stdev [REDACTED] = 1.234  
stdev [REDACTED] = 2.1  
stdev [REDACTED] = 2.298

[REDACTED] : BOXES  
[REDACTED] : PLUSES  
[REDACTED] : DIAMONDS  
[REDACTED] : X's  
[REDACTED] : CONNECTED PLUSES



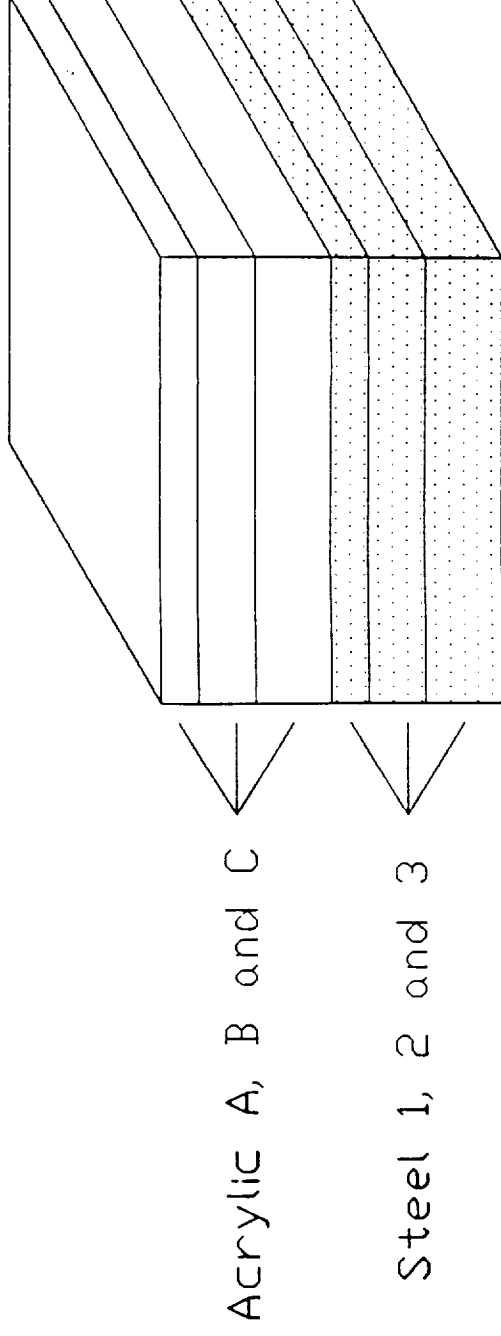
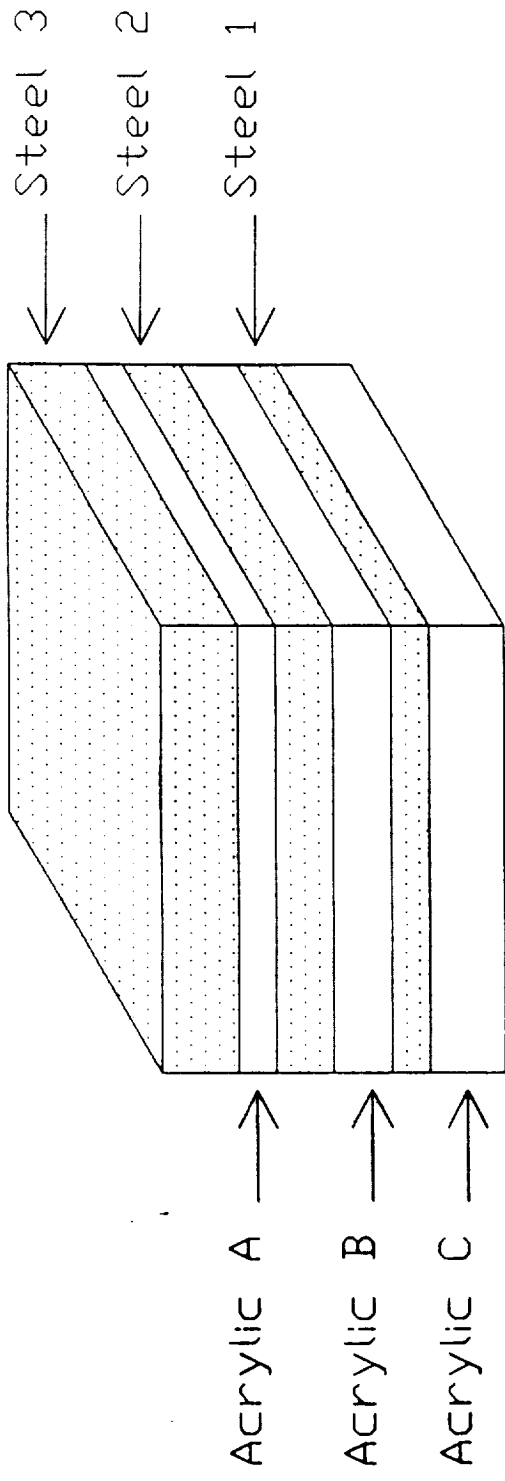
Statistics for All Lab Sites Combined:

range(all) = 13.52  
mean(all) = 1595.441

var(all) = 17.89  
stdev(all) = 4.23

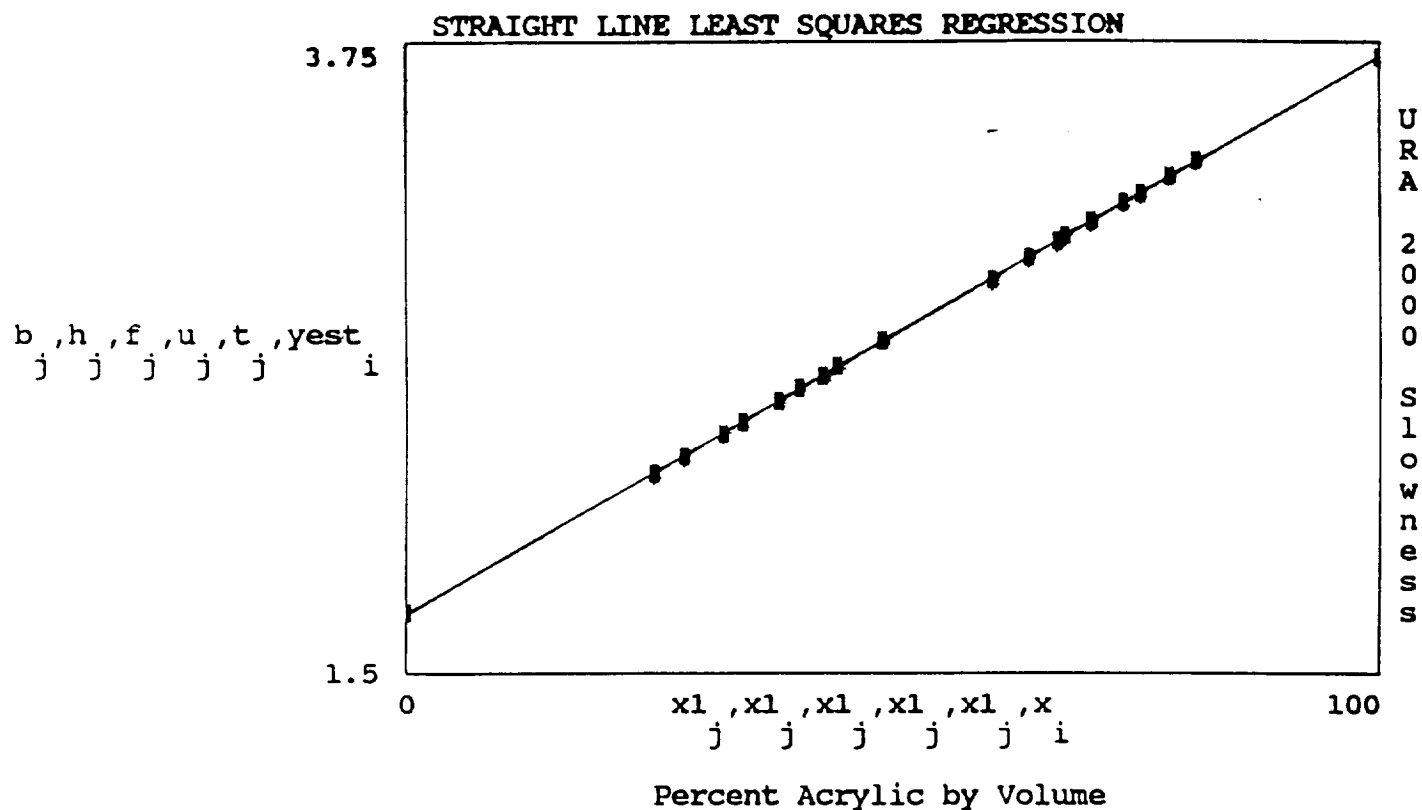
15 nsec ~ 12 PRW

# Proof of Concept Experiment



ASTM ROUND ROBIN INTER-LABORATORY ERROR ANALYSIS - COMBINED CALIBRATIONS

ACRYLIC/STEEL CALIBRATION  
ALL LAB SITES COMBINED



chi2 = 0.00365

$r = 0.99992$

mse = 0.0002

$\beta = \begin{bmatrix} 1.71018 \\ 0.01991 \end{bmatrix}$

lserr = 0.01425

$r^2 = 0.99983$

3·lserr = 0.04275

Legend:

- Lab
- 1 = [redacted]
  - 2 = pluses
  - 3 = diamonds
  - 4 = x's
  - 5 = dots

## ASTM ROUND ROBIN OUTLIER ANALYSIS

These tables contain the sample numbers (as appears in the URA 2000 data base) of designated outliers. Outliers were selected by computing standardized residuals for the regression and tagging those which were greater than 3 (standard deviations). After selection, each outlier was analyzed to determine its most probable cause. The following labels are used to explain the cause:

- D = destructive error
- M = machine error (ie software and/or hardware difficulties)
- ? = cause is not obvious
- P = wrong number of plies (even though much effort was used to correct for this problem before analysis)
- \* = time-of-flight crossing time selection difficulties

### STRAIGHT LINE LEAST SQUARES REGRESSION

	GLEX HC	GLEX TOF	KVEX HC	KVEX TOF	GREX HC	GREX TOF	UDEX HC	UDEX TOF
BAE	9 <sub>D</sub>	-	7A <sub>D</sub>	-	-	30 <sub>M</sub>	23 <sub>D</sub>	23 <sub>D</sub>
HEX	-	* <sub>M</sub>	-	1 <sub>M</sub>	N/A	N/A	N/A	N/A
ICI	N/A	N/A	N/A	N/A	17 <sub>P</sub>	17 <sub>P</sub> , 32 <sub>M</sub>	-	-
NBS	37 <sub>7</sub>	-	15 <sub>7</sub>	-	14 <sub>D</sub>	14 <sub>D</sub>	13 <sub>7</sub>	13 <sub>7</sub>
TRW	-	10 <sub>7</sub>	-	-	-	-	1 <sub>7</sub>	1 <sub>7</sub>

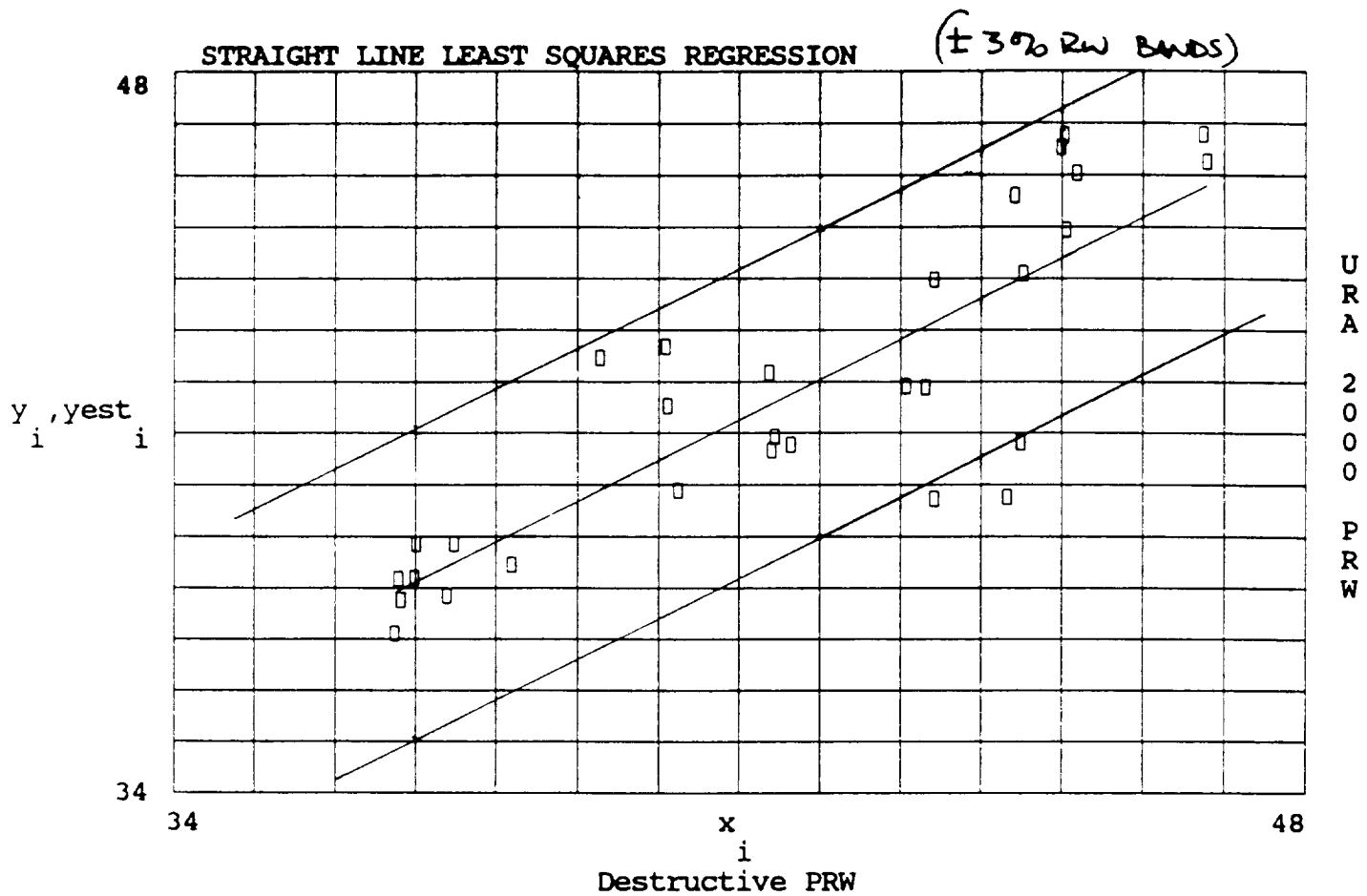
### QUARTIC POLYNOMIAL LEAST SQUARES REGRESSION

	GLEX HC	GLEX TOF	KVEX HC	KVEX TOF	GREX HC	GREX TOF	UDEX HC	UDEX TOF
BAE	9 <sub>D</sub>	-	-	-	-	30 <sub>M</sub>	23 <sub>D</sub>	23 <sub>D</sub>
HEX	-	* <sub>M</sub>	-	1 <sub>M</sub>	N/A	N/A	N/A	N/A
ICI	N/A	N/A	N/A	N/A	17 <sub>P</sub>	17 <sub>P</sub> , 32 <sub>M</sub>	-	-
NBS	3 <sub>7</sub> , 37 <sub>7</sub>	-	15 <sub>7</sub>	-	14 <sub>D</sub>	14 <sub>D</sub>	13 <sub>7</sub>	13 <sub>7</sub>
TRW	-	-	-	20 <sub>7</sub>	-	-	1 <sub>7</sub>	1 <sub>7</sub>

-----  
 ASTM ROUND ROBIN INTER-LABORATORY ERROR ANALYSIS  
 -----

Lab 5

GRAPHITE/EPOXY (CLOTH)



$\chi^2 = 75.57339$

$r = 0.84839$

$\text{mse} = 2.69905$

$\beta = \begin{bmatrix} 9.08179 \\ 0.7847 \end{bmatrix}$

$\text{lserr} = 1.64288$

$r^2 = 0.71977$

$3 \cdot \text{lserr} = 4.92864$

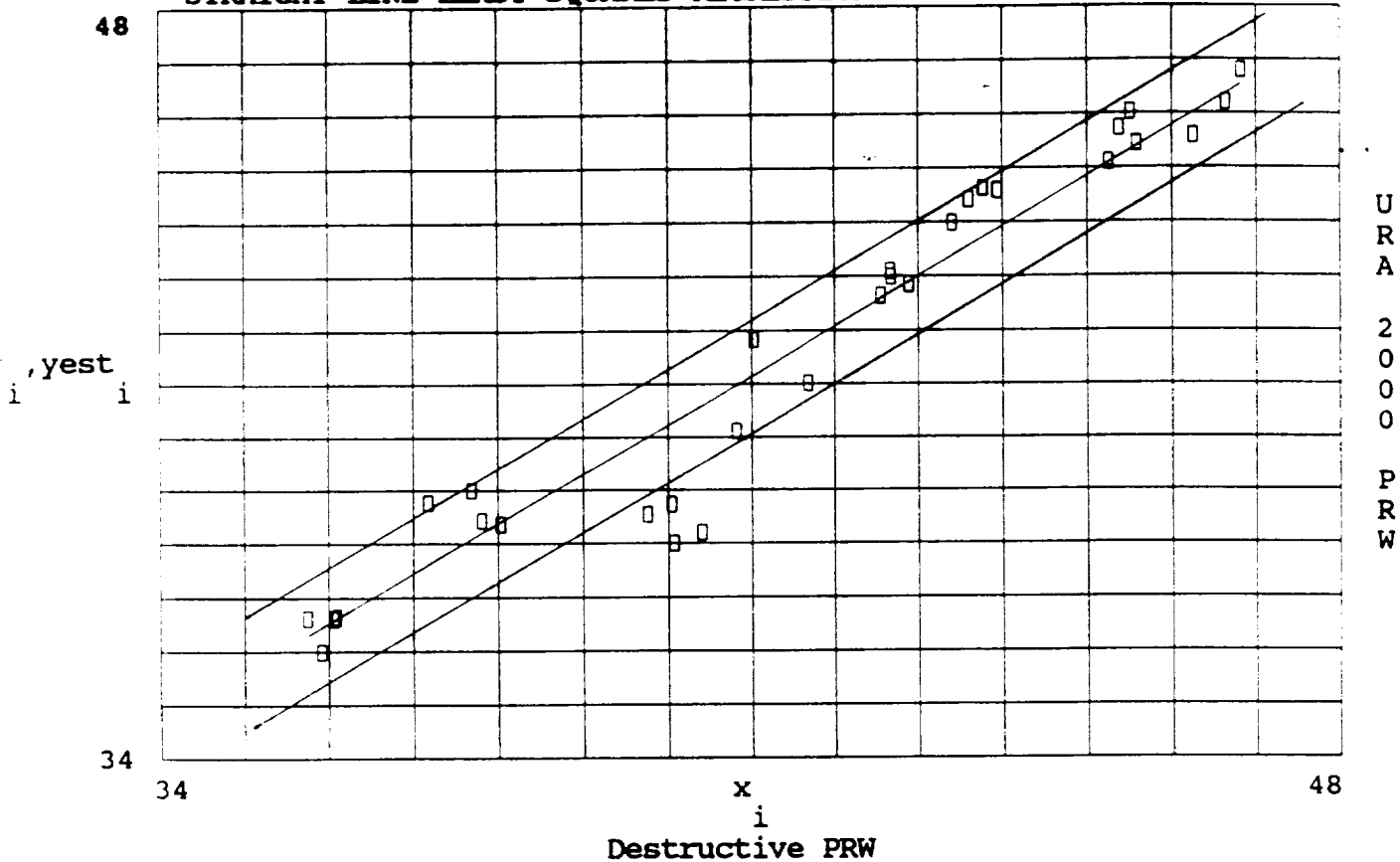
TM ROUND ROBIN INTER-LABORATORY ERROR ANALYSIS

Lab 3

GRAPHITE/EPOXY (CLOTH)

STRAIGHT LINE LEAST SQUARES REGRESSION

( $\pm 1\sigma$  RW BANDS)



chi2 = 24.85699

$r = 0.97344$

mse = 0.80184

$\beta = \begin{bmatrix} 3.23326 \\ 0.92486 \end{bmatrix}$

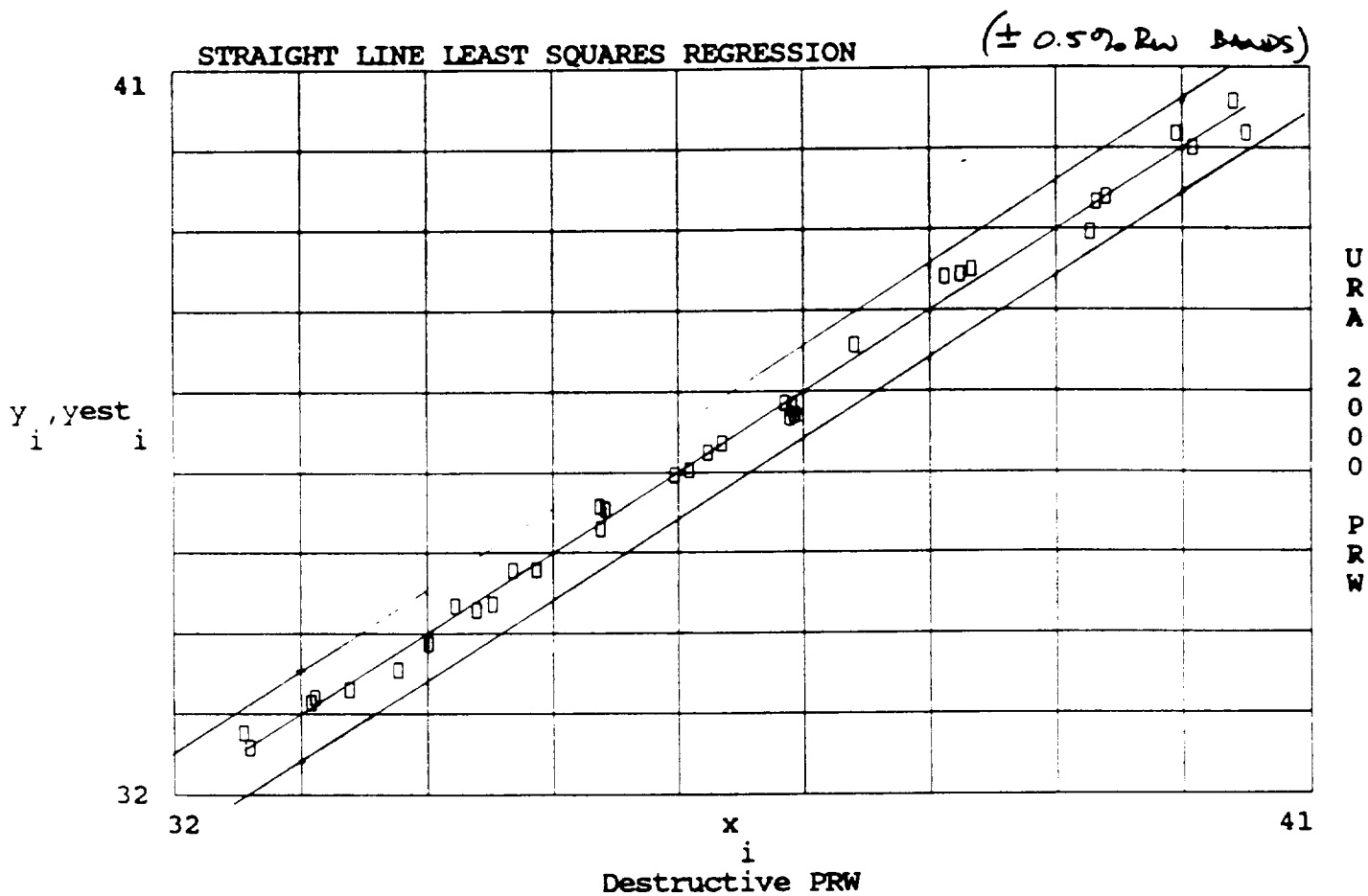
lserr = 0.89545

$r^2 = 0.94759$

3. lserr = 2.68636

-----  
 ASTM ROUND ROBIN INTER-LABORATORY ERROR ANALYSIS  
 -----

BOEING AEROSPACE  
 GLASS/EPOXY



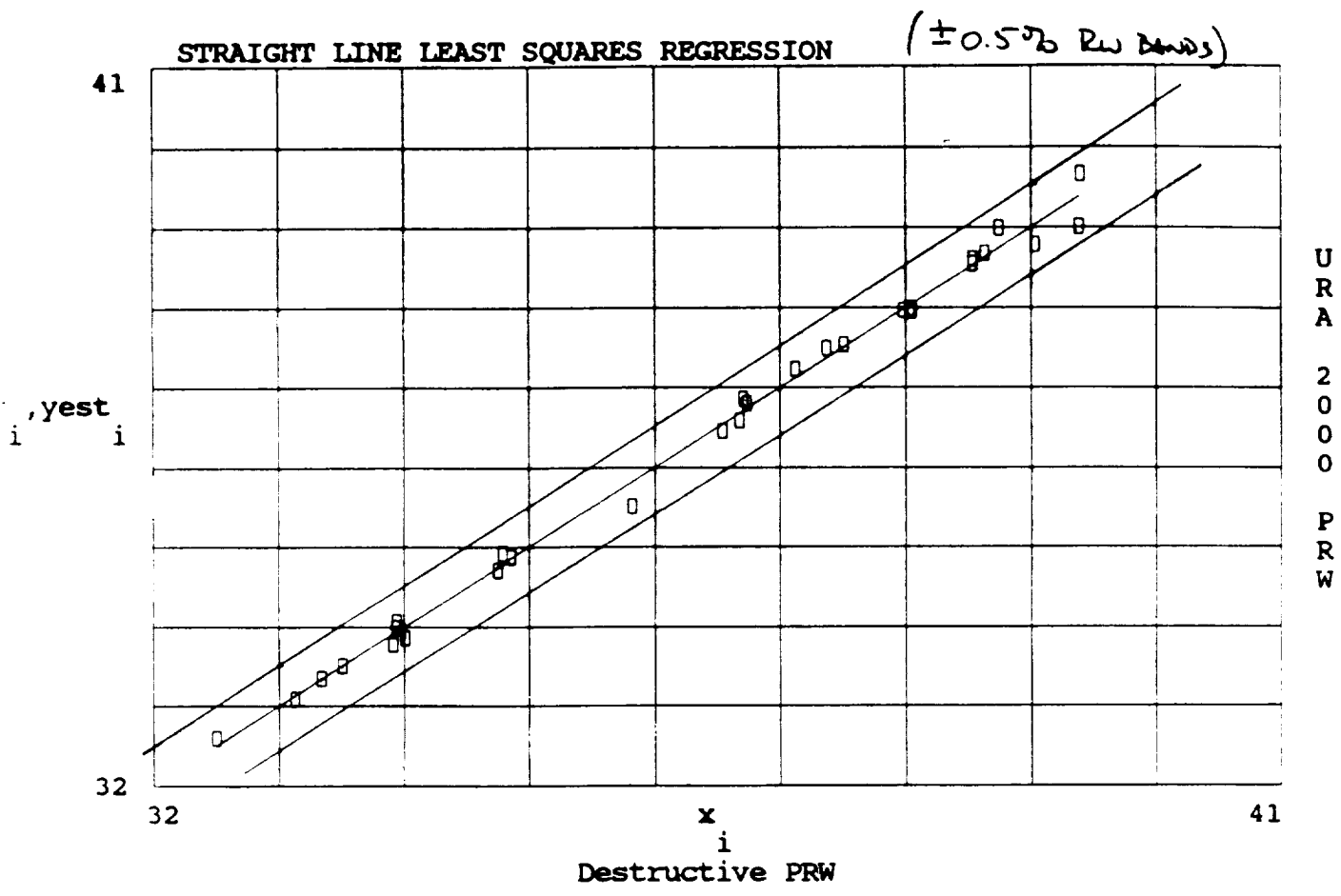
chi2 = 0.84478  
 mse = 0.0264  
 lserr = 0.16248  
 3 · lserr = 0.48744

$r = 0.99779$   
 $r^2 = 0.99558$

$\beta = \begin{bmatrix} 0.00582 \\ 0.99982 \end{bmatrix}$

STM ROUND ROBIN INTER-LABORATORY ERROR ANALYSIS

Lab #2  
GLASS/EPOXY



chi2 = 0.60103

r = 0.99771

mse = 0.02226

$\beta = \begin{bmatrix} 0.02673 \\ 0.99927 \end{bmatrix}$

lserr = 0.1492

$r^2 = 0.99542$

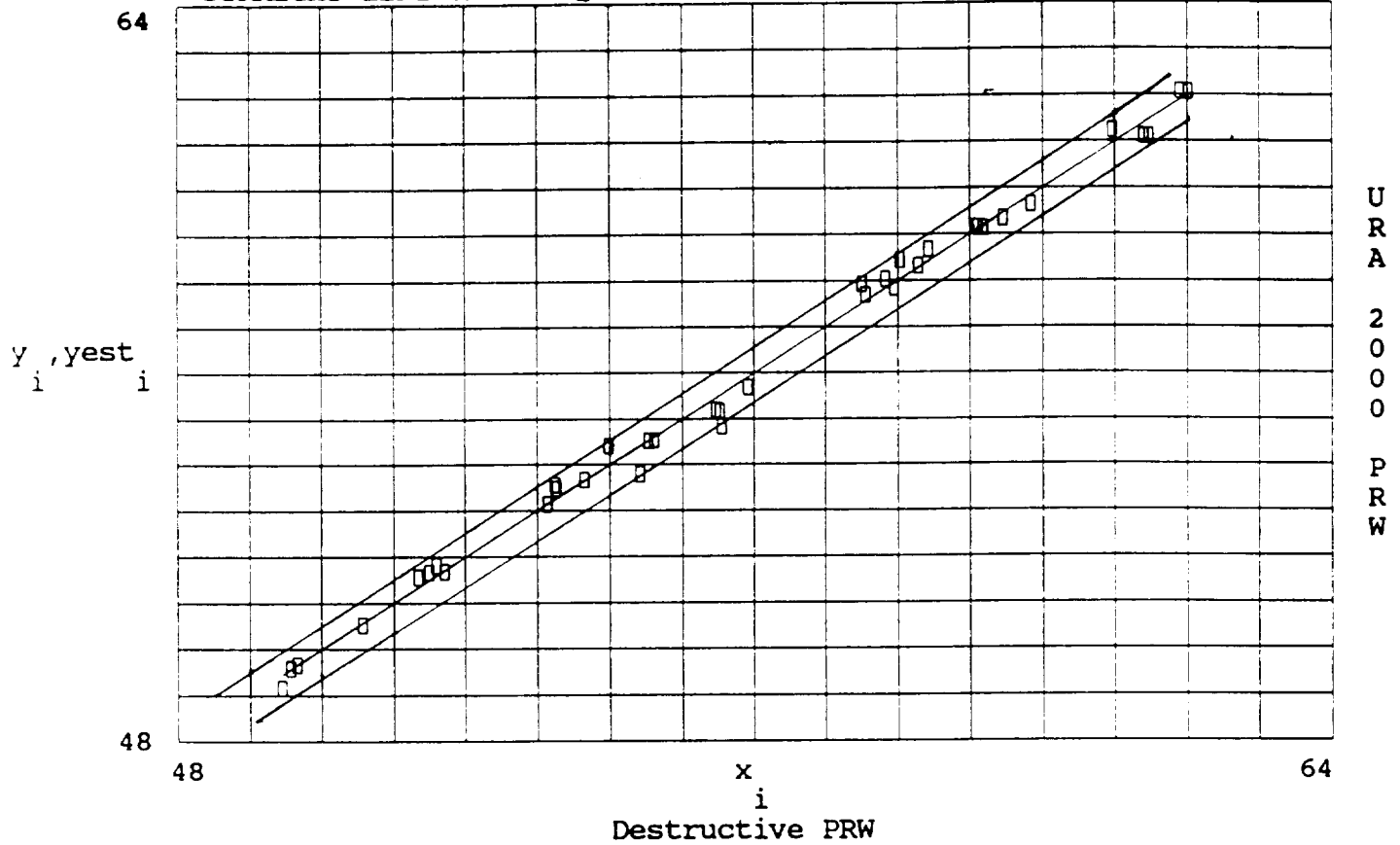
3·lserr = 0.4476



-----  
 ASTM ROUND ROBIN INTER-LABORATORY ERROR ANALYSIS  
 -----

TRW  
 KEVLAR/EPOXY

STRAIGHT LINE LEAST SQUARES REGRESSION ( $\pm 0.5\%$  RW BANDS)



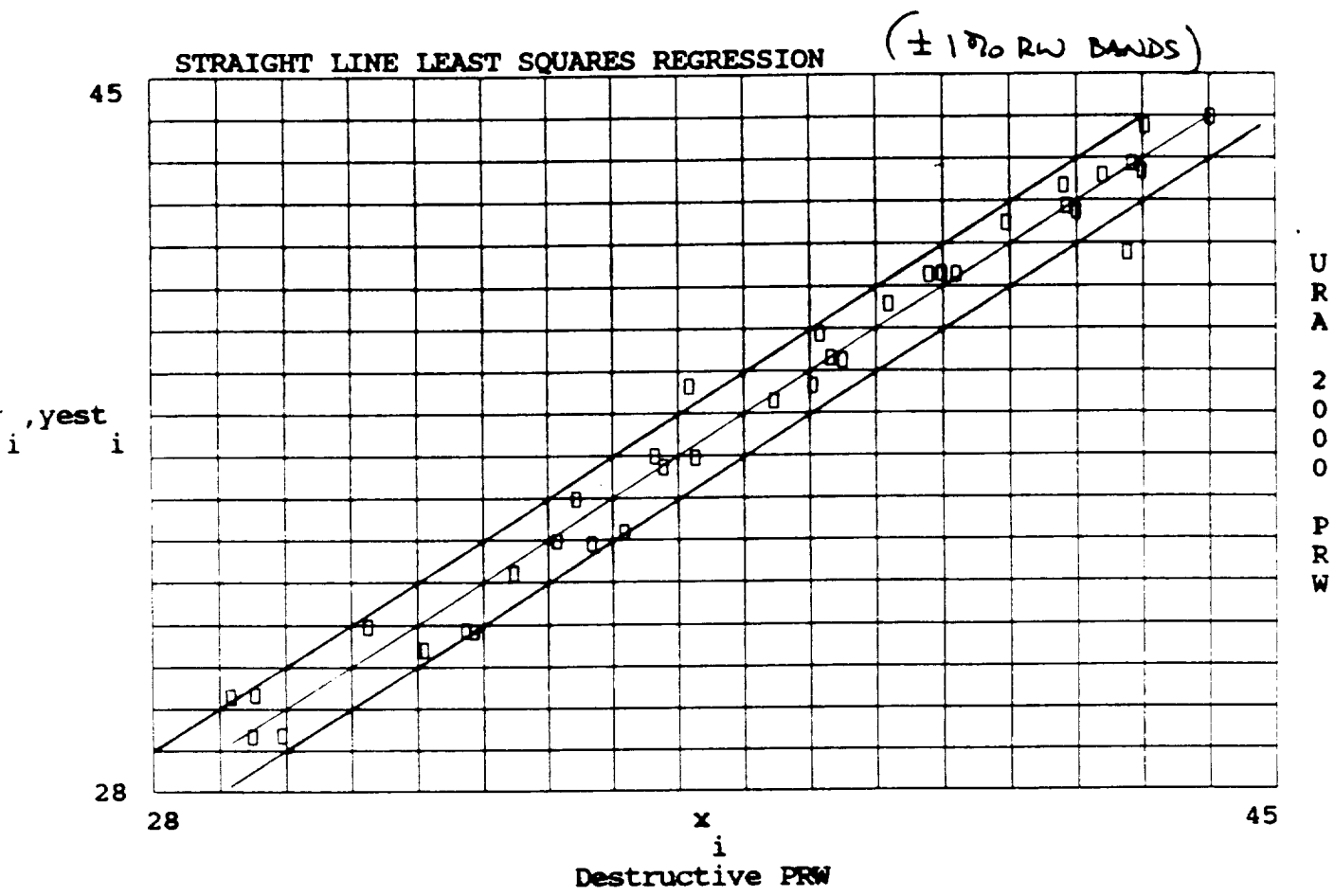
chi2 = 2.49823  
 mse = 0.07348  
 lserr = 0.27107  
 3·lserr = 0.8132

r = 0.99751  
 $r^2 = 0.99503$

$\beta = \begin{bmatrix} 0.01431 \\ 0.9997 \end{bmatrix}$

STM ROUND ROBIN INTER-LABORATORY ERROR ANALYSIS

BOEING AEROSPACE  
GRAPHITE/EPOXY (UNIDIRECTIONAL)



chi2 = 15.71938

$r = 0.98891$

mse = 0.46233

$\beta = \begin{bmatrix} 0.02942 \\ 0.99898 \end{bmatrix}$

lserr = 0.67995

$r^2 = 0.97795$

3. lserr = 2.03986

Figure 3A

KVEX  
OUTLIERS REMOVED (> 3 sigma)  
QUARTIC FIT

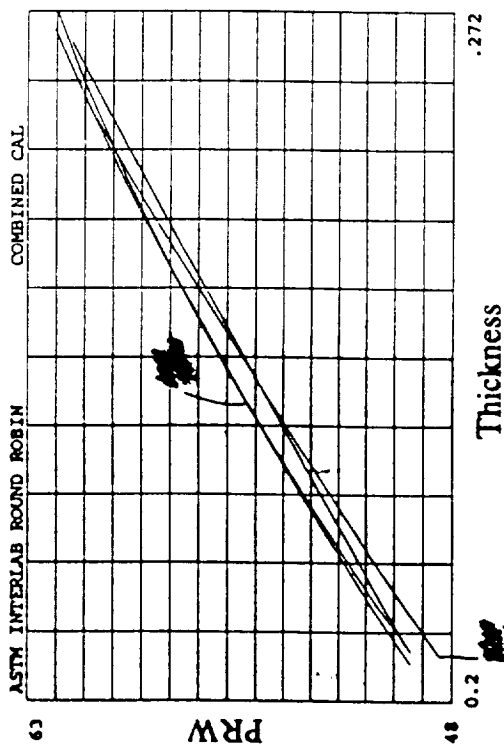


Figure 3B

KVEX  
OUTLIERS REMOVED (> 3 sigma)  
QUARTIC FIT

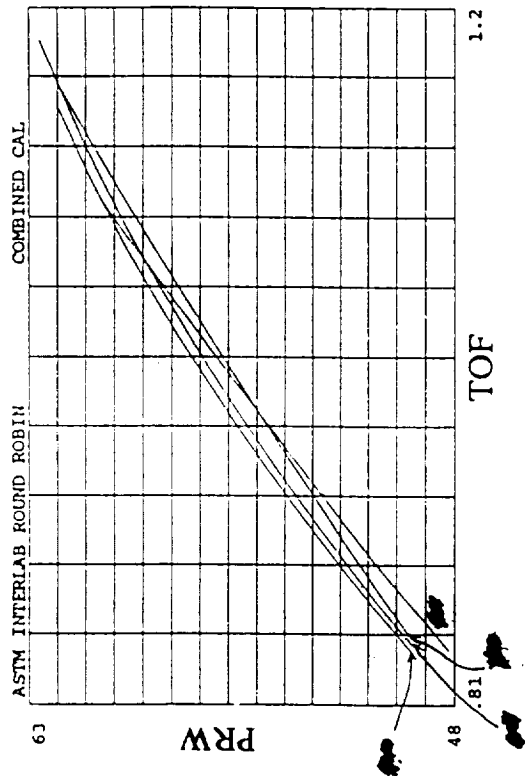


Figure 4A

INDEX  
OUTLIERS REMOVED (> 3 sigma)  
QUARTIC FIT

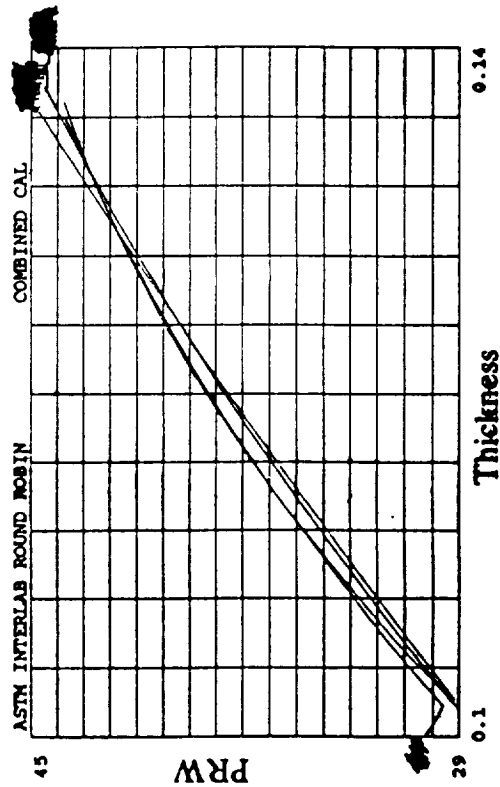
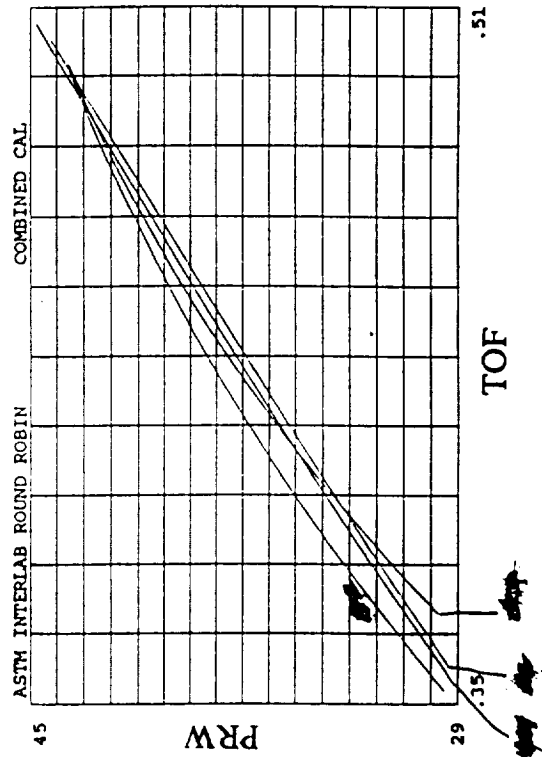


Figure 4B

INDEX  
OUTLIERS REMOVED (> 3 sigma)  
QUARTIC FIT



# SITE-TO-SITE DIFFERENCES IN DESTRUCTIVES

MATERIAL	$R_{\text{BAR}}$	$\sigma$	99% C.I.	BIAS?
GLEX	0.74	0.36	$\pm 0.924$	No
KVEX	1.84	0.89	$\pm 2.137$	Hexcel - Low
UDEX	2.77	1.345	$\pm 3.463$	No
GREX	1.14	0.55	$\pm 1.427$	No

\* Outliers removed for calculation of  $R_{\text{BAR}}$

$\sigma = R_{\text{BAR}}/d_2$  where  $d_2 = 2.06$  for sample size = 4

Figure 1A

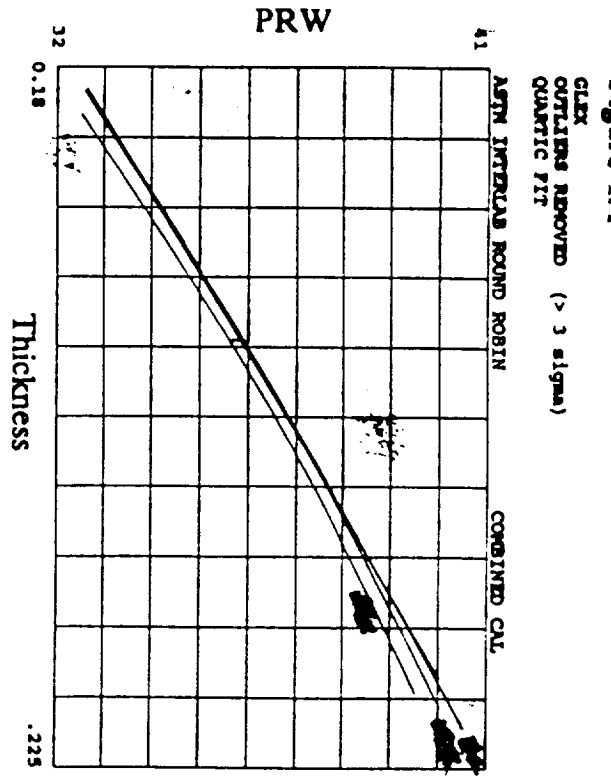


Figure 1B

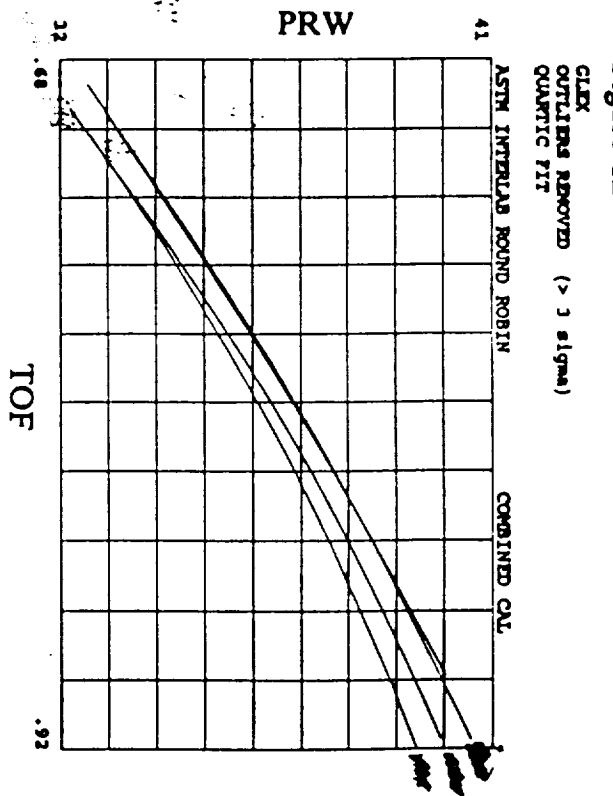


Figure 2A

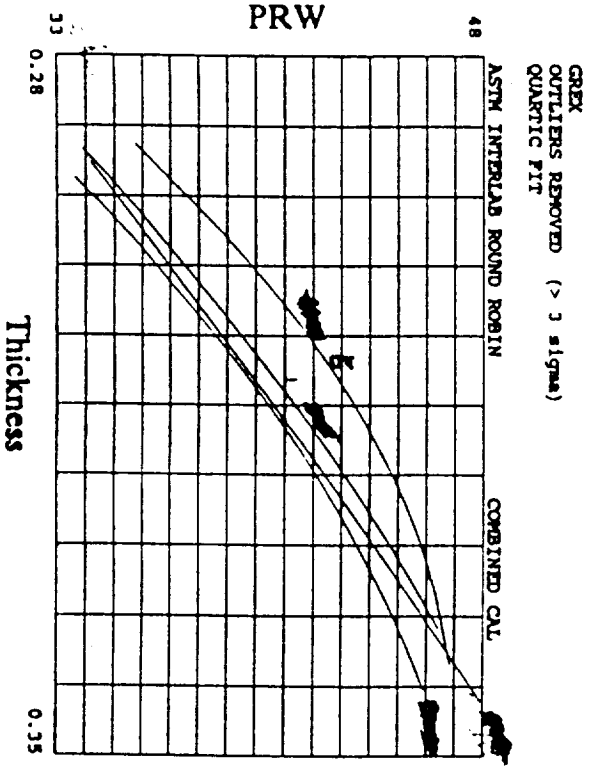
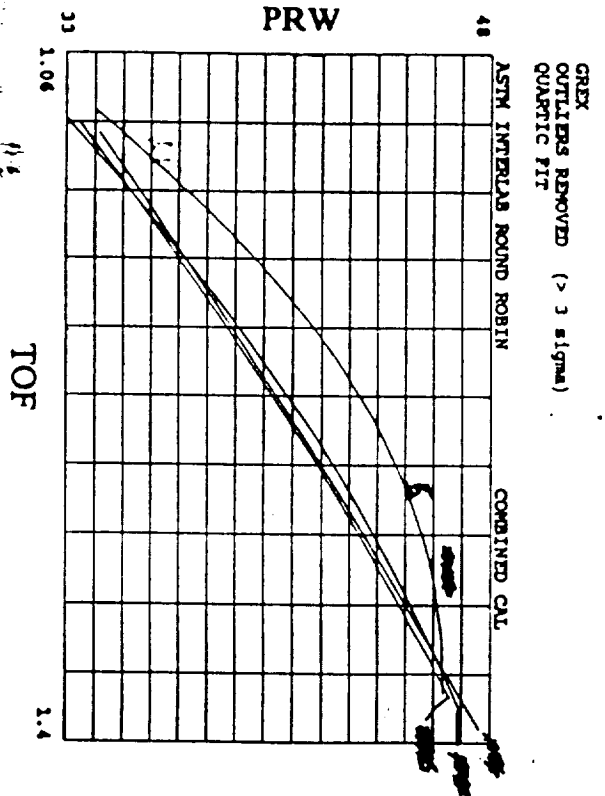
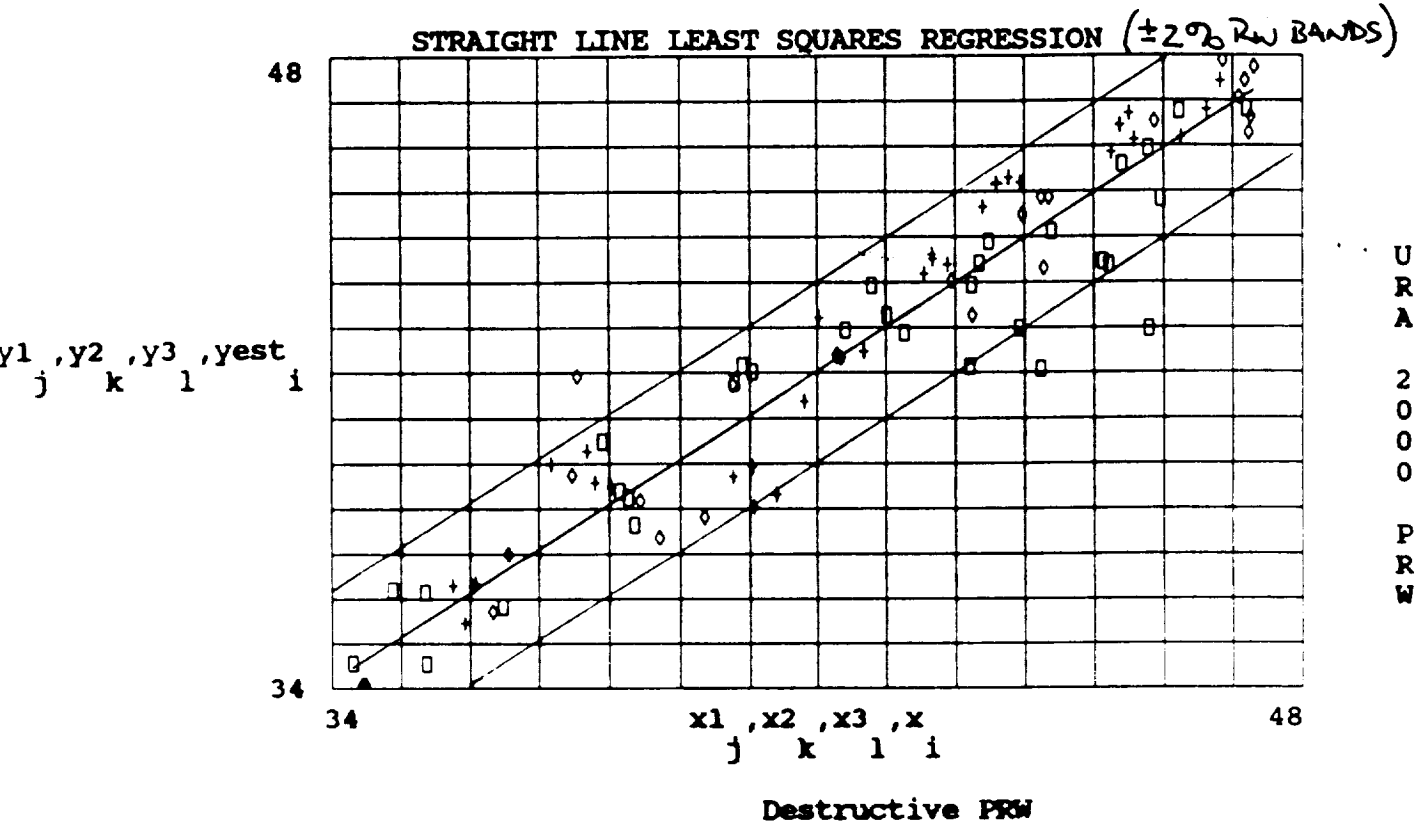


Figure 2B



GRAPHITE/EPOXY (CLOTH) **Lab 5**  
COMBINED CALIBRATION with **DATA REMOVED**



chi2 = 115.85261

r = 0.96373

mse = 1.27311

$\beta = \begin{bmatrix} 0.77842 \\ 0.98201 \end{bmatrix}$

lserr = 1.12832

$r^2 = 0.92878$

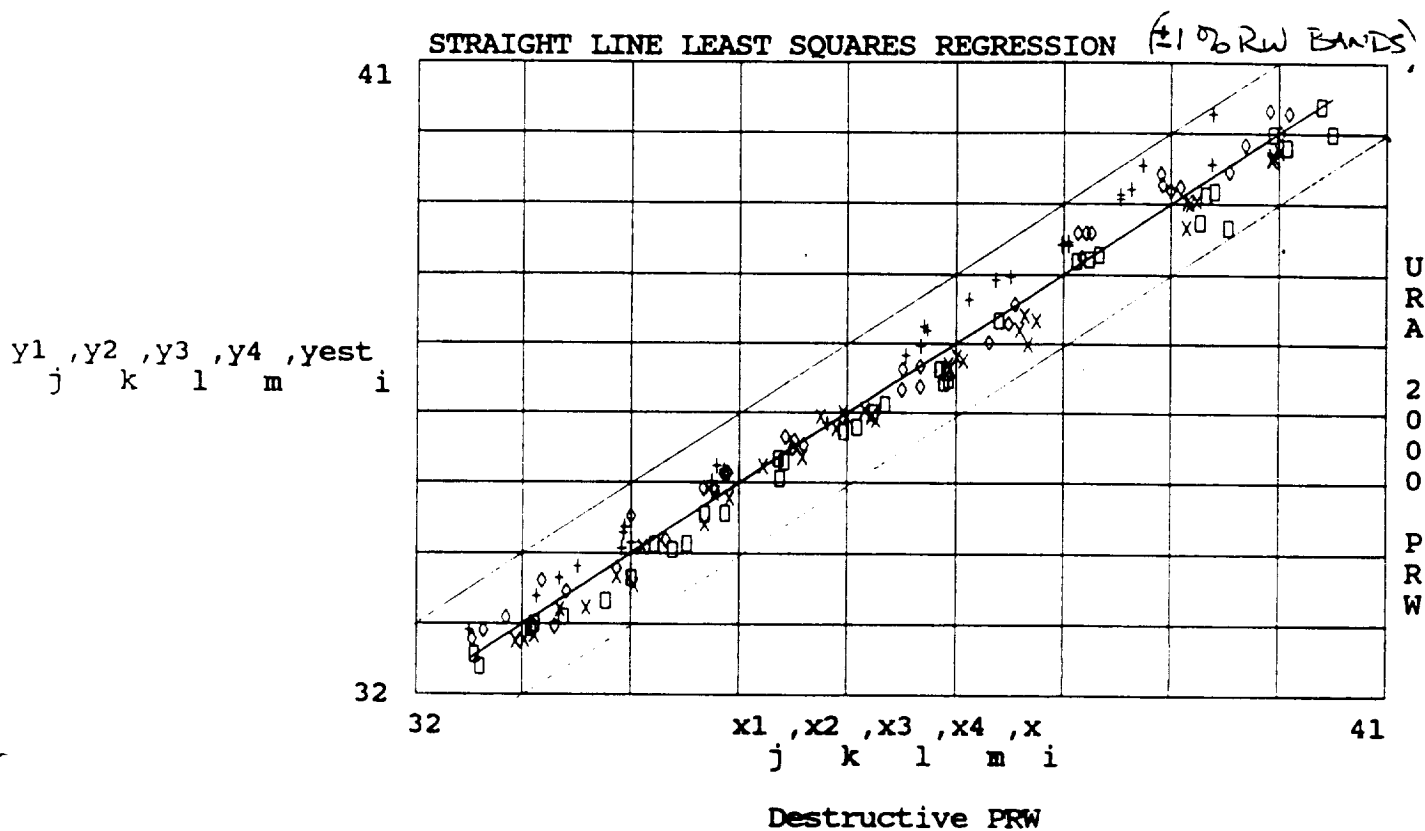
3 · lserr = 3.38496

Legend:

- = squares
- = pluses
- = diamonds

ASTM ROUND ROBIN INTER-LABORATORY ERROR ANALYSIS - COMBINED CALIBRATIONS

GLASS/EPOXY  
COMBINED CALIBRATION



chi2 = 14.20305

r = 0.99009

mse = 0.10521

$\beta = \begin{bmatrix} -0.05542 \\ 1.00149 \end{bmatrix}$

lserr = 0.32436

$r^2 = 0.98027$

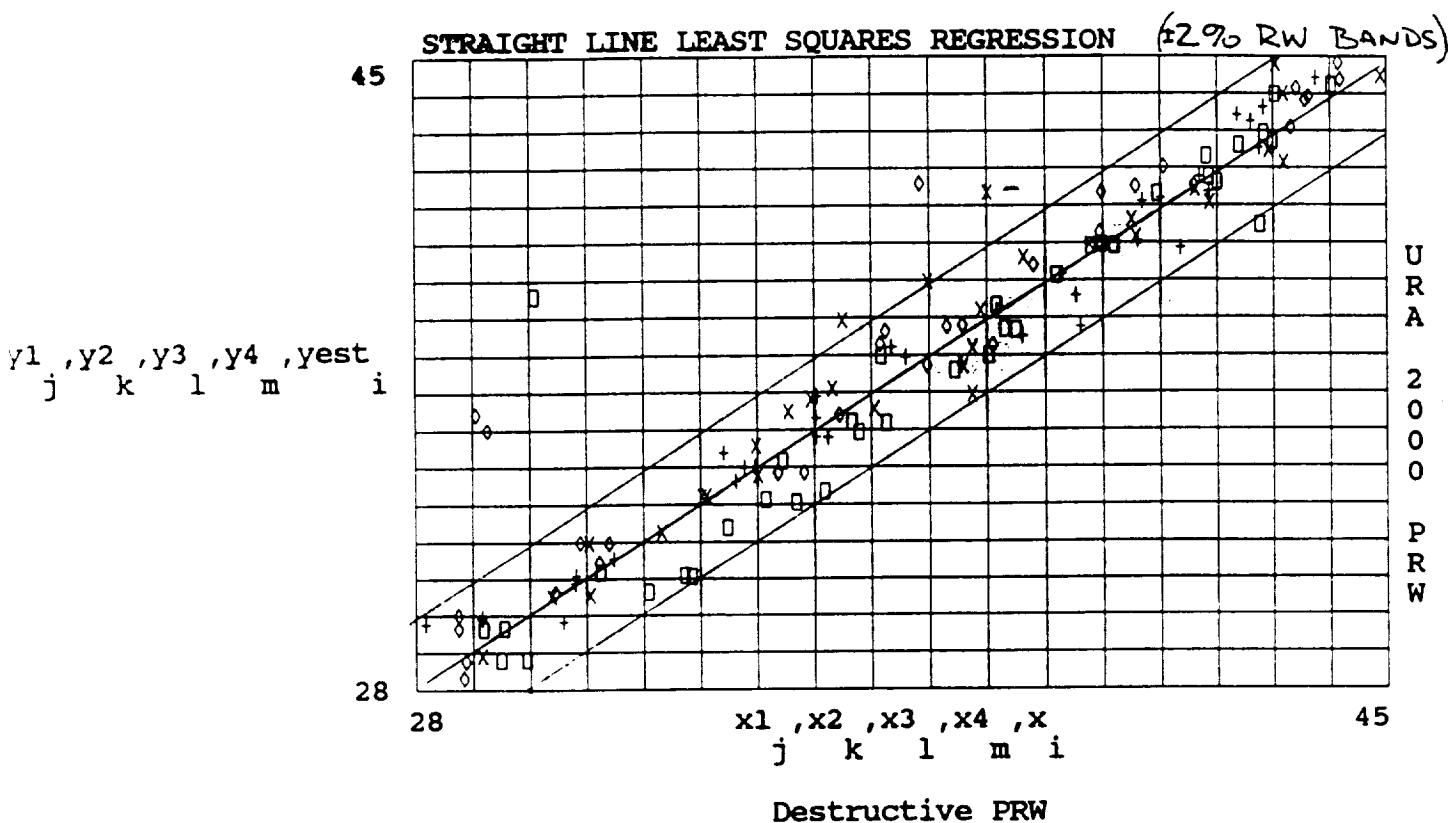
3. lserr = 0.97307

Legend:

1 = squares  
2 = pluses  
3 = diamonds  
4 = x's

ASTM ROUND ROBIN INTER-LABORATORY ERROR ANALYSIS - COMBINED CALIBRATIONS

GRAPHITE/EPOXY (UNIDIRECTIONAL)  
COMBINED CALIBRATION



$\chi^2 = 132.85348$

$r = 0.97926$

$mse = 0.99144$

$\beta = \begin{bmatrix} 0.41464 \\ 0.9873 \end{bmatrix}$

$lserr = 0.99571$

$r^2 = 0.95895$

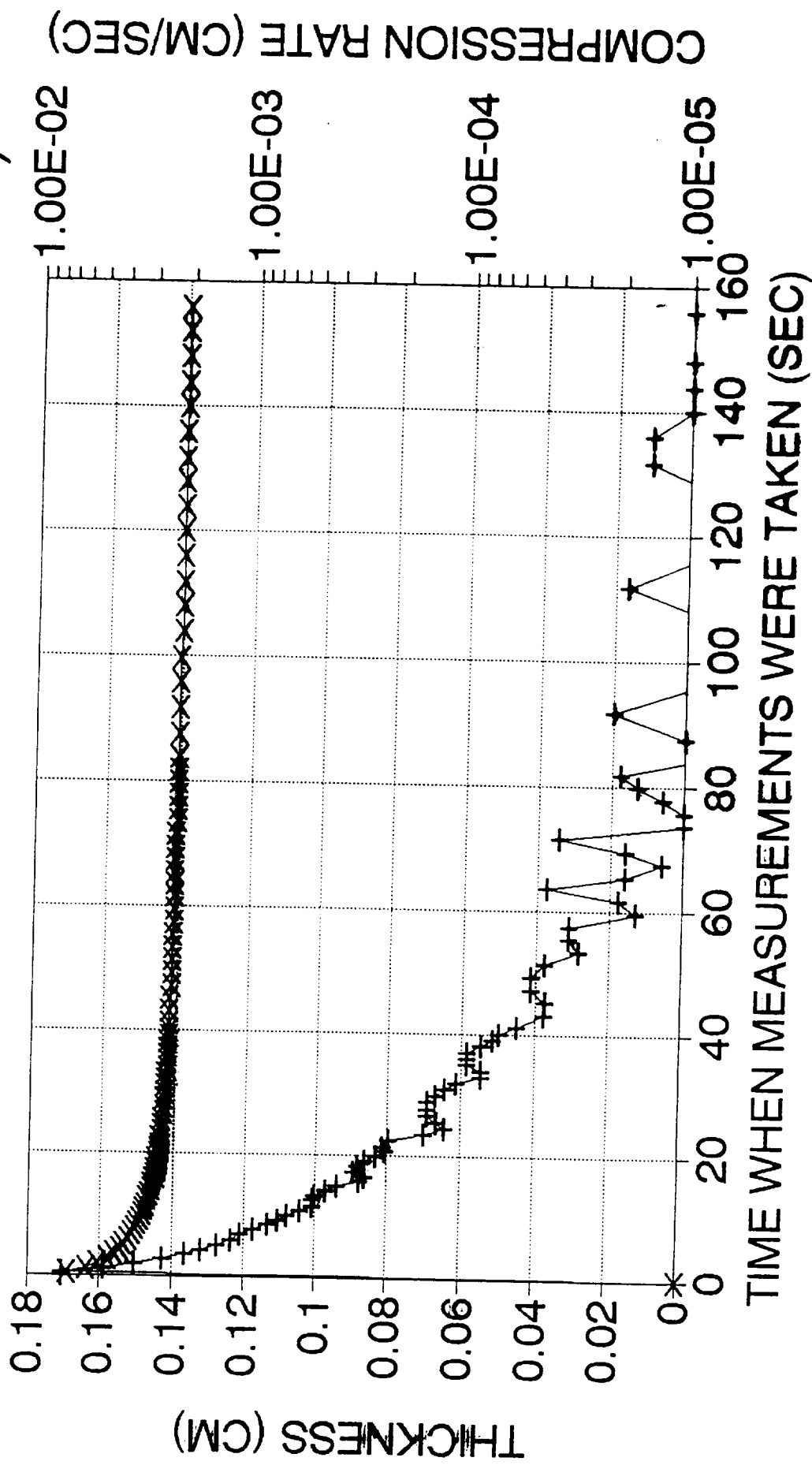
$3 \cdot lserr = 2.98714$

Legend:

squares  
pluses  
diamonds  
x's

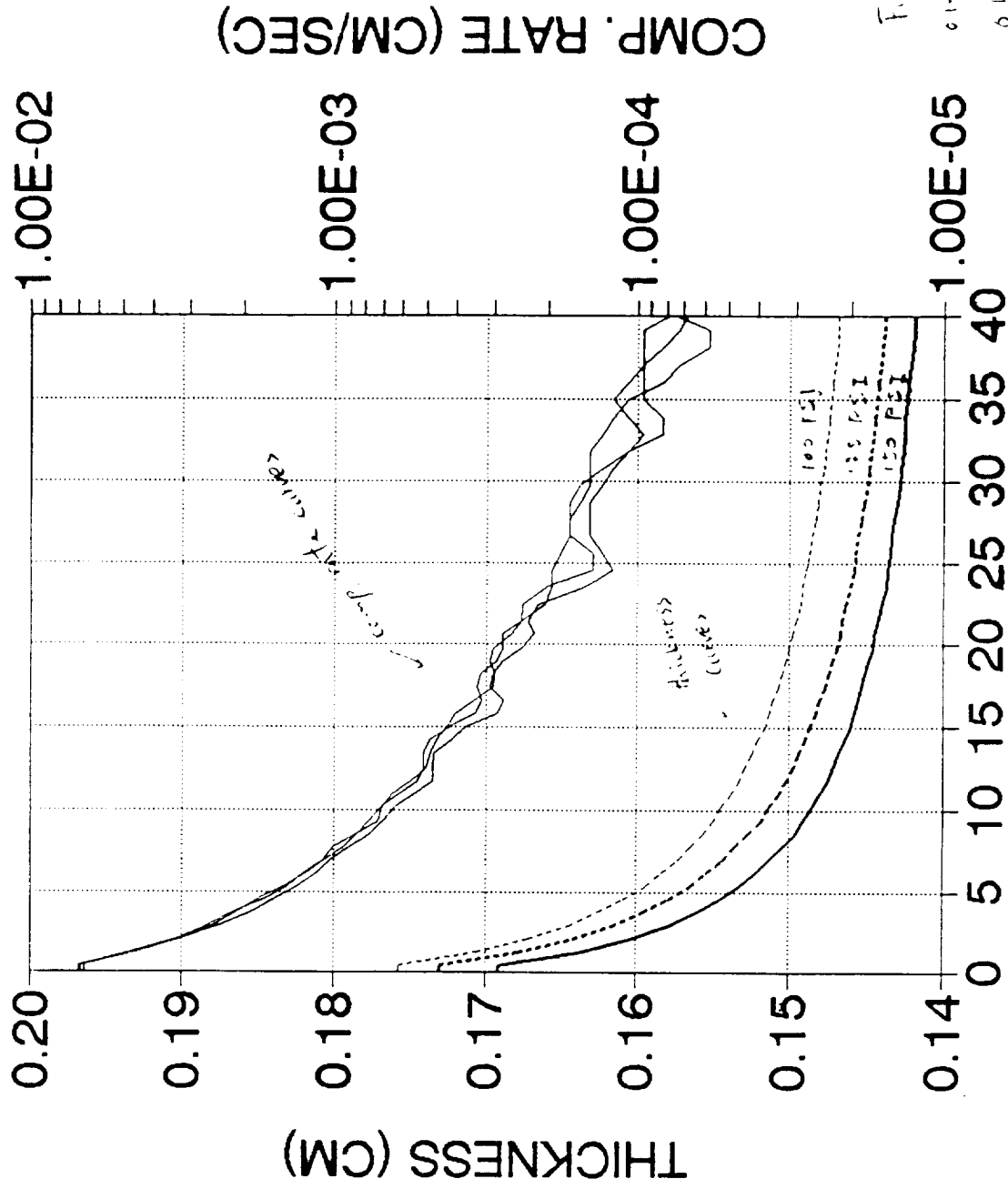


# HIGH TEMPERATURE CONSOLIDATION STUDY (HOTMXB77017781 250D 150PSI---FIBERITE)



# HIGH TEMPERATURE CONSOLIDATION STUDY

## (HOTMXB77017781 250D ALL -- FIBERITE)



COMP. RATE (CM/SEC)

.....	THICKNESS A
—	COMP. RATE A
.....	THICKNESS B
—	COMP. RATE B
—	THICKNESS C
—	COMP. RATE C

Final thk.	psi	t <sub>opt</sub>	thick <sub>opt</sub>	thick <sub>opt</sub> /th <sub>fin</sub>
0.14385	100	10.8	0.14616	1.0856
0.14140	125	10.27	0.15354	1.0859
0.13970	150	9.76	0.15105	1.0812

pressure ↗

optimum time ↗

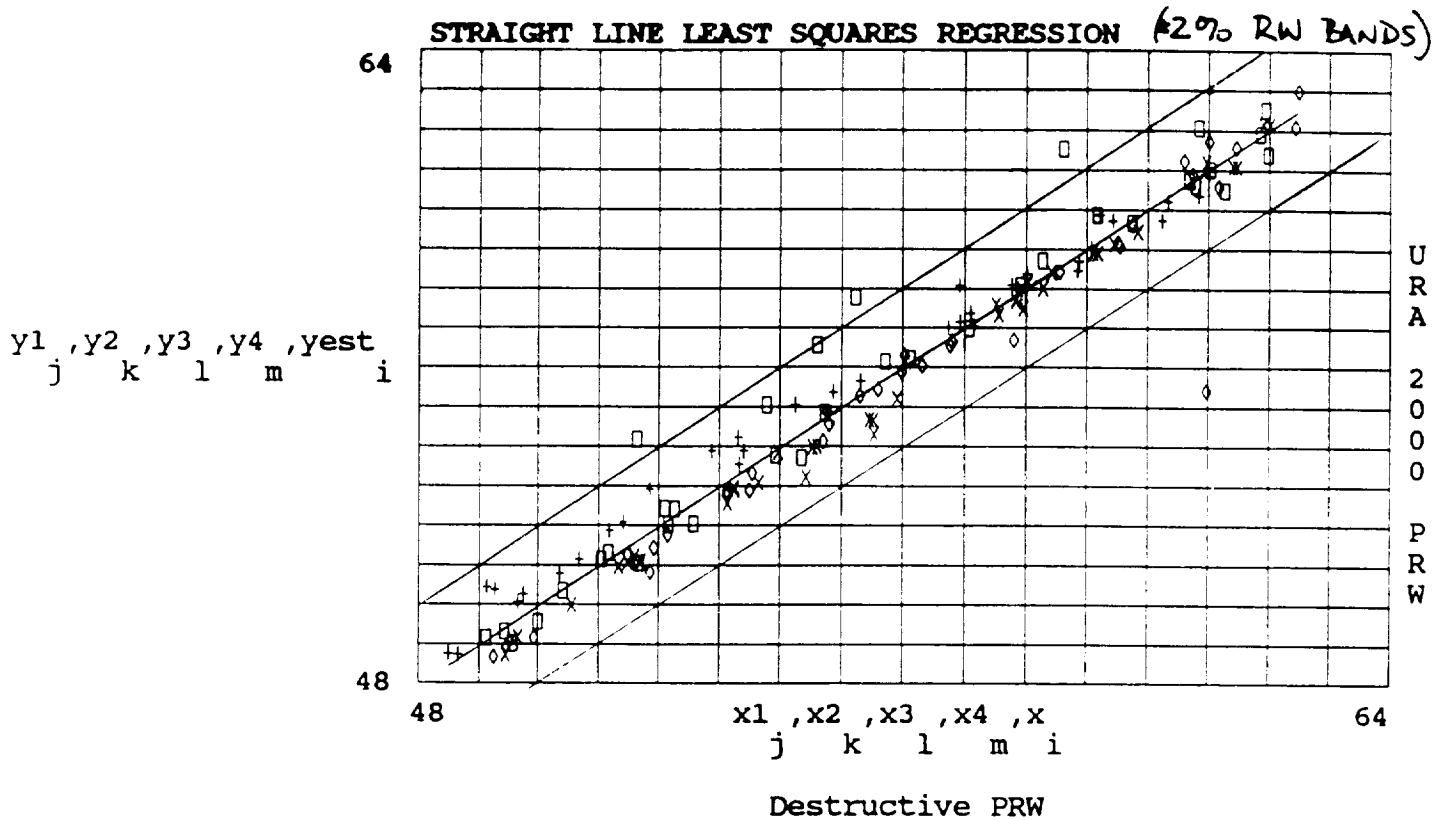
thickness at optimum time ↗

thickness at optimum time / final thickness ↗

TIME WHEN MEASUREMENTS WERE TAKEN (SEC)

ASTM ROUND ROBIN INTER-LABORATORY ERROR ANALYSIS - COMBINED CALIBRATIONS

KEVLAR/EPOXY  
COMBINED CALIBRATION



chi2 = 46.92471  
mse = 0.35018  
lserr = 0.59176  
3 · lserr = 1.77529

$r = 0.98914$   
  
 $r^2 = 0.9784$

$\beta = \begin{bmatrix} -0.29676 \\ 1.00481 \end{bmatrix}$

Legend:

1 = squares  
2 = pluses  
3 = diamonds  
4 = x's



**APPENDIX E**

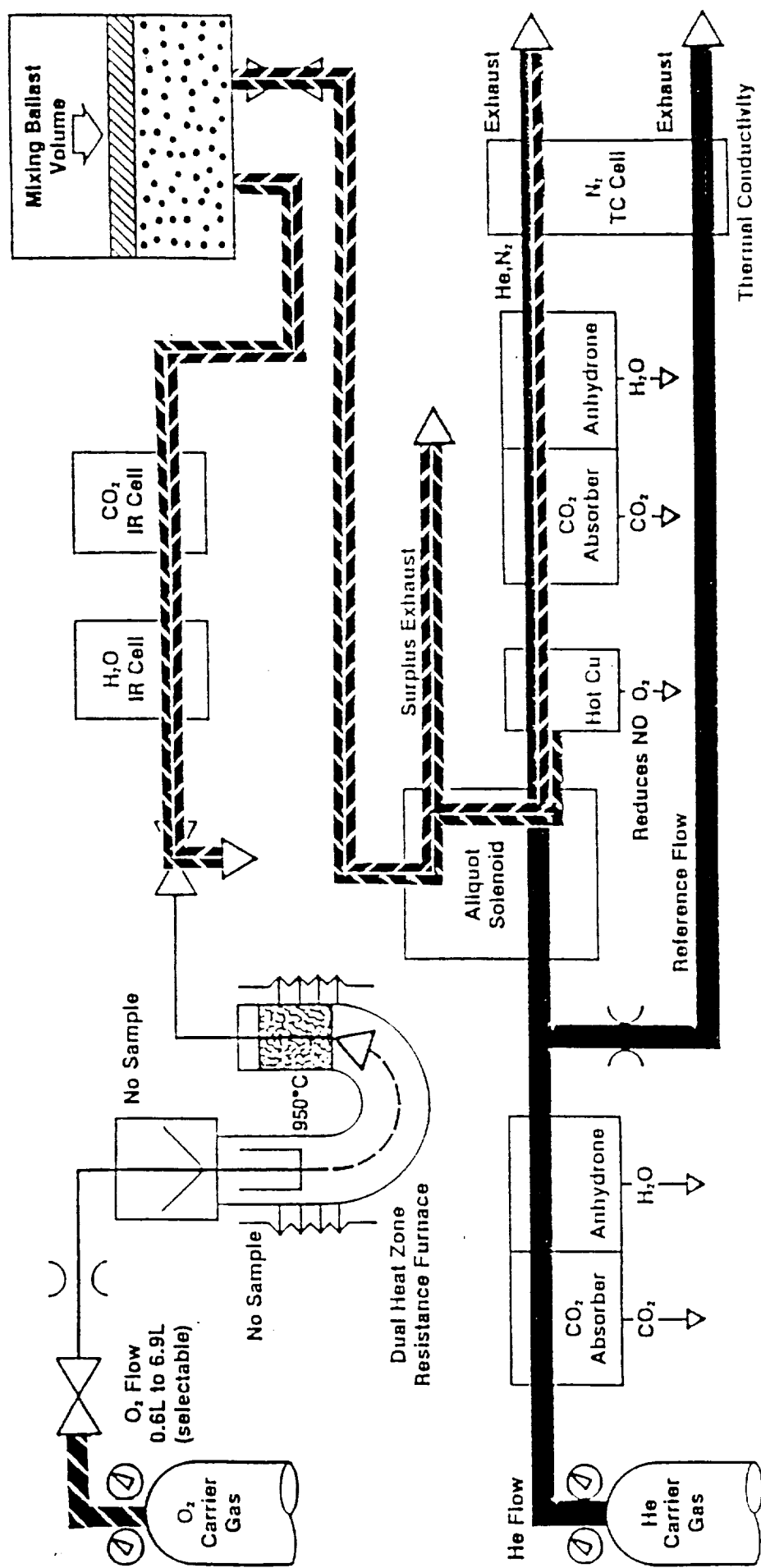
**DENNIS LAWRENZ**



## PRINCIPLE OF OPERATION OF THE CHN-600

The determination of carbon, hydrogen, and nitrogen is made by burning a weighed quantity of sample (oil, shale, coal, coke, or other organic compounds) in pure oxygen at  $\approx 950^{\circ}\text{C}$ ; carbon dioxide, water vapor, oxides of nitrogen, elemental nitrogen, and oxides of sulfur are possible products of combustion. Oxides of sulfur are removed with calcium oxide in the secondary combustion zone so that water vapor cannot combine to form sulfuric acid. The remaining gases of combustion are collected in a ballast volume and are allowed to mix thoroughly. For the nitrogen determination, a 10cc aliquot is taken. The aliquot is carried by helium into a reagent train consisting of hot copper for the removal of  $\text{O}_2$  and the reduction of  $\text{NO}_x$  to  $\text{N}_2$ , sodium hydroxide for the removal of  $\text{CO}_2$ , and magnesium perchlorate for the removal of  $\text{H}_2\text{O}$ . The remaining elemental nitrogen is measured by the thermal-conductivity cell. Simultaneous to the nitrogen measurement, the carbon and hydrogen infrared cells measure  $\text{CO}_2$  and  $\text{H}_2\text{O}$  levels. The infrared cell outputs are linearized (the thermalconductivity cell is already linear) and all outputs are multiplied by the appropriate calibration factor and "K factor" which is a composite factor that corrects for barometric pressure, ballast volume pressure, and chemical interferences. Next adjustments are made for blank and weight compensation. When these calculations are complete, the results for the three elements are displayed in percent.

This method gives the total percentages of carbon, hydrogen, and nitrogen in the organic sample as analyzed, and includes the carbon in carbonates and the hydrogen in the moisture and in the water of hydration of silicates.

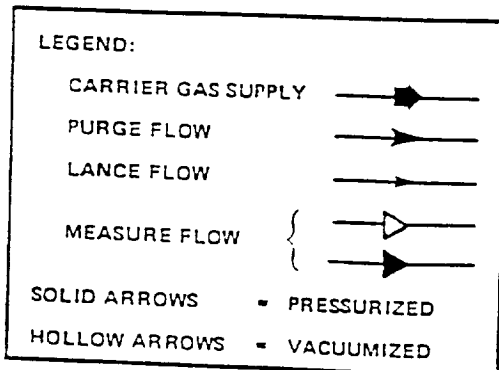
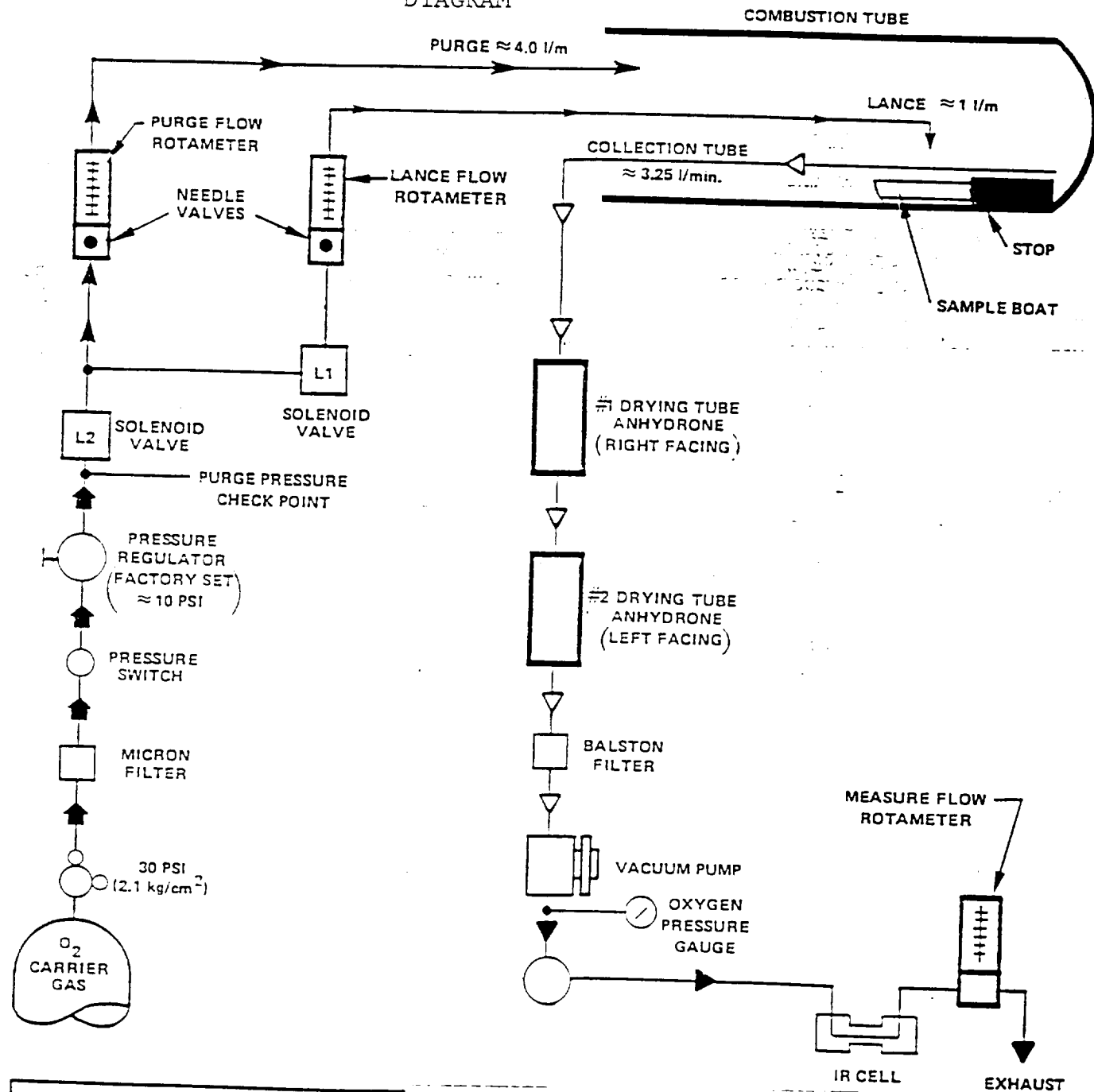


**LECO<sup>®</sup>** Flow Chart. CHN Determination



# LECO CR12 FLOW

## DIAGRAM



### NOTES:

1. O<sub>2</sub> STAYS ON FOR 10 SECONDS AFTER THE END OF ANALYSIS.

2. PURGE FLOW PROVIDES A FLOOD OF OXYGEN AT THE OPENING OF THE COMBUSTION TUBE DURING ANALYSIS THUS PREVENTING ATMOSPHERE FROM ENTERING THE SAMPLE COMBUSTION ZONE.

GAS FLOW DIAGRAM  
FIGURE S8

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# LECO CORPORATION

3000 Lakeview Avenue St. Joseph, MI 49085-2396 U.S.A.  
Phone: (616) 983-5531 • Telex: 211605 • Facsimile: (616) 983-3850

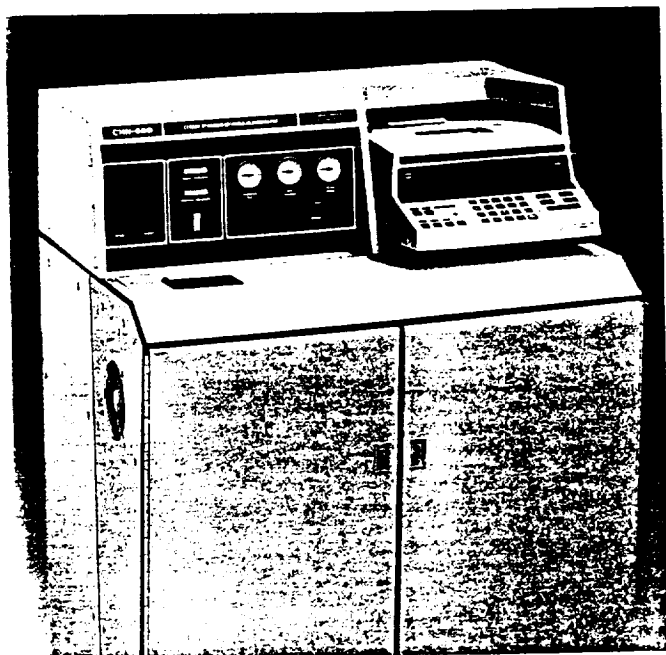
## LECO CR12 PERFORMANCE ON GRAPHITE AND COKE SAMPLES

### PARAMETERS:

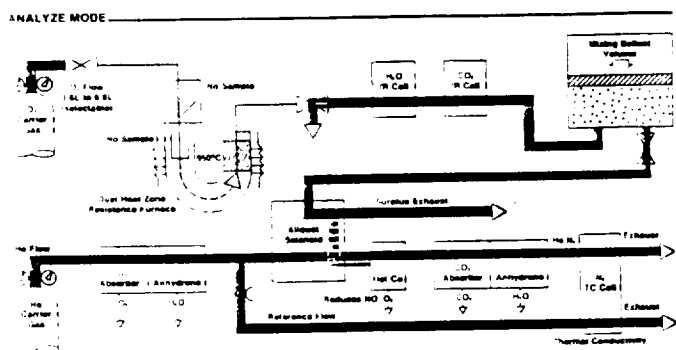
Furnace Temp: 1350°C  
Combustion Gas: Oxygen  
Lance Delay: 15 seconds  
Analysis Time: ~90 seconds  
Calibration: Outgassed graphite  
Crucible: Ceramic 528-203 Preheated at 1000° for one hour

<u>SAMPLE</u>	<u>WEIGHT</u>	<u>% CARBON</u>	<u>SAMPLE</u>	<u>WEIGHT</u>	<u>% CARBON</u>
Graphite	0.2647	100.5	BCR #3	0.1723	91.91
	0.2181	100.1	Coke	0.2130	92.34
	0.1724	99.82	@ 92.58	0.1454	91.99
	0.2158	100.0	% Carbon	0.1921	91.96
	0.2366	100.2		0.2216	91.96
	0.2035	99.92		0.1905	92.32
	0.1869	99.92		0.1983	92.07
	0.2094	99.70		0.1763	92.38
	0.1517	100.1		0.2023	92.33
	0.1383	99.73		0.2204	92.38
n = 10			n = 10		
$\bar{x} = 100$			$\bar{x} = 92.16$		
$\sigma_{n-1} = 0.24$			$\sigma_{n-1} = 0.20$		

# Rapid, Simultaneous Analysis of Carbon, Hydrogen and Nitrogen



One of the primary applications of elemental analysis is the determination of carbon, hydrogen and nitrogen in coals, cokes, oils and other organic materials. The LECO® CHN-600 and CHN-800 Elemental Analyzers simultaneously determine all three elements. Sample weights to 200 mg allow the CHN-600 to accurately analyze non-homogeneous sample materials. Sample weights from 3 mg to 15 mg employed by the CHN-800 conserve sample materials when limited amounts are available. Carbon and hydrogen are measured by infrared detection, nitrogen by thermal conductivity. Total analysis time for all three elements is 4 to 5 minutes with the CHN-600, and less than 2½ minutes with the CHN-800.



**GAS FLOW DIAGRAM**

## Principles of Operation

The combustion technique of the CHN-600 and CHN-800 is unique. A weighed sample is encapsulated in tin or copper and dropped into a reusable ceramic crucible centered in the primary hot zone of the "U" shaped combustion tube located in a resistance furnace. The

sample is burned in oxygen at 950°C. The potential combustion products are carbon dioxide, water vapor, oxides of nitrogen, elemental nitrogen, and oxides of sulfur. Oxides of sulfur are removed with a reagent in the secondary combustion zone. The secondary combustion zone also ensures complete combustion of all volatiles. The remaining products of combustion (CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub> and NO<sub>x</sub>) are collected and mixed thoroughly in a glass ballast chamber under a sliding piston. The CO<sub>2</sub> and H<sub>2</sub>O levels are constantly monitored during combustion by the CO<sub>2</sub> and H<sub>2</sub>O infrared detectors and when they return to a predetermined level, combustion is complete. An aliquot is taken and carried by helium through a reagent train for the removal of CO<sub>2</sub>, H<sub>2</sub>O and the reduction of NO<sub>x</sub> to N<sub>2</sub>. The nitrogen is then measured by thermal conductivity. Simultaneously, but separately from the nitrogen, the CO<sub>2</sub> and H<sub>2</sub>O are measured by selective infrared detectors. These measurements are weight compensated and displayed as percent C, H and N.

## Wide Range of Applications

The CHN-600 and CHN-800 successfully analyze coals, cokes, fuels, paraffin oil, benzamide, acetanilide, naphtha, rubber, shale, phenacetin, benzoquinoline, and numerous other organic substances.

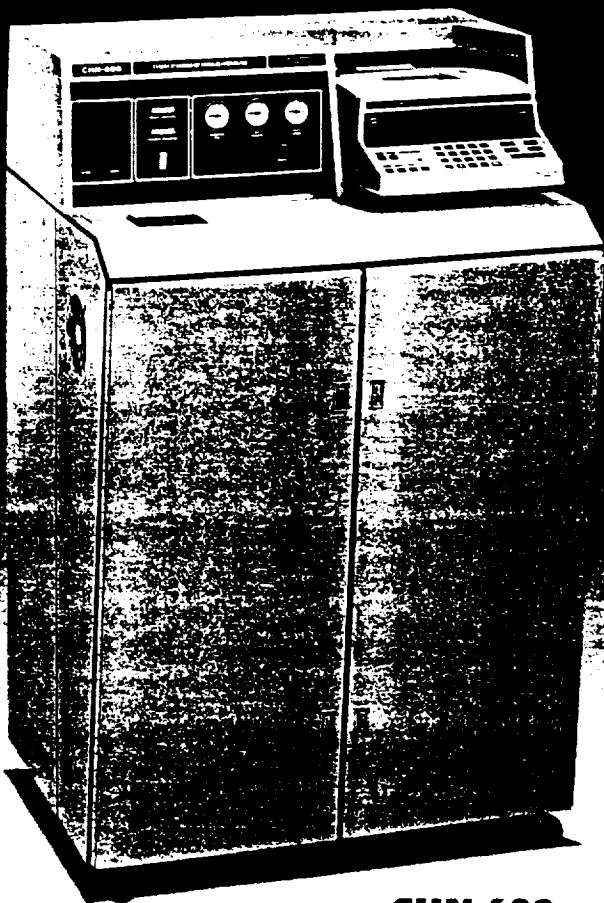
## Optional Autoloaders

When large numbers of samples must be analyzed, the optional 19 sample or 49 sample autoloaders can be utilized. The preweighed samples can then be analyzed in uninterrupted sequence without operator involvement and results will be automatically printed for each analysis.

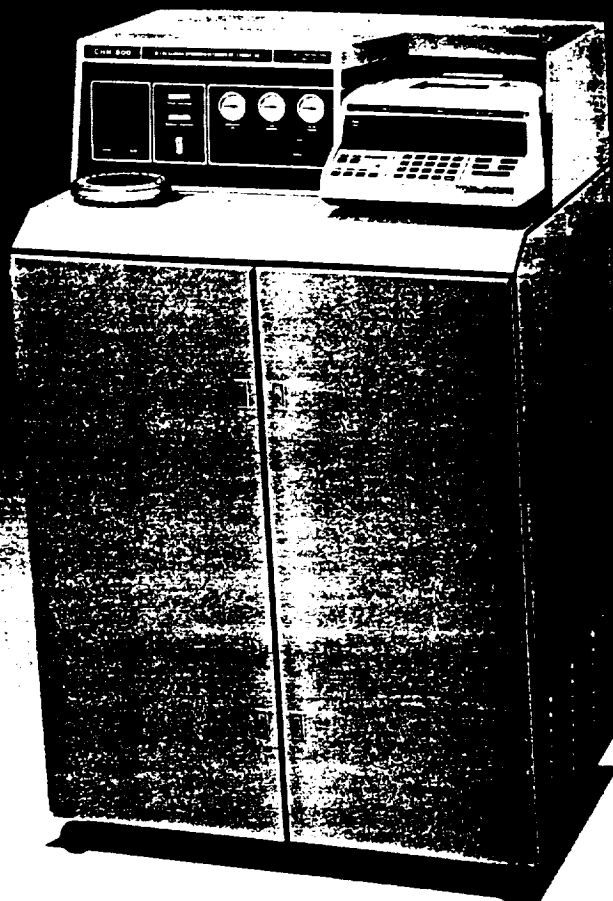


## Automatic Calibration

Both the CHN-600 and CHN-800 are calibrated by gas dosing or calibration samples of operator choice. With gas dosing, the operator selects the desired volume of CO<sub>2</sub>, N<sub>2</sub> and the number of analyses via the control console keyboard. The analyzer automatically gas doses, analyzes, and determines the appropriate calibration factor. With calibration samples, the operator analyzes as many as 49 samples, enters the value of the chosen standard at the keyboard, and the instrument automatically averages the results and sets the calibration factor.



**CHN-600**



**CHN-800**

**CHN-800 for Microsamples...from 3 to 15 mg**  
**CHN-600 for Macrosamples...100 to 200 mg**

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# and Nitrogen

## Rapid, accurate, and easy to use

The console is the operator's information and control center. It includes a numeric display, a message center, an alphanumeric printer and the keyboard.

The message center visually prompts the operator through calibration and operation with displayed commands and questions (e.g. "ENTER NEXT WEIGHT" or "GAS DOSE YES/NO"). The message center also provides diagnostic information. Both visible and audible alarms will alert the operator to procedural errors or equipment malfunction.

The integral printer will provide a permanent record of each analysis. The printed results are available in any of four formats:

The "Standard Format" (A) provides time, date, sample identification code, channel number, sample weight and the carbon, hydrogen and nitrogen contents.

An "Extended Format" (B) includes final pressure, individual blank, and calibration/correction factors for each element.

```

10 47 00 00 00
ID CODE 0000000088      CHAN #1
42 101      H 0 051
SAMPLE HEIGHT 0 1831
FINAL PRESS MM Hg 989.5
CARBON NITROGEN
ELHIP 0.00 0.00 0.35
FEHL 2377 2725 214
TIME 214 23 23
ALIE 0 0510 0 0550 0 0541
FHL 0 0541 0 054 0 0554
H+FC 0 0535 0 051 0 0000
    
```

**B**

A "Dry Answer Format" (C) includes moisture content and carbon, hydrogen and nitrogen values as received and on a "Dry Basis".

```

11 34 00 00 00
ID CODE 0000000091      CHAN #1
42 101      H 0 051
SAMPLE HEIGHT 0 1834
MOISTURE 4.30
    
```

**C**

A "Protein Format" (not shown) converts the nitrogen to a protein value using a selectable protein factor.

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## Typical Results CHN-600 ELEMENTAL ANALYZER FOR MACROSAMPLES

MATERIAL	SAMPLE SIZE (mg)	AVERAGE % CARBON	AVERAGE % HYDROGEN	AVERAGE % NITROGEN
Coal #1 n = 3	~150.0	75.52 $\sigma = 0.33$	4.83 $\sigma = 0.01$	0.95 $\sigma = 0.01$
Coal #2 n = 3	~150.0	15.26 $\sigma = 0.11$	4.42 $\sigma = 0.03$	1.20 $\sigma = 0.01$
Coke #1 n = 3	~100.0	89.58 $\sigma = 0.32$	0.29 $\sigma = 0.02$	1.08 $\sigma = 0.01$
Coke #2 n = 3	~100.0	87.41 $\sigma = 0.20$	0.23 $\sigma = 0.01$	1.18 $\sigma = 0.01$
Mineral Oil n = 3	~100.0	86.26 $\sigma = 0.07$	13.69 $\sigma = 0.03$	0.02 $\sigma = 0.01$
Heavy Oil n = 3	~100.0	86.59 $\sigma = 0.02$	9.93 $\sigma = 0.06$	0.34 $\sigma = 0.01$
Soil n = 3	~200.0	23.33 $\sigma = 0.01$	0.50 $\sigma = 0.02$	0.22 $\sigma = 0.01$
Plant Tissue n = 3	~200.0	43.43 $\sigma = 0.09$	6.11 $\sigma = 0.06$	2.27 $\sigma = 0.01$
Peat Moss n = 3	~100.0	53.42 $\sigma = 0.15$	5.50 $\sigma = 0.02$	0.93 $\sigma = 0.01$
Rubber n = 3	~120.0	84.92 $\sigma = 0.45$	9.07 $\sigma = 0.11$	4.23 $\sigma = 0.01$
Wheat n = 3	~200.0	45.75 $\sigma = 0.03$	6.46 $\sigma = 0.02$	2.03 $\sigma = 0.01$
Clay n = 3	~250.0	None Detected	0.63 $\sigma = 0.05$	3.01 $\sigma = 0.01$
Limestone n = 3	~100.0	11.97 $\sigma = 0.01$	0.03 $\sigma = 0.01$	0.08 $\sigma = 0.01$
Marl n = 3	~250.0	0.04 $\sigma = 0.00$	0.35 $\sigma = 0.04$	6.78 $\sigma = 0.01$
Petroleum Coke n = 3	~100.0	96.21 $\sigma = 0.08$	0.04 $\sigma = 0.01$	0.86 $\sigma = 0.01$

## Typical Results CHN-800 ELEMENTAL ANALYZER FOR MACROSAMPLES

MATERIAL	NOMINAL SAMPLE SIZE (mg)	CARBON	HYDROGEN	NITROGEN
Acetanilide n = 3	~7.00	71.14 $\sigma = 0.09$	6.68 $\sigma = 0.09$	10.32 $\sigma = 0.01$
Benzamide n = 3	~8.00	69.38 $\sigma = 0.02$	5.78 $\sigma = 0.02$	11.56 $\sigma = 0.01$
Nicotinamide n = 3	~8.00	59.00 $\sigma = 0.05$	5.04 $\sigma = 0.04$	22.92 $\sigma = 0.01$

## Specifications

<b>Range*</b>		<b>Regulators Required</b>	
Carbon	0.01% min. - 100.0% max.	Oxygen	0-125 PSI, CGA 540, 7/8-14 Male R.H.
Hydrogen	0.01% min. - 100.0% max.	Helium, Nitrogen	0-125 PSI, CGA 580, 15/16-14 Female R.H.
Nitrogen	0.01% min. - 50.0% max.	Carbon Dioxide	0-125 PSI, CGA 320, 13/16-14 Male R.H.
<b>Accuracy**</b>		Air	0-125 PSI, CGA 346, 13/16-14 Male R.H.
CHN-600	±0.04% carbon or ±0.3% of reading, whichever is greater ±0.02% hydrogen or ±1.5% of reading, whichever is greater ±0.03% nitrogen or ±3% of reading, whichever is greater	Carrier Gases†	Oxygen, 99.99% pure, 40 PSI (2.8 kg/cm <sup>2</sup> ) ±10% Helium, 99.99% pure, 40 PSI (2.8 kg/cm <sup>2</sup> ) ±10%
CHN-800	±0.04% carbon or ±0.3% of reading, whichever is greater ±0.02% hydrogen or ±1.5% of reading, whichever is greater ±0.03% nitrogen or ±2% of reading, whichever is greater	Pneumatic Gas	Nitrogen or instrument air, source must be oil and water free, 40 PSI (2.8 kg/cm <sup>2</sup> ) ±10%
<b>Nominal Sample Size</b>		Dose Gases	Carbon dioxide, 99.9% pure, 40 PSI (2.8 kg/cm <sup>2</sup> ) ±10% Nitrogen, 99.5% pure, 40 PSI (2.8 kg/cm <sup>2</sup> ) ±10%
CHN-600	200 milligrams	<b>Power</b>	
CHN-800	10 milligrams	Requirements	230 VAC ±10%, 50/60 Hz, 3000 watts warm up, 800 watts continuous
<b>Analysis Time</b>		<b>Dimensions</b>	
CHN-600	4 to 5 minutes including purge	Height	48 inches (122 cm)
CHN-800	2 minutes 20 seconds including purge	Width	30 inches (76 cm)
<b>Chemical Reagents</b>		Depth	27 inches (69 cm)
Anhydrous Magnesium Perchlorate (MgClO <sub>4</sub> ) Sodium Hydroxide on an inert base Copper Metal Turnings N-Catalyst		Weight	400 lbs (182 kg)

\* The rate of oxidation and volume of gas produced determine the sample size that can be used to achieve the maximum range limit.

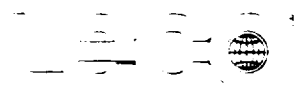
\*\* Calibrated and conformance tested by gas dose analysis.

† The nitrogen blank is directly related to nitrogen and argon contamination in the oxygen supply.

## Part Numbers

785-500 CHN-600 Elemental Analyzer for Macrosamples Pkg.	501-291 Oxygen Regulator
600-700 CHN-800 Elemental Analyzer for Microsamples Pkg.	764-216 Helium, Nitrogen Regulator
778-470 19-Sample Autoloader	768-593 Carbon Dioxide Regulator
781-570 49-Sample Autoloader	766-036 Compressed Air Regulator
778-440 Vacuum Cleaner Attachment	777-147 Data Transmit Card

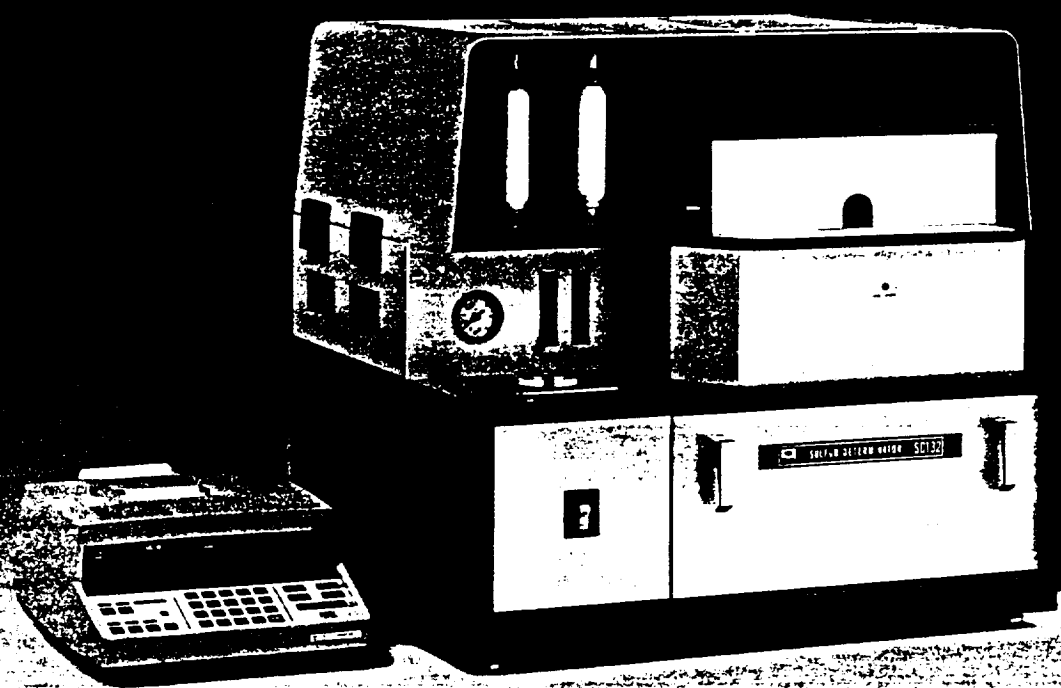
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**LECO CORPORATION**  
3000 Lakeview Avenue  
St. Joseph, MI 49085-2396  
U.S.A.



Phone: (616) 983-5531  
Facsimile: (616) 983-3850



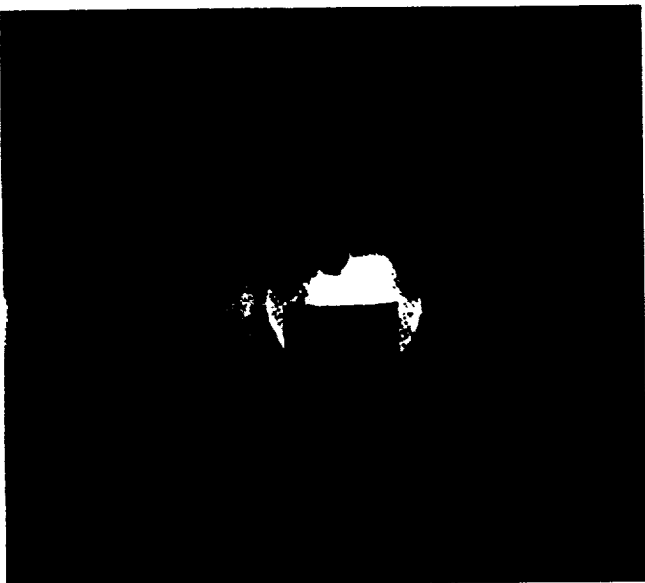
***Accurate determination of total carbon or total sulfur in organic and fossil fuel materials.***

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**LECO®**

## Advanced instrumentation for the organics and inorganics laboratory

The LECO® CR-12, SC-32, SC-132 and SC-232 permit the organic and inorganic laboratory to determine total carbon or sulfur with optimum speed and accuracy. The combination of a dependable molybdisilicide resistance heated furnace with a patented open-end combustion system allows samples of a nominal 0.5 gram weight to be totally combusted in a pure oxygen environment.



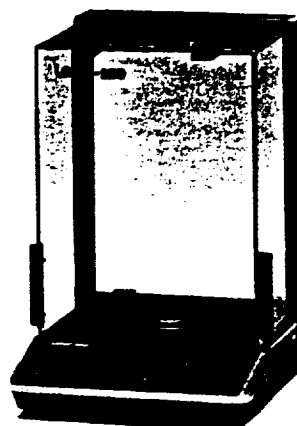
The oxygen environment is provided in two separate patterns. A purge flow of oxygen around the front of the combustion area provides a blanket to keep atmosphere out while acting as the primary source of oxygen for combustion. The second oxygen flow pattern is delayed to turn on after the bulk of the sample has combusted and provides a direct lance flow of oxygen onto the sample to combust the remaining sample material. The released  $\text{SO}_2$  and  $\text{CO}_2$  gases are drawn from the combustion area by a pump and directed to a highly selective solid-state infrared detection system. The microprocessor-based system handles all the signal processing functions, integration, blank compensation and calibration and weight correction. The system's control console provides a display and printed copy of the final result.

The microprocessor system allows the analysis to be performed with the utmost of ease. Analysis parameters, including minimum analysis time, lance delay, calibration correction and blank correction, can be entered into four individual analysis channels to accommodate different sample types. Then, to perform an analysis, the operator selects the channel to be used and places an empty combustion boat on the integral balance. The microprocessor automatically tares the weight of the boat, and the operator then presses the ID CODE key to enter a sample identification consisting of up to eight digits.

After weighing a nominal 0.5 gram weight into the combustion boat (the sample weight is displayed on the system's control console), the operator presses the ENTER key and the sample weight and ID code are automatically transferred into memory. As many as 50 samples can be weighed and entered into memory prior to analysis.

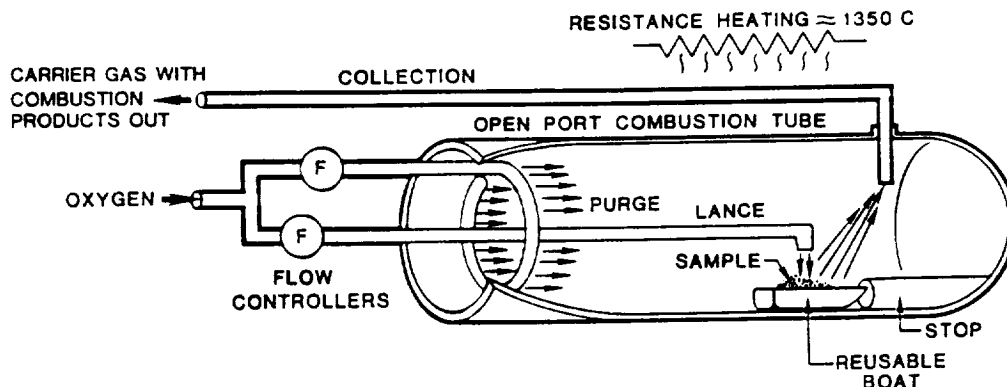
Next, the operator presses the ANALYZE key and after an initial purge period has been completed, the microprocessor prompts the operator to load the sample (combustion boat) into the combustion system. The microprocessor starts and ends the analysis automatically.

### Optional External Balance interface



When analyses require a sample weight of 0.1 grams or less, the LECO® 250 Electronic Balance can be interfaced with the unit by installing the optional balance interface kit. When used, the LECO® 250 allows accurate, automatic weight entry from 0.0001 to 121 grams with readability of  $\pm 0.0001$  grams. Nominal stabilization time with the LECO® 250 is 3 seconds.

### UNIQUE LECO COMBUSTION SYSTEM



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## CR-12 Carbon Determinator

The LECO® CR-12 Carbon Determinator is designed for organic materials with a carbon concentration of 0.005% to 10% based at 1 gram. Higher concentrations can be analyzed by using smaller sample sizes. Materials such as graphite, calcium carbonate, limestone and nicotonic acid can be determined within 120 to 150 seconds with an accuracy of  $\pm 1\%$  of the carbon present.

### CR-12 Typical Results

Material	Sample Weight (grams)	% Carbon Expected	% Carbon Determined
Graphite	0.1	100.00	100.1
			99.9
			99.8
Nicotonic Acid	0.1	58.54	58.52
			58.64
			58.45
Calcium Carbonate	1.0	11.99	11.99
			11.99
			12.00

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## SC-132 Sulfur Determinator

The SC-132 will analyze the same materials as the SC-32, but is best suited for analyses of lower sulfur concentrations (ranging from 0.001% to 2% for a 1 gram sample). The speed and accuracy of the SC-132 is identical to that of the SC-32, and results may also be programmed to be displayed and printed in percent S,  $\text{SO}_3$ , or  $\text{SO}_4$ .

### SC-132 Typical Results

Material	Comb. Aid	Sample Weight (grams)	% Sulfur Exp.	% Sulfur Det.
Orchard Leaves	$\text{V}_2\text{O}_5$ Powder 501-636	0.25 to 0.3	0.19	0.194
				0.190
				0.192
Carbon Black	None	0.2 to 0.5	Unknown	0.042
				0.041
Doiomite	Sulfcel® 502-032	0.5 to 1.0	Unknown	0.0052
				0.0054
Coal	None	0.2 to 0.5	1.03	1.03
				1.02
				1.03

## SC-32 Sulfur Determinator

The SC-32 is ideal for coal, coke and hydrocarbon materials with sulfur concentrations ranging from 0.005% to 4% for a 1 gram sample. The flexibility of the system makes the SC-32 useful for other materials as well, including tobacco, cement and plant tissue. Each of these materials can be determined with an accuracy of  $\pm 1\%$ . Through the system's programming, values can be calculated and displayed in percent S,  $\text{SO}_3$ , or  $\text{SO}_4$ .

### SC-32 Typical Results

Material	Comb. Aid	Sample Weight (grams)	% Sulfur Exp.
Residual Oil	Com-Aid® 501-427	0.1 to 0.2	1.05
Tobacco	None	0.25 to 0.3	Unknown
Portland Cement	Sulfcel® 502-032	0.2 to 0.5	2.83
Shampoo	$\text{V}_2\text{O}_5$ Powder 501-636	0.2 to 0.4	Unknown
Coal	None	0.2 to 0.5	Unknown

## SC-232 Sulfur Determinator

The SC-232 contains the same features as the SC-32 and SC-132, but is designed for the high sulfur materials such as ore concentrates or unvulcanized rubber that contain sulfur concentrations from 0.05% to 75% at 1 gram.

### SC-232 Typical Results

Material	Comb. Aid	Sample Weight (grams)	% Sulfur Exp.
Zinc Concentrate	$\text{V}_2\text{O}_5$ Powder 501-636	0.5	30.6
Lead Concentrate	$\text{V}_2\text{O}_5$ Powder 501-636	0.5	Unknown
Unvulcanized Rubber	$\text{V}_2\text{O}_5$ Powder 501-636	0.1	Unknown



**APPENDIX F**

**CINDY UPTON**



**NMR**

**NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY**

CINDY UPTON  
NASA/MSFC

## **NUCLEAR SPIN**

- AS IN THE CASE OF ELECTRONS, THE NUCLEI OF CERTAIN ATOMS ARE CONSIDERED TO SPIN.
- THE CIRCULATION OF CHARGE GENERATED BY THIS SPINNING CAUSES A MAGNETIC MOMENT ALONG THE AXIS OF SPIN - THE NUCLEI ACT LIKE TINY BAR MAGNETS.

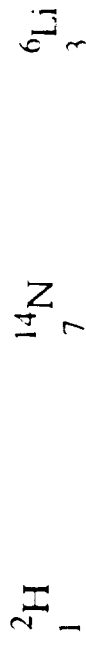
### NUCLEI WHICH HAVE THE PROPERTY OF SPIN

1. Nuclei with an ODD mass have half-integral spin.



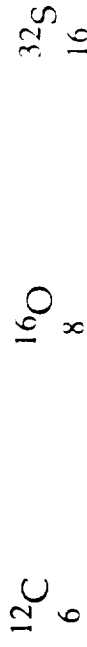
$$I = \underline{1/2}$$

2. Nuclei with an EVEN mass number, but an ODD charge number, have an integral spin.



$$I = \underline{1}$$

3. Nuclei with an EVEN mass number and an EVEN charge number have zero spin.



$$I = \underline{0}$$

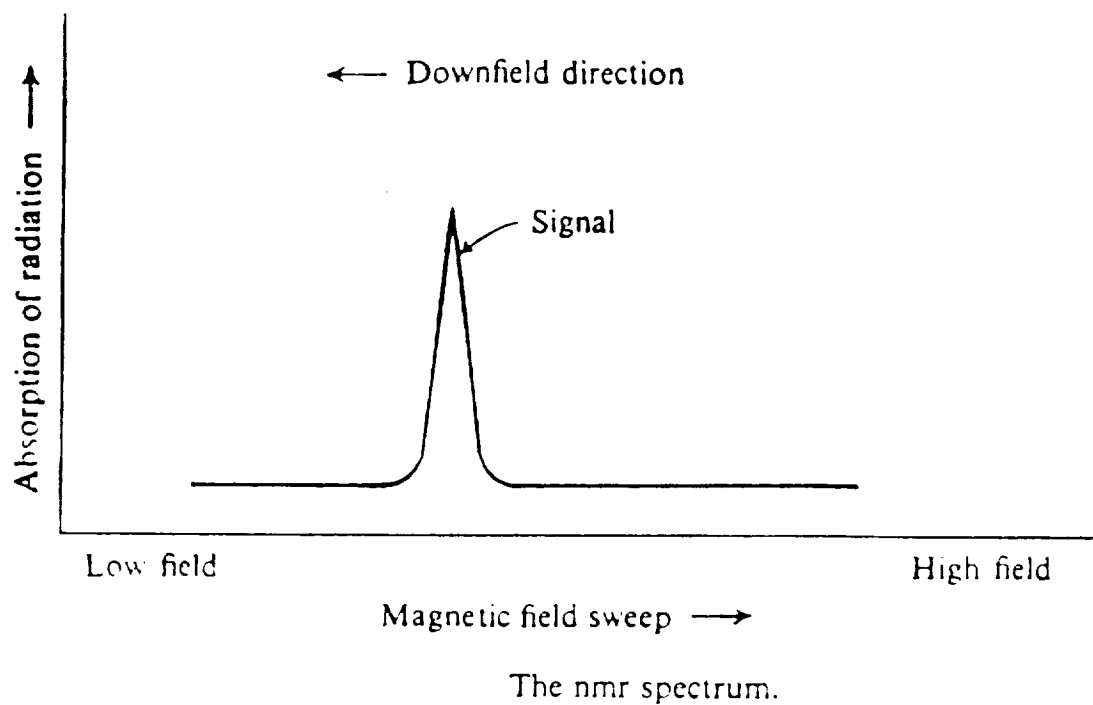
## ALIGNMENT OF NUCLEI WITHIN A MAGNETIC FIELD

- If a nucleus possessing the property of spin is placed in an external magnetic field, quantum mechanics predicts that the magnetic moment of the nucleus can be aligned two different ways:
  - With the magnetic field, which is more stable, or
  - Against the magnetic field.
- If the magnetic moment is aligned with the field, energy must be applied and absorbed by the nucleus in order to flip the "magnet" over to an alignment to the less favored position, against the field.



## SPECTROSCOPIC ANALYTICAL TECHNIQUES

- IR & UV spectra are obtained by passing radiation of steadily changing frequency through a substance and observing the frequency at which radiation is absorbed.
- NMR: Keep radiation frequency constant, and vary the strength of the magnetic field; at some value of the field strength, the energy required to flip the nucleus equals the energy of the radiation, absorption occurs, and a signal is observed. This is a NMR spectrum.



This diagram may be found in "Organic Chemistry",  
by Robert Morrison and Robert Boyd, 3rd edition, page 415.

## APPLIED FIELD STRENGTH VS. EFFECTIVE FIELD STRENGTH

- Resolution of structures via NMR spectra is due to the fact that a nucleus absorbs at a frequency on the magnetic field that it experiences. This is the EFFECTIVE FIELD STRENGTH, and at each nucleus it depends on its own unique environment, including such things as its electron density and the presence of neighboring nuclei. The effective field strength is not exactly equal to the APPLIED FIELD STRENGTH. Each nucleus (or set of equivalent nuclei) will have a slightly different environment from its neighbor. So, a different applied field strength will be necessary to produce the same effective field strength.
- We can say then that given a certain radiofrequency, all nuclei absorb at the same effective field strength, but at a different applied field strength. This applied field strength is measured and is plotted against absorption.

## EQUIVALENT NUCLEI

- Within a molecule, nuclei with the **same environment** absorb at the same applied field strength. Those nuclei with the same environment are said to be equivalent. Using carbon as an example, note the differences between each a, b, or c by looking at the attached groups. Either there is a different number of hydrogens, or there is a chlorine:



**2 NMR Signals**  
**Ethyl Chloride**



**2 NMR Signals**  
**Isopropyl Chloride**



**3 NMR Signals**  
**Propylchloride**

### SOME SAMPLE DATA

- The following spectra were obtained by Dr Robert Wardle (Thiokol/Wasatch). These spectra are preliminary. More scans are needed for improved resolution.

## PROTON NMR

.  $^1\text{H}$  NMR SPECTRA MEASURES THE NUMBER OF AROMATIC PROTONS AND COMPARES THEM TO METHYLENE BRIDGE PROTONS TO OBTAIN DEGREE OF CURE, AND INFORMATION ON THE SOLVENT AND CATALYST.

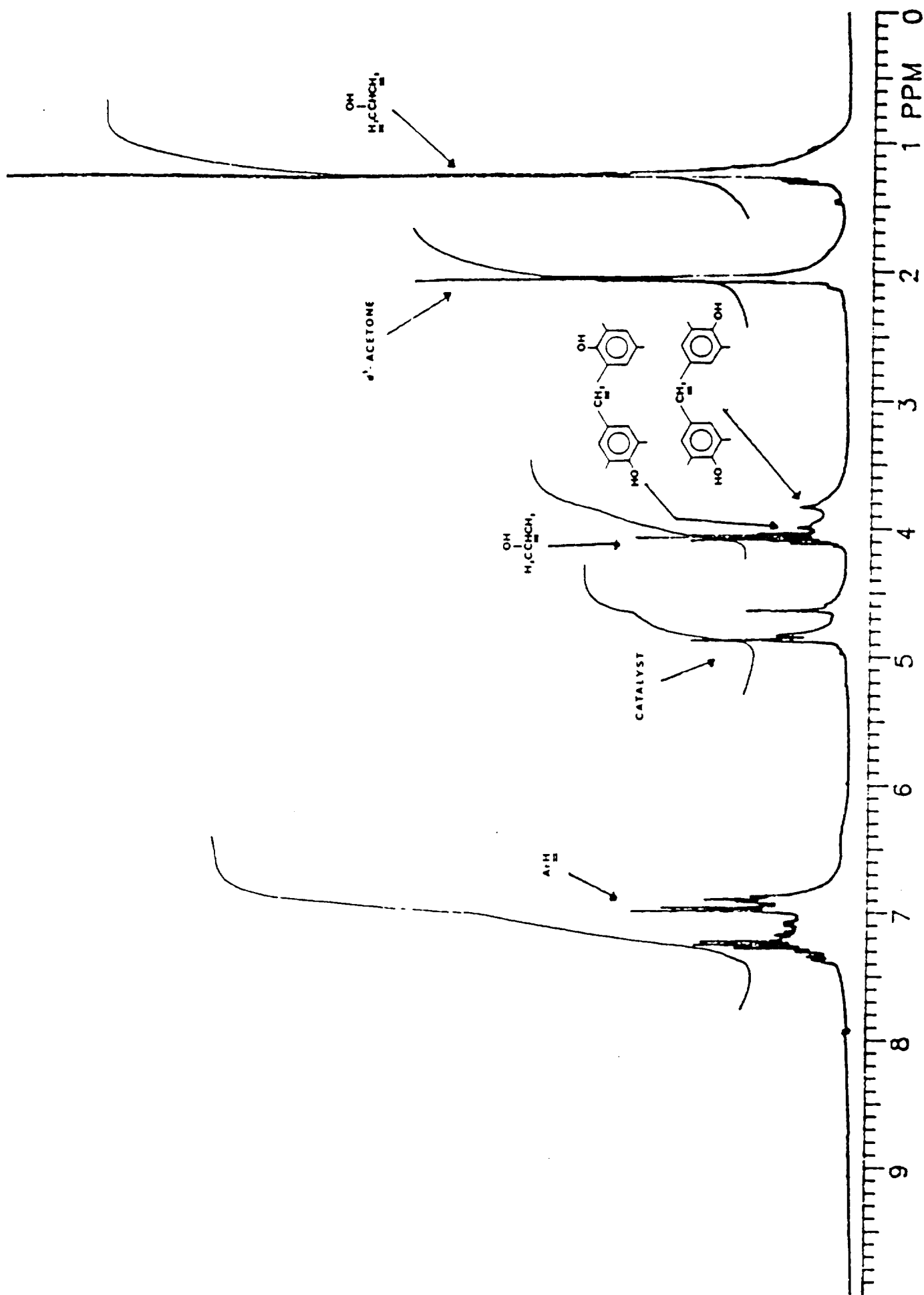


Figure 1. This  $^1\text{H}$  spectrum was obtained on a  $d^6$ -acetone solution of Borden L6J-159 phenolic resin. Assignments are as noted on the spectrum, with the observed protons being double underlined. Most significant to this project is the lack of definable resolution of the aromatic signals and the overlap of the isopropanol methine and the 2,4'-connected phenol

## CARBON - 13 NMR

- $^{13}\text{C}$  NMR MEASURES THE NUMBER OF AROMATIC CARBONS, AND COMPARES THEM TO NUMBER OF METHYLENE BRIDGE CARBONS TO OBTAIN DEGREE OF CURE, MEASUREMENT OF SOLVENT, AND CATALYST.



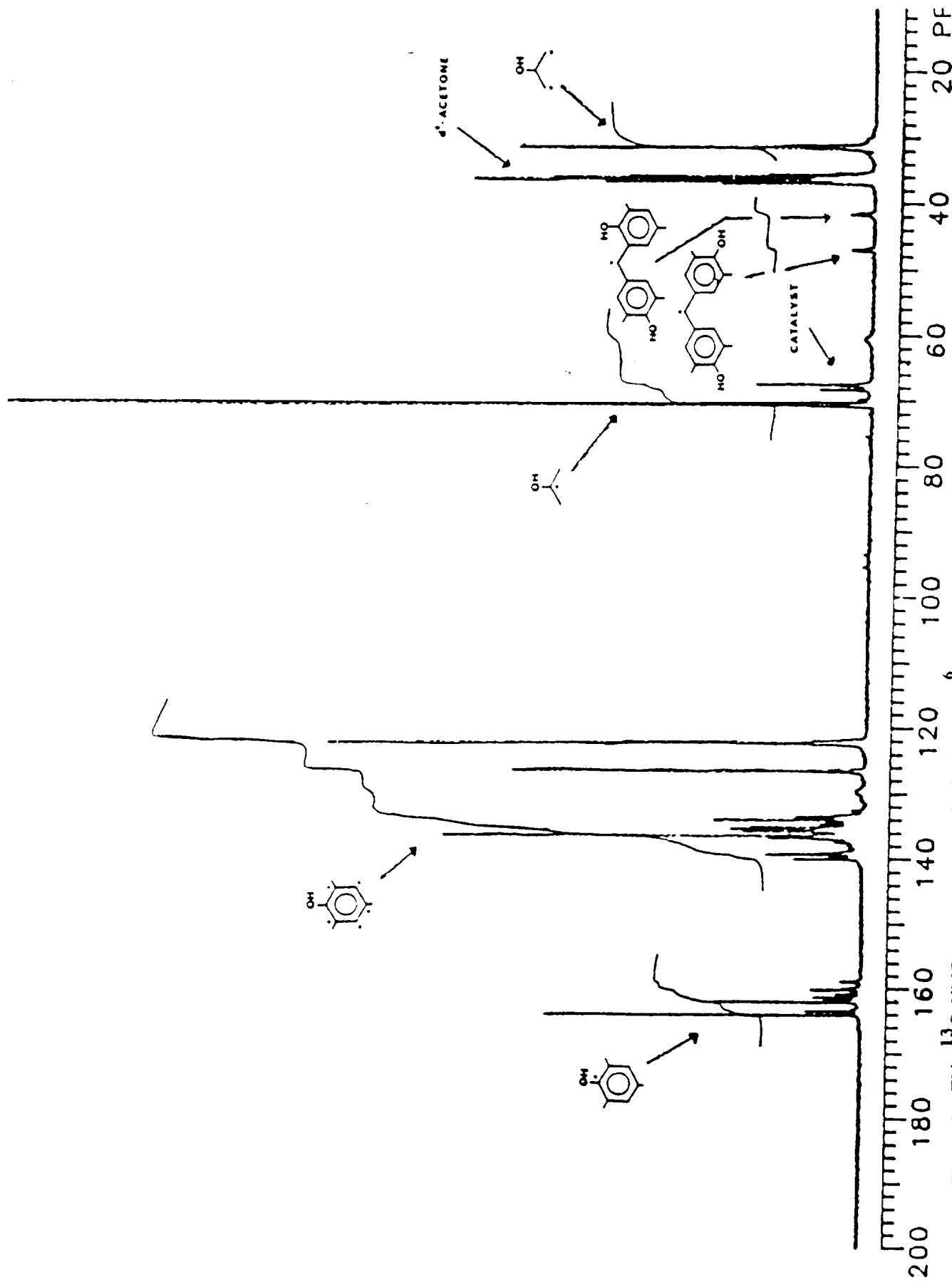


Figure 2. This  $^{13}\text{C}$  NMR spectrum was obtained on a  $\text{d}^6$ -acetone solution of Borden L6J-159 using gated decoupling and a long relaxation time. Assignments are as noted on the spectrum with the observed carbons being marked with dots (•). Most significant to this effort is the good separation and resolution of all significant resonances allowing accurate determination and qualification of species.

## DISTORTIONLESS ENHANCEMENT with PROTON TRANSFER

- DEPT ALLOWS THE DETERMINATION OF DEGREE OF SUBSTITUTION AT A CARBON CENTER. QUATERNARY CARBONS (NO PROTONS ATTACHED) DO NOT APPEAR. METHINES (-CH-), AND METHYLS ( -CH<sub>3</sub>-) APPEAR AS POSITIVE PEAKS, AND METHYLENES (-CH<sub>2</sub>-) ARE NEGATIVE PEAKS.

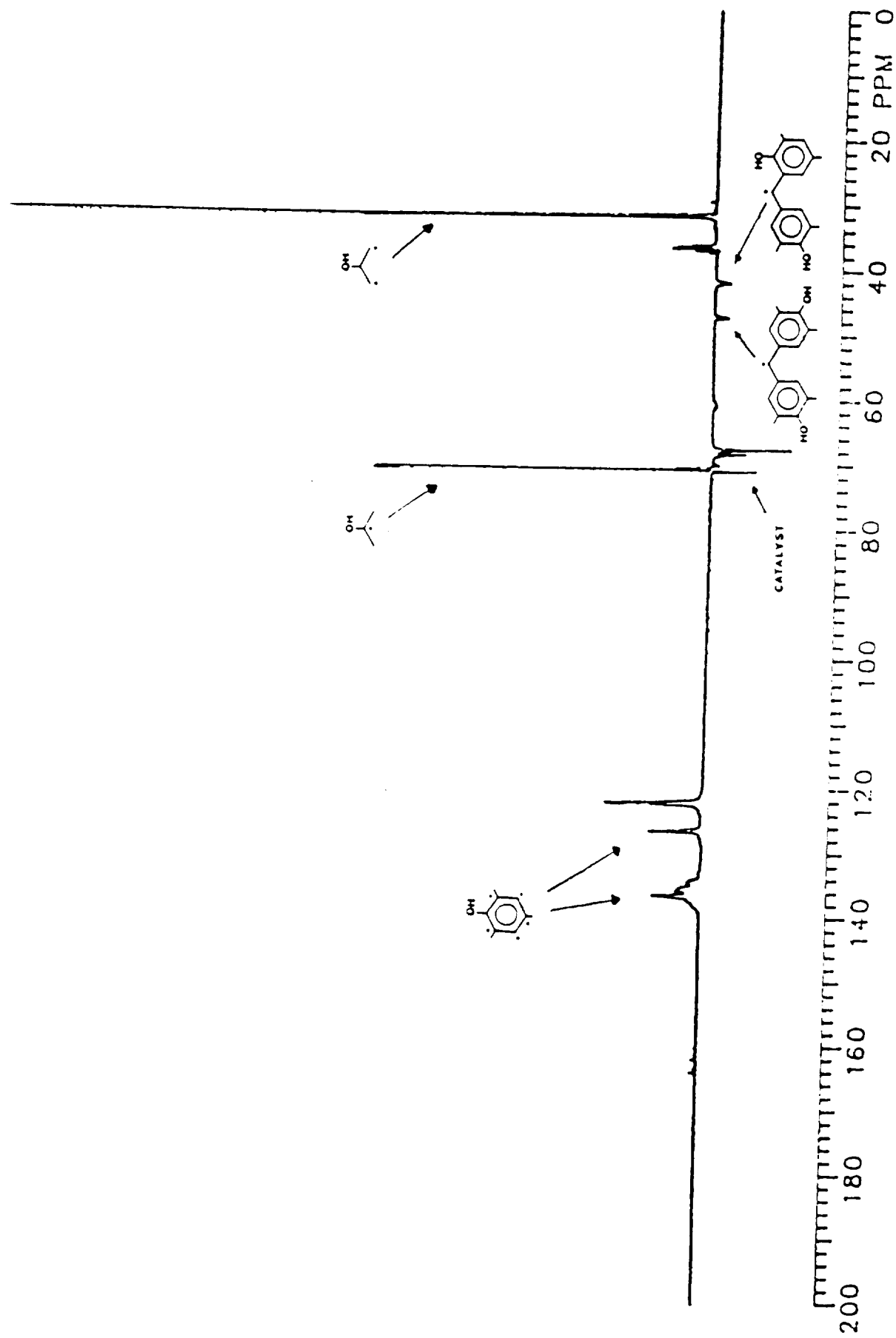


Figure 3. This DEPT (Distortionless Enhancement with Proton Transfer) spectrum was obtained on a  $\text{d}^6$ -acetone solution of Borden L6J-159 using standard parameters. Assignments are as noted on the spectrum with the observed carbons being marked with dots (•). This spectrum should be compared to the standard  $^{13}\text{C}$  NMR shown in figure 2. It should be noted that quaternary carbons are not in this spectrum, methines and methylenes are positive peaks and methylenes are negative peaks.

## QUANTITATIVE AND QUALITATIVE INFORMATION EXPECTED FROM NMR STUDIES:

- BOND LENGTHS
- CHAIN GROWTH AND CROSS-LINKING OF ORTHO- AND PARA- METHYLENE BRIDGES FORMED DURING THE CURE MECHANISM
- EXTENT OF DESOLVATION
- KINETIC INFORMATION - PREVIOUSLY UNABLE TO MEASURE DUE TO NUMEROUS POSITIONAL ISOMERS IN CONDENSATION PROCESS
- STRUCTURE ELUCIDATION AT VIRTUALLY ANY POINT DURING THE CURE PROCESS
- LOT -TO - LOT VARIATIONS - PHENOL/FORMALDEHYDE RATIO, CATALYST, SOLVENT
- DIRECT EXAMINATION OF PRE- AND POST- FIRED MATERIALS - e.g. MICROCRACKING

### **DOWNSIDE:**

- NOT SUITABLE FOR ROUTINE ON-LINE PROCESS CONTROL OR QUALITY ASSURANCE, DUE TO LENGTH OF TIME IN OBTAINING SPECTRA, COST OF EQUIPMENT, AND OPERATOR TRAINING

**APPENDIX G**

**JIM KIRKHART**



**GENCORP  
AEROJET**

**SPIP ADVISORY COMMITTEE**

**CARBON FIBER ELECTRICAL RESISTIVITY TESTING**

**ROUND ROBIN RESULTS**

**16 MAY 1991**

**Jim Kirkhart**

**Aerojet Propulsion Division  
Sacramento, CA**

**Pat Pinoli**

**Lockheed Research and Dev.  
Palo Alto, CA**

**Propulsion Division**

## **TEST OBJECTIVES**

**Determine Variation In Data Analysis Method**

**Determine Variation In Test Methodology**

**Assess Variation Between Test Facilities**



## **TEST FACILITIES**

**BP Chemicals, Fibers and Materials  
(Tested First and Last)**

**Polycarbon**

**Lockheed R & D**

## **TEST PLAN SUMMARY**

**Utilize NARC 23 Carbon Fabric (Special Heat Treatment,  
Roll #70513-2C)**

**Removed 15 Warp Yarns; 1.5 Meter In Length**

**Each Test Facility Used Their Own Standard Test  
Technique To Measure Resistance**

**Resistance Measured At 100 cm and 50 cm Intervals  
(ASRM Test Technique Included as Reference)**

## **VARIATION IN TEST METHODOLOGY**

### **BP Chemical**

**Flat Plate With Copper Pads, One End Taped Down and  
60 gm Clip/Weight On Other End**

### **Polycarbon**

**Yarn Over Copper Pins, With One End Tied and  
60 gm Clip/Weight On Other End**

### **Lockheed**

**Yarn Over Copper Pins, Pulled Tight**

## **VARIATION IN DATA ANALYSIS METHOD**

**ASRM Method, Resistance 100 - 50 cm**

**BP CHEMICALS Method, Resistance of Delta 50 cm**

**AMOCO Method, Resistance of Lowest Delta 50**

**50 cm Direct, Resistance at 50 cm**

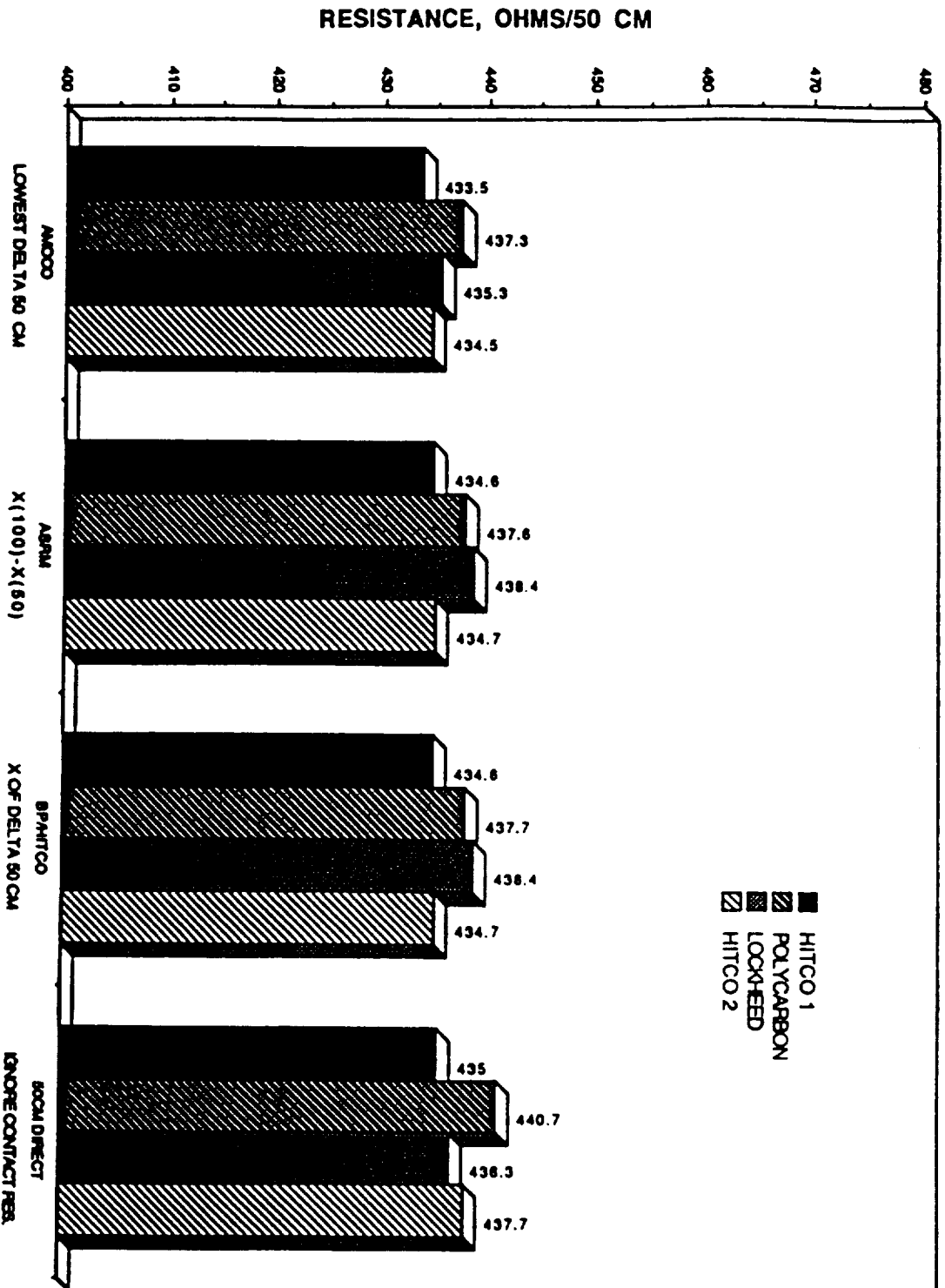
# RAW TEST DATA

SAMPLE #	TEST FACILITY										HITCO 2		
	HITCO 1		POLYCARBON		LOOK-HEAD		100 CM		50 CM		100 CM	50 CM	DELTA OHM
	100 CM	OHM	100 CM	OHM	DELTA OHM	DELTA OHM	OHM	OHM	DELTA OHM	DELTA OHM	OHM	OHM	DELTA OHM
1	858	432	862	433	429	429	866	434	432	432	857	431	426
2	923	456	935	470	465	465	864	433	431	431	931	471	460
3	870	435	878	442	436	436	861	429	432	432	873	439	434
4	851	425	856	431	425	425	859	430	429	429	848	425	423
5	856	429	863	434	429	429	872	436	436	436	856	428	428
6	869	435	879	439	440	440	872	436	436	436	875	438	437
7	895	447	908	455	453	453	852	425	427	427	896	450	446
8	856	427	863	434	429	429	935	454	481	481	856	429	427
9	863	431	871	437	434	434	858	432	426	426	868	433	435
10	893	447	903	454	449	449	870	434	436	436	896	448	448
11	891	446	900	453	447	447	903	449	454	454	895	449	446
12	849	428	860	430	430	430	860	429	431	431	853	427	426
13	863	433	869	436	433	433	854	428	426	426	865	433	432
14	852	428	864	432	432	432	897	449	448	448	858	431	427
15	855	438	864	430	434	434	897	446	451	451	858	433	425

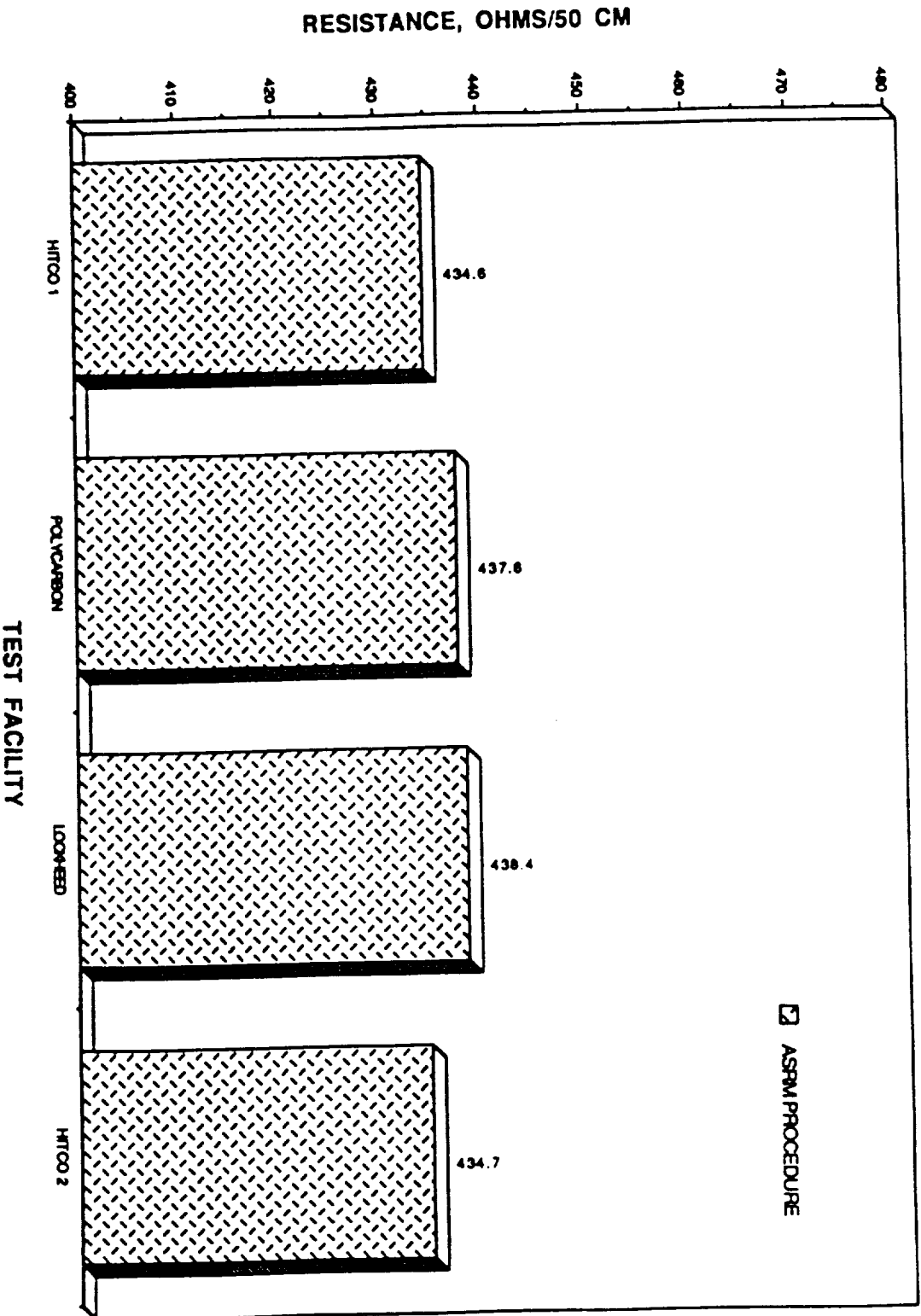
# **DATA ANALYSIS SUMMARY**

	AMOCO PROCEDURE LOWEST DELTA 50 CM RESISTANCE	ASPM PROCEDURE AVG (100)-AVG(50)	BP/HITCO PROCEDURE AVG OF DELTA 50	IGNORE CONTACT RESISTANCE PROCEDURE 50 CM DIRECT
HITCO DATA AVG, OHMS/50 CM STD DEV	433.5 10.5	434.6	434.6 12.1	435 9.5
POLYCARBON DATA AVG, OHMS/50 CM STD DEV	437.3 11.2	437.6	437.7 11.1	440.7 11.9
LOCKHEED DATA AVG, OHMS/50 CM STD DEV	435.3 9.4	438.4	438.4 14.7	436.3 8.9
HITCO DATA 2 AVG, OHMS/50 CM STD DEV	434.5 10.8	434.7	434.7 10.8	437.7 12.2

**ASRM ROUND ROBIN TEST ANALYSIS ON BP/HITCO PREWOVEN FABRIC YARN**  
**VARIATION IN DATA ANALYSIS METHOD**

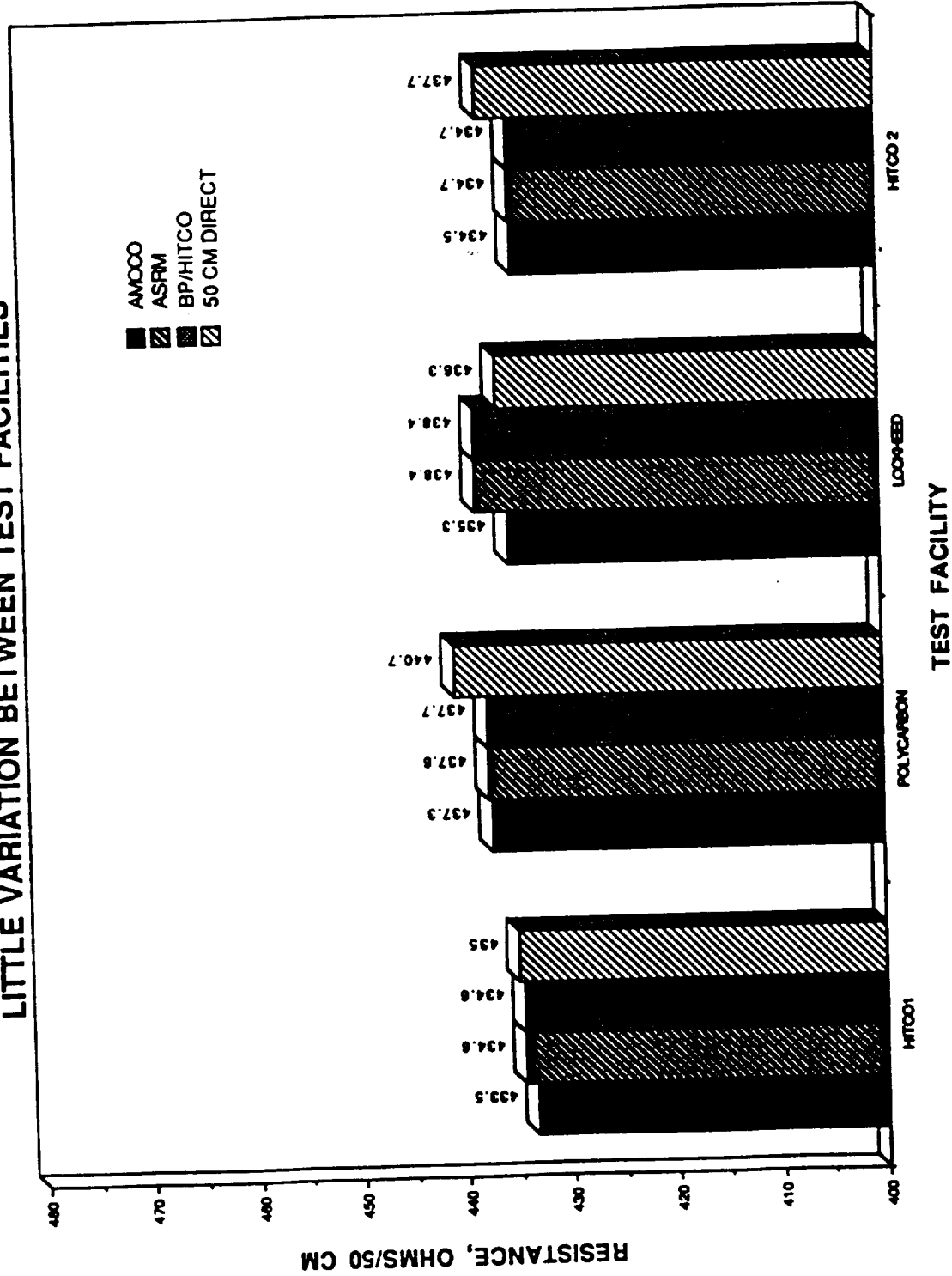


**ASRM ROUND ROBIN ANALYSIS ON BP/HITCO PREWOVEN FABRIC YARN**  
**VARIATION IN TEST METHODOLOGY**





# ASRM ROUND ROBIN TEST ANALYSIS ON BP/HITCO PREWOVEN FABRIC YARN - LITTLE VARIATION BETWEEN TEST FACILITIES



## **SUMMARY AND CONCLUSIONS**

**Very Little Variation Exists That Can be Related to:**

**Test Facility**

**Test Technique**

**Data Analysis Method**

**Recommend Using ASRM-Y2 "Carbon Fabric and Yarn Electrical Resistivity, Yield and Density" as Industry Syandard**

TEST METHOD NO. ASRM-Y2 REV. N/A DATE 01 FEB. 1991

SUBJECT: CARBON FABRIC AND YARN ELECTRICAL RESISTIVITY, YIELD AND DENSITY

## 1.0 SCOPE

This test method is a technique to measure the electrical resistivity yield and density of unsized carbon fiber.

## 2.0 EQUIPMENT AND MATERIALS

- 2.1 Ohm meter calibrated to read resistance to  $\pm 0.1$  ohm.
- 2.2 Fixed copper rods (1/4" diameter) set at 50 cm and 100 cm distance. Polish rods with 600 grit paper prior to measurement.

## 3.0 PROCEDURE

### 3.1 Resistance Measurement

- 3.1.1 Cut 5 yarn tows approximately 1 1/2 meter length each. For fabric extract 5 each warp yarn tows for measurement.
- 3.1.2 Measure resistance of each tow specimen individually at 100 cm and again at 50 cm.
- 3.1.3 Determine x resistance for 100 cm and 50 cm.
- 3.1.4 Subtract 50 cm x value from 100 cm x value to establish resistance for 50 cm w/o contact resistance.
- 3.1.5 Record resistance as ohms/cm.

### 3.2 Yarn Yield (unsized)

- 3.2.1 Measure length of each specimen, to the nearest 0.1 cm, 5 total, and coil each specimen into one tared aluminum dish.
- 3.2.2 Vacuum dry specimens for 2-16 hours at  $105^{\circ} \pm 5^{\circ}$  C.
- 3.2.3 Remove specimens quickly from vacuum oven and weigh to nearest 0.1 mg.
- 3.2.4 Record yield as mg/cm.

### 3.3 Yarn Density (Unsize)

- 3.3.1 Vacuum dry fiber for 2-16 hours prior to density measurement. Weigh to the nearest 0.1 mg (A).
- 3.3.2 Place the coiled sample in a 50 ml beaker containing 0-dichlorobenzene, ultrasonic for  $5 \pm 1$  minutes to remove trapped air from specimen. Remove sample and place in large beaker of 0-dichlorobenzene located under the analytical balance (See Density Apparatus, Figure 1). Shake the sample vigorously to completely wet sample and remove entrapped air. Place it on the lower (immersed) weighing pan of the balance and weigh to nearest 0.1 mg. Record as "B".
- 3.3.3 Read the liquid specific gravity from hydrometer immersed in the 0-dichlorobenzene and record as "L".
- 3.3.4 Record yarn density, gm/cc.

## 4.0 CALCULATION

### 4.1 Yarn Yield

$$\text{Yarn Yield} = \frac{\text{Dried Fiber Wt.}}{\text{Total Specimen Lengths}}$$

### 4.2 Yarn Density

$$\text{Yarn Density, g/cm}^3 = \frac{L \times A}{C}$$

where:

- A = Dry weight of yarn  
 B = Wet weight of yarn  
 C = Weight difference between dry and wet yarn  
 L = Liquid specific gravity

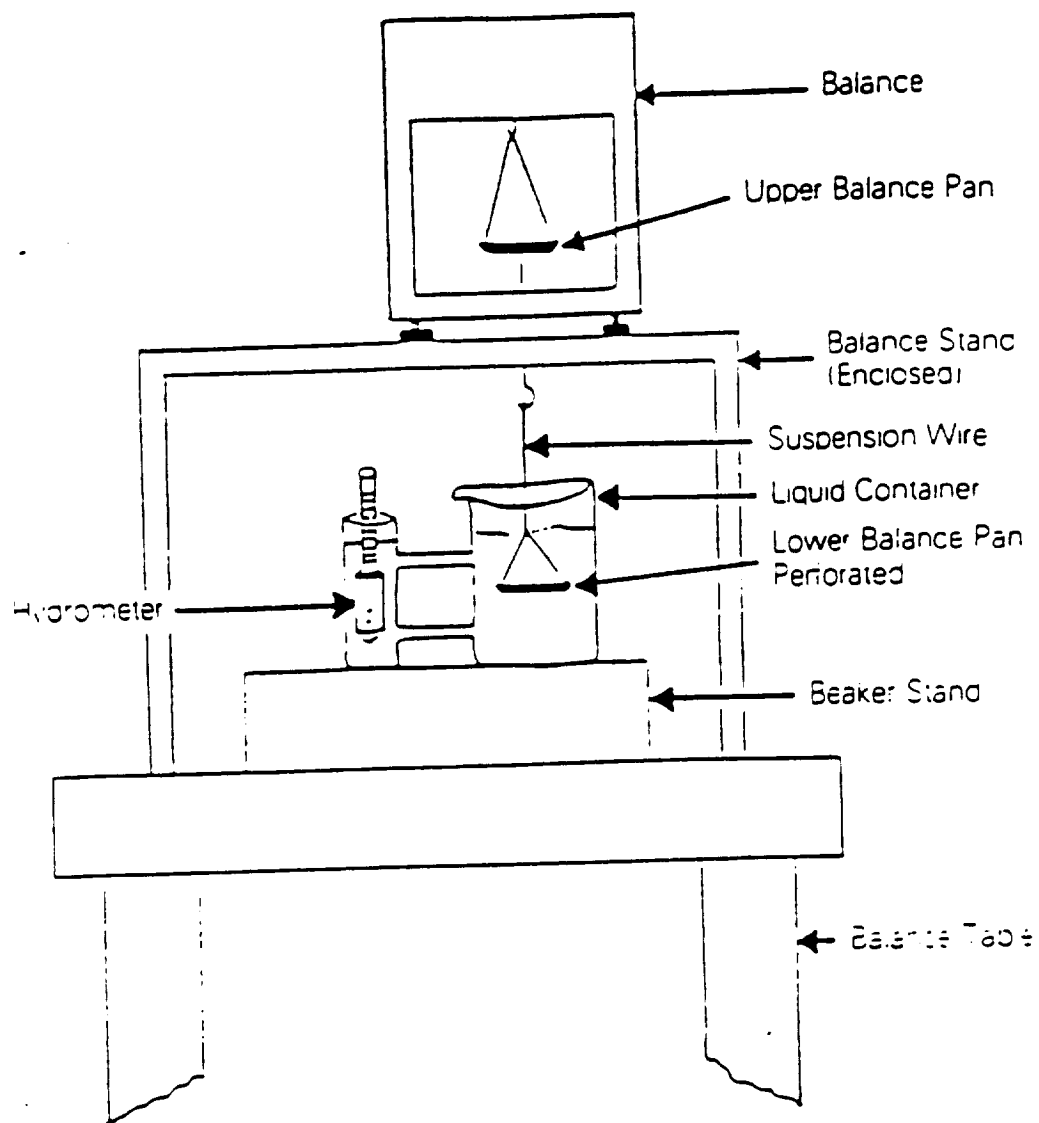
### 4.3 Electrical Resistivity

$$\text{Electrical Resistivity } (\mu\Omega \times M) = \frac{\text{Resistance (ohm/cm} \times \text{Yield (ohm/cm)} \times 10^4}{\text{Fiber Density (g/cm}^3)}$$

## 5.0 REPORTING

Report individual values and average.

Figure 1





## **APPENDIX H**

**JACK WILLIAMSON**





**SPIP ACTIVITY**

**PRODUCT IDENTIFICATION CODE**

**Presented to**

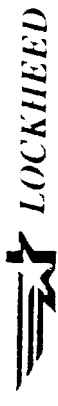
**The Industry Advisory Committee for  
Carbon Phenolic Constituent Test Methodology**

**Amoco R&D Center  
Alpharetta, Georgia  
May 16, 1991**

**Jack Williamson  
Consultant**



## PRODUCT IDENTIFICATION CODE



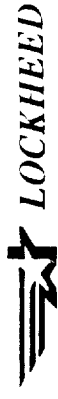
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### BACKGROUND

NASA/MSFC has expressed/concern with regards to inadequate identification codes employed by aerospace suppliers. Potential differences in products are not traceable by routine product code changes.



## PRODUCT IDENTIFICATION CODE



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### SPIP TASK APPROACH

- Held open forum on issue at the November, 1990 meeting at NARC
- Presented comprehensive SPIP code outlines for carbon fabric and prepreg
- Executive committee reviewed SPIP code outlines and recommends:
  - The entire committee review all potential product changes which should be traceable by product code change.
  - Vote on all issues to develop a consensus.
  - The executive committee prepare a letter to NASA/MSFC and the suppliers to reference the committee conclusions.

**SPIP - Nozzle Initiative Advisory Committee on  
Standardization of Carbon-Phenolic  
Constituent Test Methodology**

**Advisory Committee Ballot  
May 16, 1991**

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(Check those changes which should initiate a product code change)

**Carbon Yarn/Fabric Code**

- ☐ Fiber Precursor (PAN, Rayon, etc.)
- ☐ Precursor Source
- ☐ Heat Treatment Temperature
- ☐ Postwoven/Prewoven
- ☐ Fabric Weave
- ☐ Filament Count
- ☐ Yarn Construction
- ☐ None of the Above
- ☐ Other Attributes

**Pre-Preg Code**

- ☐ Fiber Precursor (PAN, Rayon, etc.)
- ☐ Fabric Postwoven/Prewoven
- ☐ Fabric Manufacturer
- ☐ Fabric/Yarn Heat Treatment
- ☐ Resin Manufacturer
- ☐ Resin Specification
- ☐ Filler Manufacturer
- ☐ Filler Specifications
- ☐ Resin Filler Level
- ☐ Impregnation Method
- ☐ (Solvent/Hot Melt)
- ☐ None of the Above
- ☐ Other Attributes

This vote represents a:

- Product Supplier ☐
- Product User ☐
- Product Designer ☐

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- ☒ Yarn Construction
- ☐ None of the Above
- ☒ Other Attributes
  - SIZING
  - CONTINUOUS VS. SPUN
  - DENIER

UNTIL WE KNOW WHICH INDEPENDENT  
VARIABLES AFFECT THE CURED  
COMPOSITE AND HOW THEY AFFECT  
THE MATERIAL WE NEED TO  
MONITOR AS MANY OF THESE  
VARIABLES AS POSSIBLE

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- ☒ Fabric Postwoven/Prewoven
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- ☒ Resin Manufacturer
- ☒ Resin Specification
- ☒ Filler Manufacturer
- ☒ Filler Specifications
- ☒ Resin Filler Level
- ☒ Impregnation Method
- ☒ (Solvent/Hot Melt)
- ☐ None of the Above
- ☒ Other Attributes
  - VOLATILES
  - FLOW

This vote represents a:

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- Product Designer ☒

*All Future Product Codes should  
be unique to a specific MTH!*

**SPIP - Nozzle Initiative Advisory Committee on  
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- ☐ Filament Count
- ☐ Yarn Construction
- ☐ None of the Above
- ☒ Other Attributes
- ☒ Thickness

OTHER  
LOT NO.

KEEP IT AS IS

**Pre-Preg Code**

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- ☒ Fabric Manufacturer
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- ☐ Filler Manufacturer
- ☒ Filler Specifications
- ☒ Resin Filler Level
- ☐ Impregnation Method
- ☐ (Solvent/Hot Melt)
- ☐ None of the Above
- ☒ Other Attributes
- ☒ Cured Thickness

- ☒ Vol %
- ☒ Flow
- ☒ Resin Content

This vote represents a:

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- Product Designer ☒

OTHER  
LOT NO.



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This vote represents a:

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- Product Designer ☐

*Supplier of weaving.  
Prepreg definition much better  
left to Prepregger.*

*[Signature]*

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*Sizing*

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- ☒ Other Attributes

*Pre preg Spec.  
Straight/Bias*

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- Product Designer ☐

*WOULD LIKE TO SEE A CODE TO PROVIDE ALL THE ABOVE  
INFORMATION. IN RECOGNITION OF THE RELUCTANCE TO  
USE OVERLY LONG CODES, A GOOD COMPROMISE WOULD  
BE TO ADD A THREE LETTER CODE TO SPECIFY THE RESIN,  
THE FIBER, AND THE FILLER MATERIALS. THE RELEASE OF  
THE "GRADE CODE" INFORMATION FROM B/P CHEMICAL AND  
FIBERITE TO THE COMMUNITY SHOULD ALSO HELP IN UNDERSTANDING  
THE MATERIAL DESIGNATIONS.*

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- ☐ None of the Above
- ☒ Other Attributes

ABSTRACT

This vote represents a:

- Product Supplier ☒
- Product User ☐
- Product Designer ☐

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# **SPIP - Nozzle Initiative Advisory Committee on Standardization of Carbon-Phenolic Constituent Test Methodology**

**Advisory Committee Ballot  
May 16, 1991**

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- ☒ Fabric/Yarn Heat Treatment
- ☒ Resin Manufacturer
- ☐ Resin Specification *should not*
- ☒ Filler Manufacturer
- ☐ Filler Specifications *should not*
- ☒ Resin Filler Level
- ☒ Impregnation Method
- ☒ (Solvent/Hot Melt)
- ☐ None of the Above
- ☐ Other Attributes

This vote represents a:

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**ORIGINAL PAGE IS  
OF POOR QUALITY**

# SPIP - Nozzle Initiative Advisory Committee on Standardization of Carbon-Phenolic Constituent Test Methodology

Advisory Committee Ballot  
May 16, 1991

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ORIGINAL PAGE IS  
OF POOR QUALITY

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- Product User ☐
- Product Designer ☐

*I am a member of the*

*Ballot = question how far I, as a member, want to go in changing the numbering system. The first number will be the number of the question and the second the answer.*





**APPENDIX I**

**KENNETH DEVANE**



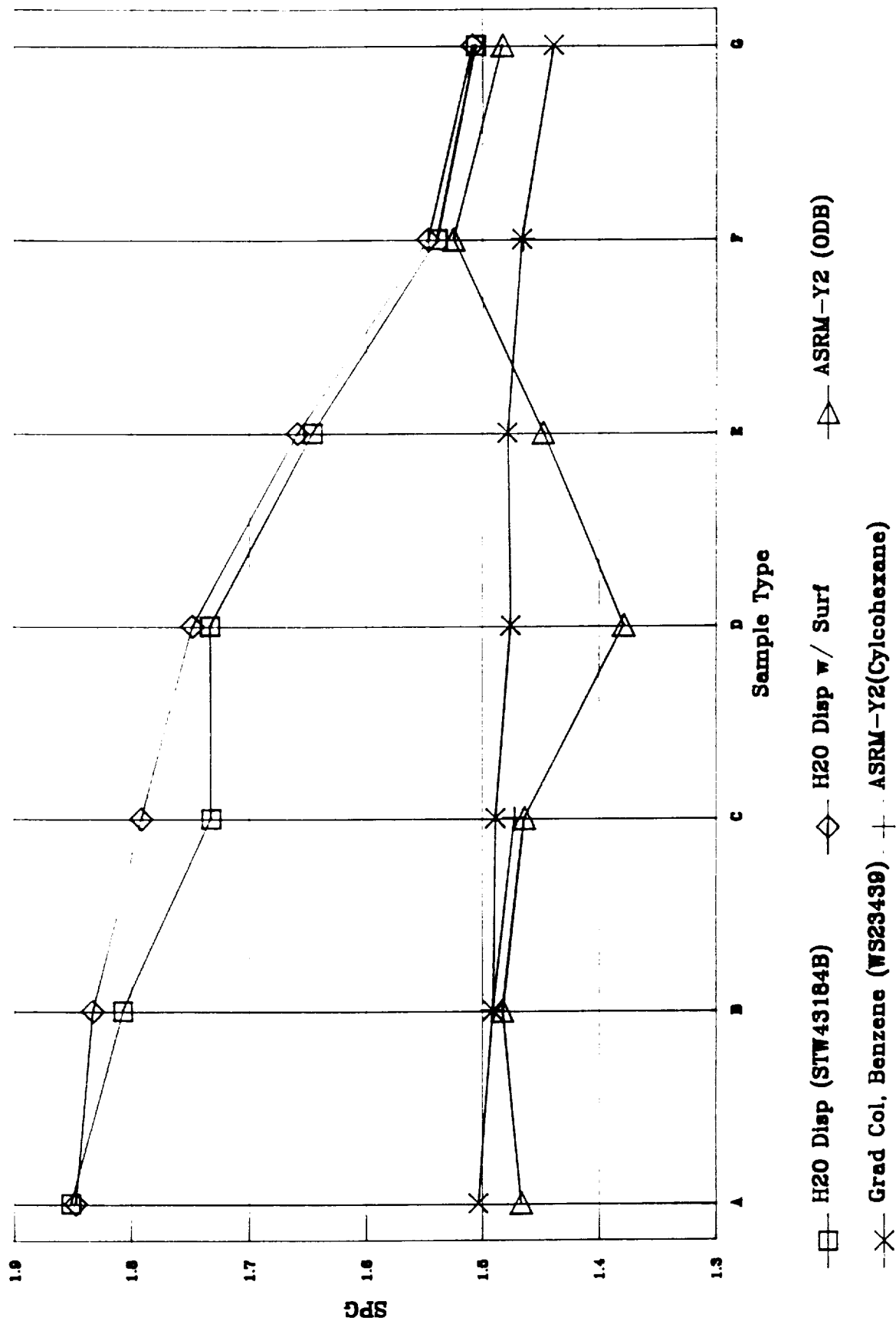
**KENNETH A. DE VANE**  
**BP CHEMICALS (Hitco) Inc.**

**ADVANCED MATERIALS DIVISION**  
**FIBERS AND MATERIALS**  
**GARDENA, CALIFORNIA**

**PRESENTED AT THE**  
**SPIP INDUSTRIAL ADVISORY COMMITTEE**  
**ON**  
**STANDARDIZATION OF CARBON-PHENOLIC**  
**TEST METHODS AND SPECIFICATIONS**

# Density Method Comparison

BPCHI Fibers & Materials - Gardena



## **DENSITY MEASUREMENT**

- **7 FABRIC TYPES**

- **5 MEASUREMENTS**

- **GRADIENT COLUMN - BENZENE**
- **DISPLACEMENT - WATER**  
**WATER W/SURF.**  
**ODB**  
**CYCLOHEXANE**  
**(WILL DO HEXANE)**

## **CONCERNS**

- **TECHNIQUE** - **DEGAS...**
- **SAFETY** - **SOLVENT-TOXIC...**  
**FIRE...**
- **SOLVENT DISPOSAL**

**DO WE NEED THIS?**

**I.E. SOLVENT BASED DENSITY  
ARE OTHER TESTS ADEQUATE?**

**IF YES → REDUCED FREQUENCY**

## SOLVENTS

	<u>TLV<sup>1</sup> ppm</u>	<u>FIRE</u>	<u>ENTRY ROUTE</u>
ODB	50	"MODERATE"	SKIN-RESPIRATORY
CYCLOHEXANE	300	"DANGEROUS"	RESPIRATORY
HEXANE	50	"DANGEROUS"	RESPIRATORY
BENZENE	10 (1?)	DANGEROUS	-





## **APPENDIX J**

### **EDWARD MILLS**



**SPIP ACTIVITY**

**PRODUCT IDENTIFICATION CODE**

**Presented to**

**The Industry Advisory Committee for  
Carbon Phenolic Constituent Test Methodology**

**Amoco R&D Center  
Alpharetta, Georgia  
May 16, 1991**

**Edward Mills  
UT/CSD Materials**

## **Argument for Establishment of a Standard Carbon / Graphite Phenolic Grade Coding System**

### **To Support Design, Analysis, and R&D thru Material Test / Database Identification**

- Allows Cataloging of Test Results (SRI etc.) and Establishment of Industry Database
- Allows Extrapolation of Existing Test Database for similar Materials
- Allows Educated Selection of Firing Temperatures, Weave Forms, Resin systems, etc.

### **To Facilitate Purchasing and Eliminate Unapproved Substitution or Changes**

- Allows Configuration Management of Critical Features
  - Most Nozzle Applications have "No Changes ... after Qualification" clauses
  - Variants include Cloth Type, Fillers, Resin System Modifications
  - Example of potential problem: MX4926 may be either VCK or CSA Carbon Cloth
    - VCK is Intermediate Fired 5 Harness Satin 1100d
    - CSA is Low fired 8 Harness Satin 1650d
- Allows Procurement and Inventory by standard Computer Programs (CULLINET etc.)
  - Keep code under 15 Alpha Numeric digits total including any prefix
  - Maintain Certification to Existing Specs with maximum Cross-certification

## **Critical Parameters for Carbon and Graphite Phenolic Prepreg Coding**

### **Basic Nomenclature**

Graphite, Carbon, Low Density Carbon, etc.

### **Cloth Parameters**

#### **Firing Temperature**

Low ( $\approx 1200^{\circ}\text{C}$ ), Med ( $\approx 1500^{\circ}\text{C}$ ), High ( $\approx 2500^{\circ}\text{C}$ ), Other (Proprietary)

#### **Weave Type**

Standard (Woven as Rayon then Heat Treated), Woven Post Heat Treat, other

#### **Weaver**

Highland, Miliken, etc.

#### **Weave Description**

3 Ply Plain, 2 Ply 5 Harness Satin, 1 Ply 8 Harness Satin, etc.

#### **Yarn**

Avtex 1650d, Avtex 1100d, NAR 1650d, NAR 1100d, other

### **Manufacturer of Prepreg**

BP Chemicals, Fiberite, etc.

### **Resin System**

Monsanto SC1008, Borden SC1008, 91LD, other (Proprietary), etc.

### **Resin Application**

Wet resin, film, etc

### **Fillers**

Various (may use Specific Designation in lieu of Proprietary description)

### **Form**

Broadgoods, Bias Tape, Straight Tape

### **Width (*for Procurement / Logistics only*)**

Broadgoods Width or Tape Roll Widths

# Typical Carbon and Graphite Phenolic Materials Qualified for CSD Applications

## Carbon Phenolic

MX4926	VCK	Bias Tape	Titan 4 IUS I-VI	SE0116 Prepreg SE0858 Prepreg SM1132 Prepreg	SE0091 Cloth SE0965 Cloth SM1135 Cloth
MX4926	VCK	Straight Tape	IUS I-VI	SE0858 Prepreg SM1132 Prepreg	SE0965 Cloth SM1135 Cloth
MX4926		Bias Tape	D5 Mk111 Aegis MM-III Other	WS23447 Prepreg JCM13152 Prepreg L6520496 Prepreg AGC34306 Prepreg SE1403 Prepreg	WS23444 Cloth No Separate Cloth Spec No Separate Cloth Spec No Separate Cloth Spec SE1401 Cloth
MX4926		Straight Tape	D5 Mk111 Aegis MM-III Other	WS23447 Prepreg JCM13152 Prepreg L6520496 Prepreg AGC34306 Prepreg SE1403 Prepreg	WS23444 Cloth No Separate Cloth Spec No Separate Cloth Spec No Separate Cloth Spec SE1401 Cloth
MX4926LD		Straight Tape	D5 Other	WS23446 Prepreg SE1410 Prepreg	WS23444 Cloth SE1401 Cloth

## Typical Carbon and Graphite Phenolic Materials Qualified for CSD Applications

### Carbon Phenolic

FM5055	Bias Tape	D5	WS23447 Prepreg	WS23444 Cloth
		IUS	SE0858 Prepreg	SE0965 Cloth
		I-VI	SM1132 Prepreg	SM1135 Cloth
		Mk111	JCM13152 Prepreg	No Separate Cloth Spec
		Aegis	L6520496 Prepreg	No Separate Cloth Spec
		MM-III	AGC34306 Prepreg	No Separate Cloth Spec
		Other	SE1403 Prepreg	SE1401 Cloth
			WS23447 Prepreg	WS23444 Cloth
			SE0858 Prepreg	SE0965 Cloth
			SM1132 Prepreg	SM1135 Cloth
FM5055	Straight Tape	D5	JCM13152 Prepreg	No Separate Cloth Spec
		IUS	L6520496 Prepreg	No Separate Cloth Spec
		I-VI	AGC34306 Prepreg	No Separate Cloth Spec
		Mk111	SE1403 Prepreg	SE1401 Cloth
		Aegis	WS23447 Prepreg	WS23444 Cloth
		MM-III	SE0858 Prepreg	SE0965 Cloth
		Other	SM1132 Prepreg	SM1135 Cloth
			JCM13152 Prepreg	No Separate Cloth Spec
			L6520496 Prepreg	No Separate Cloth Spec
			AGC34306 Prepreg	No Separate Cloth Spec
FM5055LD	Straight Tape	D5	SE1403 Prepreg	SE1401 Cloth
		Other	WS23446 Prepreg	WS23444 Cloth
			SE1410 Prepreg	SE1401 Cloth

## Typical Carbon and Graphite Phenolic Materials Qualified for CSD Applications

### Graphite Phenolic

FM5014	Broadgoods	Titan 4	4MDS40721 Prepreg	4MDS40752 Cloth
FM5014	Straight Tape	Titan 4	4MDS40721 Prepreg	4MDS40752 Cloth
FM5064	Broadgoods	IUS	SE0999 Prepreg	SE0998 Cloth
FM5064	Bias Tape	I-VI	SM1138 Prepreg	SM1137 Cloth
FM5064	Straight Tape	IUS	SE0999 Prepreg	SE0998 Cloth
FM5064		I-VI	SM1138 Prepreg	SM1137 Cloth
FM5064		IUS	SE0999 Prepreg	SE0998 Cloth
FM5064		I-VI	SM1138 Prepreg	SM1137 Cloth



