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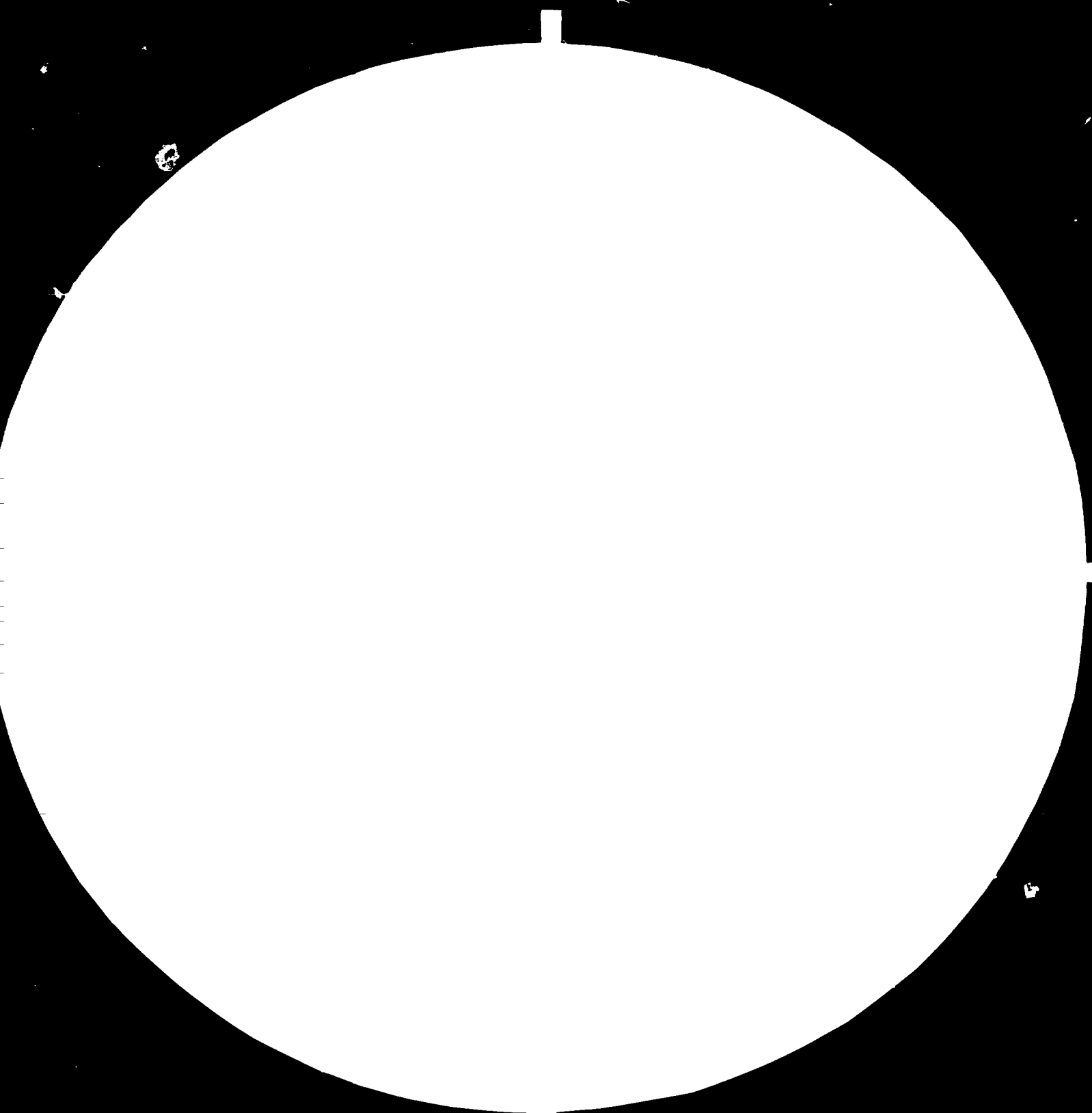

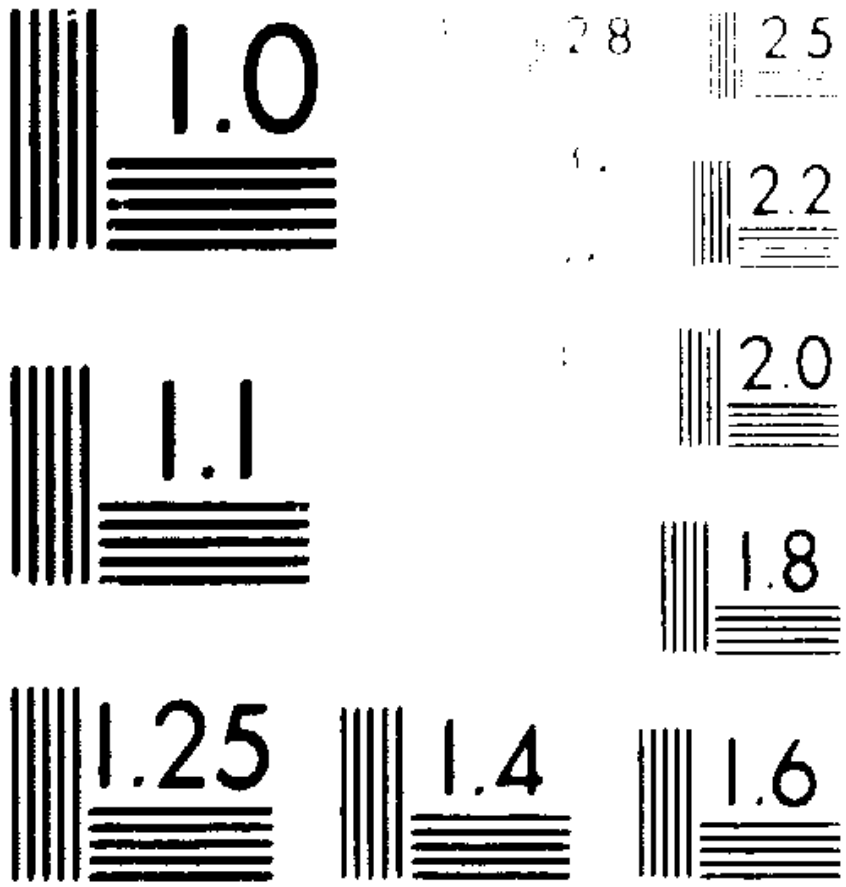
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Durmersheim, 21.August 1982

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REPORT OF MY ACTIVITIES AS UNIDO-CONSULTANT IN THE

CARBON FIBRE PROJECT IN SAO JOSE DOS CAMPOS, BRAZIL

ST/BRA/81/001/11-63/32.1.H

Duration: Three months; from 6.May to 5.August

Activities in general

My activities as UNIDO-expert in the carbon fibre project in Brazil from the 6.May 1982 to the 5.August 1982 are mainly covered by the following items:

a. Introduction of analytical methods for the characterization of PAN-precursor fibres, oxidized PAN-fibres and carbon fibres as well as for the study of the progress of the stabilization and carbonization reactions during the manufacture of carbon fibres from PAN.

b. Stabilization and carbonization experiments of PAN-fibres from COURTAULDS (S.A.F.) with variation of process parameters in order to improve the properties of the resulting carbon fibres.

c. Stimulation of basic research work in the carbon fibre field including the modification of initial PAN-fibres by chemical treatment.

d. Teaching the brazilian staff in the understanding of the basic chemical and physical changes during the processing of C-fibres from PAN.

Detailed description of my activities

Item a

Differential thermal analysis (DTA)

The techniques and evaluation of data from DTA-experiments with initial PAN-fibres and oxidized PAN-fibres have been teached, using the new DTA-equipment, purchased by the UNIDO. By the results from experiments with linear heating rate it was possible to explain the different thermal behaviour of PAN according to a different chemical composition of the tested polymer samples.

By performing systematic isothermal DTA-experiments between 220 and 270°C using PAN-samples with different comonomers and different atmospheres (air, nitrogen) and evaluation of the kinetic data for the cyclization and the oxidation of PAN

the influence of the comonomers (e.g. in case of itaconic acid as comonomer an accelerating effect on the cyclization and oxidation rates) could be shown to the brazilian staff.
Furthermore I have shown to the brazilian staff how to measure quantitatively the progress of the cyclization in the different zones of the continuous oxidation furnace by performing DTA-experiments with linear heating rate with fibre samples collected from each zone of the furnace.
I have trained the engineer Arnaldo, since April in the brazilian team, in all details of the experimental DTA-techniques as well as in the interpretation of the DTA-results.

Infrared spectroscopy (IR)

Two techniques for the sample preparation have been introduced. The spectra were obtained from a Perkin-Elmer spectrometer, which is located in the chemical department of the ITA, but can be used by the carbon fibre team without limitations.
By dissolving PAN-fibres in a suitable solvent and reprecipitating the polymer as a film it is possible to get IR-spectra with good resolution and high reproducibility. This is a precondition for the evaluation of quantitative data from the spectra.
I have teached the brazilian staff (Eng. Arnaldo, Eng. Simionato) to use this technique for the quantitative determination of the comonomer content after calibration with samples of known comonomer content.
I have shown furthermore how the IR-spectra, received from oxidized PAN-fibres and prepared as KBr-disks, can be interpreted with respect to the progress of the cyclization of PAN by comparing the extinction of characteristic groups in the spectrum of untreated PAN with the spectra of PAN-samples, heattreated at different temperatures and different times.

Method for the measurement of the fibre density

A sink-float method for the density measurement of fibres was introduced by me. By this very simple and quick method it is possible to measure the density of initial PAN-fibres, of oxidized fibres as well as of C-fibres. In combination with the measured weight of a certain length of a fibre sample it is possible to calculate the average cross-section of the fibres.

The increase of the fibre density of oxidized PAN-fibres with stabilization time and temperature gives usefull qualitative and quantitative informations on the stabilization reactions. The results of the density measurements of the fibres in the different stages of the C-fibre processing were discussed intensively with the brazilian team with respect to the optimization of the process and theproperties of the resulting C-fibres.

Item b

Stabilization experiments

The stabilization parameters for the COURTAULDS-fibre, used by the brazilian team, have been 220°C for 3 hours at an overall elongation of the fibres of 6%. No variations of these parameters have been done in this continuous one step experiments before my arrival in Brazil. In order to find optimized stabilization parameters for the future two step or three step stabilization in the pilot plant, the brazilian team started under my advice systematic stabilization experiments with varied stabilization temperatures and times, also in two step experiments, where the first step was a stretching step at temperatures between 150 and 220°C, and the second step was a stabilization (oxidation) step at 220°C and higher temperatures (isothermal and programmed temperature profile) for different times.

All fibres resulting from the experiments already performed during my stay have been analysed by means of the analytical methods, described in Item a of this report. The results of the experiments have been discussed with the brazilian team (Eng. Simionato, Eng. da Silva, Eng. Arnaldo). The properties of C-fibres resulting from the oxidized PAN-fibres of these experiments have been compared with earlier results. The tensile strength of the C-fibres was in nearly all cases higher than before. Especially by the introduction of the stretching step (up to 45% elongation) the tensile strength of the C-fibres could be improved up to about 50% (highest tensile strength 3.1 GPa). An optimal stretching temperature of 190°C was found.

The experiments could not be finished during my stay because of the great number of variations necessary for an optimization of all parameters. But the results showed already the direction for the further experiments, which will be done by the brazilian team after my leave.
The experiments were accompanied by discussions about the basic changes caused by the variations of the parameters in order to teach the brazilian team to perform similar optimization studies with other fibres than the exclusively used COURTAULDS-fibre.

Carbonization experiments

Before my arrival in Brazil, it was already known to me, that the brazilian team used a carbonization temperature of 1000°C. With respect to a maximum tensile strength of C-fibres, a heat treatment to higher temperatures is necessary. To find out the optimum heat treatment temperature (HTT) and to show to the brazilian team the increase of the Youngs modulus with increasing HTT, I have initiated systematic discontinuous heat treatments between 1000 and 2500°C with C-fibres, continuously carbonized up to 1000°C (COURTAULDS-fibres, stabilized 220°C, 3 h, 6% elong; carbonization with 7% shrinkage). Similar earlier experiments failed because of a contamination fo the purge gas in the graphitization furnace. By a carefull oxygen and moisture removement and, more important, by a change in the purge gas flow direction inside of the furnace these problems could be solved.
Maximum tensile strength of at about 2.6 GPa was found between 1200 and 1400°C (1000°C: 2.1 GPa), the Youngs modulus increased linearly from 165 GPa at 1000°C to 280 GPa at 2500°C. The carbon fibre yield after the heat treatment was between 55 and 50%, depending on the HTT.

Item c

Because I have found, that there exist severe lacks in the basic understanding of the chemical and physical changes in the fibres during the processing of C-fibres from PAN, I have initiated some small research programmes, which can help to improve the knowledge of the brazilian team.

One of these programmes consists of the modification of initial PAN-fibres by a treatment in nitric acid. The first experiments have already shown, that the rate constant of the cyclization can be increased considerably (e.g. 50% for PAN-fibres, treated for 1 hour in boiling nitric acid, 10%). The experimental work consists of the treatment of different PAN-fibre types for different times in nitric acid of various concentrations, IR- and elemental analysis of the modified fibres, DTA-experiments with the treated fibres (evaluation of stabilization kinetics), isothermal stabilization experiments and subsequently carbonization and testing of the resulting carbon fibres. The experimental part of this program will be done mainly by Eng. Arnaldo, because he is already common with various analytical techniques to be used in this work.

Item d

After my arrival in Brazil, I didn't see a chance to teach the brazilian team by giving some lectures or seminars because of the limited knowledge of the English language of the team members.
I found a better way to improve the theoretical knowledge by discussing intensively the different theoretical aspects of the carbon fibre manufacture using the experiments performed during my stay as a starting point. This discussions covered a relatively long time of my daily work, but were successfull because the language problems could be overcome in this way.

Comments and recommendations

My general impression of the carbon fibre project is, that it will be possible for the brazilian team with the help of UNIDO-exports, to produce carbon fibres with properties comparable to those of commercial C-fibres. This is the case, if the COURTAULDS-fibre (S.A.F.) is used, which is a fibre especially for the manufacture of C-fibre.
But I see problems, if brazilian PAN-fibres, which are still to develop, are used as procursor material. Only with a good basic knowledge it will be possible to find out the suitability of new fibre types. Therefore I recommend strongly, to bring

the knowledge of the brazilian in the near future on a higher level. Otherwise also the work of Dr. Nagabushnam can fail, because a succes of his work depends strongly on carefull and completo experimental stabilization and carbonization work in the carbon fibre group with the PAN-fibres developed by him.