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OPTIMIZATION AND DEVELOPMENT OF CARBON FIBRES TECHNOLOGY

ST/BRA/81/T01

BRAZIL

Terminal Report *

Prepared for the Government of Brazil
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Financing System for
Science and Technology for Development

Based on the work of Mr. J. Renato
National Project Leader

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United Nations Industrial Development Organization
Vienna

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1. OBJECTIVE OF THE PROJECT

The main objectives of the project were to complete the adaptation and development of the technology to produce carbon fibres using national raw materials in Brazil and to complete the formation of a team that could help further improve this technology or do developmental work related to other structural fibres and their products. That team would then have the capacity to start work at laboratory scale, continue to pilot scale and finish with the technology introduced in the industrial system.

The project was planned for a duration of 36 months and was extended to five years during project life.

2. THE "CENTRO TECNICO AEROESPACIAL" (CTA) - THE BRAZILIAN COUNTERPART

CTA was the Brazilian counterpart organization which carried out the project work. It had functions reaching from development work at laboratory scale, through pilot scale, to the final introduction of the process of production in the industrial sector of the country.

CTA started a national programme in 1976 at laboratory scale with the aim of developing competence and technology in the area of carbon fibres. At the end of nearly four years' work, considerable progress had been achieved.

However, despite the efforts made before 1982, it was not possible at that time to produce an appropriate fibre for industrial use. There were problems with availability of suitable precursors. The quality of the resulting carbon fibre could not be systematically assured. Furthermore, there were problems with surface treatment.

Further training and the help of external assistance were needed to complete the work up to the development of the process at industrial scale for the production of carbon fibres.

3. COMPOSITION OF THE WORKING GROUP AT CTA

At the beginning of the project, the team directly involved in the programme included eight trained professionals under the direction of a Brazilian aeronautical engineer, holding a PhD in Engineering from the Massachussetts Institute of Technology (Mr. Faria). Mr. Bahel, from NPL in New Delhi, acted as Chief Technical Adviser (CTA) supported by UNFSSTD/UNIDO. From the beginning of 1982 towards February 1987 changes in the personal structure of the project management occurred.

1983 - Mr. Robert Kessel - Chief of Materials Division within IPD/CTA took the responsability as project leader.

Mr. Nagabushanam from LOWELL University, USA followed Mr. Bahel as CTA mid 1982 and also acted as internal programme coordinator at PMR (Materials Division) within IPD (Research and Development Inst.) at the Centro Tecnico Aeroespacial. Mr. Nagabushanam had to return to Lowell University, USA at the end of 1984. The Brazilian team member, Mr. Scyllas, was nominated then as internal Project Leader within the Materials Division under Mr. Kessel.

1985 - The Chief of IPD/PMR was changed from Mr. Kessel to Mr. Runivan Wellington Silva and in October 1985 Mr. João Renato became the responsible of the programme under Mr. Runivan. He therefore is the author of this Final Report.

July 1986 The leadership of PMR was awarded to Mr. Paulo Remi Guimarães Santos.

The size of the group itself has not changed during the first three years (1982-1984). Some personal replacements however became necessary due to the loss of specialists to the aeronautical industry. Fortunately, some key scientists first of all Mr. Simionato, remained with the team and guaranteed not only conservation of the experience elaborated so far but also the training of new coworkers.

During the last two years, 1985 - 1986, the number of coworkers in the group increased to 26 people consisting of 10 researchers and 16 technicians. The names of the present carbon fibre team (87) is compiled in enclosure 5.

4. REPORTS AND TRIPARTITE REVIEW MEETINGS

The work performed between 1982 and 1984 and the results obtained during this period is comprehensively compiled in the Final Report of Dr. Nagabushanam (December 1984), the responsible project coordinator and Chief Technical Adviser at that time. The report was arranged as follows: Chapters on

- Polymerization studies, studies in spinning, heat treatment (oxidation and carbonization) and development activities on surface treatment.

the respective parts 2, 3 and 4 of this Final Report (Dec 84) are attached as enclosure 1.

The evaluation of the results obtained during this period is compiled in the report on the December 1984 Tripartite Review Meeting.

Pages 9 to 13 of that report are attached as enclosure 2. They also include external accomplishments as well as the working programme and proposals for 1985.

Two further Tripartite Review Meetings were held, one on 10/11 Dec 85 in Rio and the second one on Feb 18th, 1986 at CTA. Parts of the 1986 Review Meeting Report are attached as enclosure 3.

The state of the Carbon Fibres programme in February 1986 with regard to the objectives of the Project Document as formulated by the Special Adviser of the project-at that time Prof. Fitzer-is given in Chapter 5.

5. CONCLUSIONS ON THE STATUS OF THE CARBON FIBRES PROGRAMME IN FEB 86

Objective 1: "Formation of a team capable to absorb western technology and to apply for own research and development".

Since the Tripartite Review Meeting in 1985, the project leadership was changed from Cap. Scyllas to Mr. Renato. Taking into account the starting difficulties it must be stated that the present team is the best since the beginning of the project. The motivation of the team members is very good, and the cooperation between them is steadily improving. Some members exhibit enthusiasm in demonstrating the successful work. Here Mr. Rheder should personally be mentioned. Although his speciality is the spinning department, he was charged with the repair and start of the carbonization equipment and was successful in solving all difficulties in cooperation with the technical staff members of PMR.

Nevertheless, the number of members of the team has to be increased further to avoid that experience gained so far is lost because of split obligations within the team and restricted numbers of coworkers.

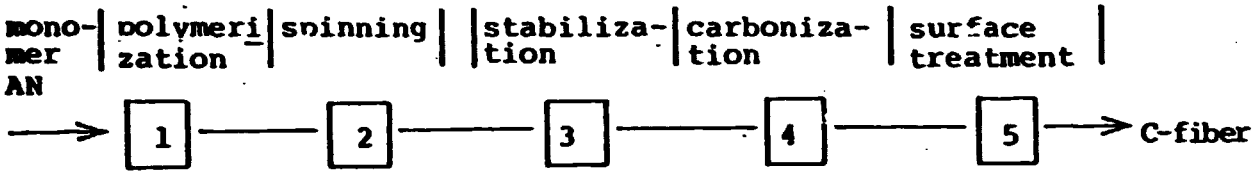
The team is strong in the fields of:

- wet spinning (DMF) in the laboratory, but not in pilot scale;
- stabilization in the laboratory scale and obviously in future pilot scale;
- carbonization in laboratory and pilot scale;
- surface treatment in laboratory and pilot scale

but extremely weak in polymerization, even in laboratory scale. This polymer preparation was the speciality introduced by the former Chief Technical Adviser, Dr. Nagabushanam. Within the co-operation with COPENE, a polymer chemist is expected to be delegated to CTA, in order to continue the polymer department.

Objective 2: "Development work on carbon fibre fabrication up to pilot scale and transfer to industry"

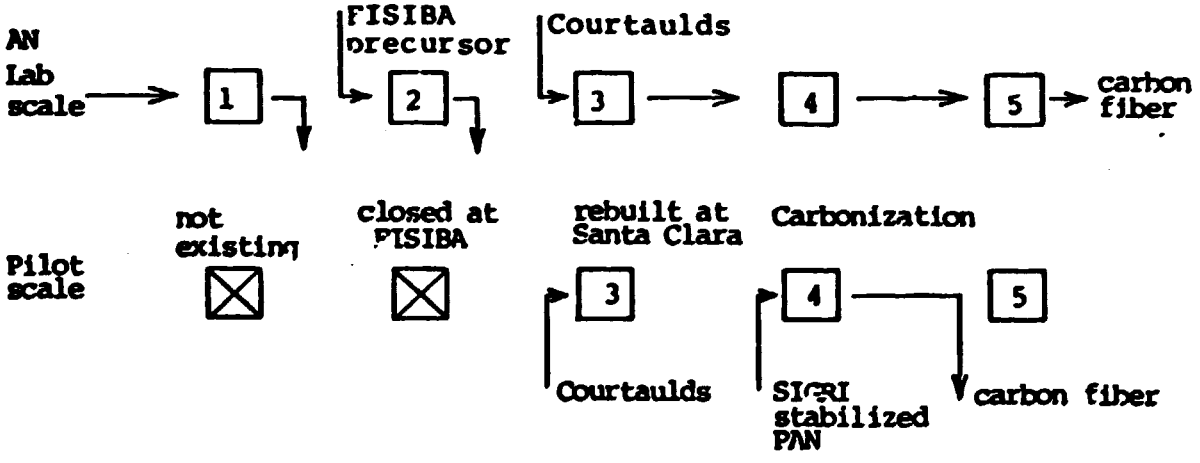
The carbon fibre fabrication consists of a sequence of process steps.



Planned from the beginning, the program included all steps. It was, however, pointed out repeatedly during the last three years that it is completely unrealistic to expect that the final C-fibre can be made from own polymer within these short years.

Fortunately not only PAN precursor fibres suitable for C-fibre fabrication became commercially available during the last years, but recently also stabilized Courtaulds precursor (by courtesy of SIGRI, which company has delivered the pilot carbonization furnace).

The following material flow is indicated below:



Step 3

in pilot scale depends on the availability of the Santa Clara oven. This oven was delivered in the fall of 1985 already, but so badly designed that it worked as room heater but not as yarn heater. It is hoped that additional thermal insulation will improve the situation. Santa Clara takes the oven back next week. Perhaps rebuilding will successfully be finished in April/May 1986. Then in the middle of the year the pilot line could work in the same way as the laboratory line.

Step 1

Polymerization, urgently needs experts' help even for laboratory scale. The former Chief Technical Adviser would be an ideal help.

Step 2

because of non-availability of spinnable own polymers laboratory scale spinning work is concentrated on spinning experiments and optimization of FISIBA polymers. Perhaps a carbon fibre with lower final mechanical properties can be achieved from this precursor, too if stabilization carbonization treatment will be optimized.

Spinning at FISIBA plant with UNIDO spinning equipment is stopped since long time already. Unfortunately, most officials in CTA and especially in COPENE do not remember that this spinning equipment is owned to CTA by UNFSSTD (UNIDO). The plant was only established in Salvador because FISIBA has promised to run the equipment with own labour team and at own cost.

It seems necessary that at that time COPENE will be reminded of this obligation.

6. THE WORK PERFORMED AFTER FEB 86 UP TO THE PROJECT TERMINATION END OF FEB 87 AND FINAL RESULTS.

The report in this chapter comprises :

6.1 - UNFSST/UNIDO contribution

6.2 - The cooperation between CTA and COPENE

6.3 - The stabilization furnace, built by SANTA CLARA

6.4 - The carbonization furnace, built by SIGRI/RUHSTRAT

6.5 - Summery of the activities 86-87

6.1 UNFSST/UNIDO contribution

The UNFSST/UNIDO support until 85 is compiled in the Enclosure 4.

The support in the last year (5^{th}) of the furtherly extended programme was small only but effective from view point of finalization of the overall concept.

It consisted of :

a. Two visits of Special Technical Adviser (first one in Feb 86 for preparation of the Tripartite Meeting, and the second, in Feb 87, for assist in finalization of the Project and preparation of the Second Phase).

b. Visit of the expert Josef Steinhart, with the aim of running the carbonization furnace, using stabilized multi-filament fibers from SIGRI, and to propose apparative improvements.

c. Two Study-tours of CTA members:
Firstly, Mr. Polidoro, to Europe, in September 1986, with the important task to prepare the visit of the expert, Mr. Steinhart, mentioned in (b) above.

The second study tour was performed during the first half of 1987 by two leading members of CTA (Mr. Kessel, as the new Technical Vice-Director of IPD/CTA and Mr. Remi, the Chief of Materials Division) to the People's Republic of China, following an invitation of the Chinese visitors from BICT and BIAM during June 1986 at CTA. (Programme as enclosed).

6.2 The cooperation with COPENE

6.2.1. Contract

The most successful achievement of adapting the research results to industrial application was the co-operation contract between CTA and COPENE, no 004-IPD-C/86, signed on January 22, 1986. The effective co-operation started in April 1986. This contract is planned for two years. It covers a COPENE input in the order of magnitude of Cz$8.000.000,00 split into a part of Cz$6.000.000,00 to be used for expenses at CTA and Cz$2.000.000,00 for expenses for polymerization and spinning works at COPENE. The part for CTA covers:

a. Laboratory equipment (US$235.000,00)
b. Personnel expenses
c. Exchange of measuring data and sample materials with FISIBA.

6.2.2. Results on polymerization

As reported to COPENE in October 1986 the polymer group at CTA has developed a good precursor polymer (PAN), in the laboratory scale, with the following chemical composition, and properties:

Acrylonitrile	93%
Methyl acrylate	6%
Itaconic acid	1%
Intrinsic viscosity /n/	1,63
Numerical molecular weight ($\bar{M}_n$)	114,828
Ponderal molecular weight ($\bar{M}_w$)	213,467
Polydispersion ($\bar{M}_w/\bar{M}_n$)	1,86

The chemical composition and properties of the FISIBA polymer, used so far at CTA laboraotry-scale spinning plant, and also, at FISIBA spinning plant is:

Acrylonitrile	94%
Methyl acrylate	6%
Intrinsic viscosity /n/	1,60
Numerical molecular weight ($\bar{M}_n$)	127,982
Ponderal molecular weight ($\bar{M}_w$)	255,642
Polydispersion ($\bar{M}_w/\bar{M}_n$)	1,99

As a comparison, the imported COURTAULDS polymer (from the finished PAN fibre precursor) shows the following properties (see table 2):

Chemical composition:

Acrylonitrile	93%
Methyl acrylate	6%
Itaconic acid	1%
Intrinsic viscosity /n/	1,60
Numerical molecular weight ($\bar{M}_n$)	149,390
Ponderal molecular weight ($\bar{M}_w$)	244,215
Polydispersion ($\bar{M}_w/\bar{M}_n$)	1,73

The polymer technology reached by CTA group is already available to

be transferred to the Brazilian partner COPENE, since they have the Polymerization plant ready.

CHARACTERIZATION	POLYMER	
	CTA	COURTAULDS
Mw	387485	257670
Mn	143407	149390
Polydispersion	2,70	1,72
η	2,44	1,6

TABLE 1 - RESULTS ON POLYMERIZATION

6.2.3 Results on spinning at CTA and FISIBA

The properties of the PAN precursor from FISIBA spun at CTA plant are the following:

Tensile Strength (GPa) : 0,4

Elasticity Modulus (GPa) : 6,0

Tenacity (g/Dm) : 4,2

Denier : 1,2

Density (g/cm^3) : 1,16

The properties of the PAN precursor spun at CTA spinning plant from the polymer developed at CTA Polymerization group are :

Tensile Strength (GPa) : 0,32

Elasticity Modulus (GPa) : 8,14

Tenacity (g/Dm) : 3,18

Denier : 2,0

Density (g/cm^3) : 1,17

(see also tabel 2)

According to the opinion of Dr Falkai, who was the UNIDO Consultant in 1984 and is now private consultant at FISIBA the CTA laboratory scale spinning plant has achieved the limit of its capacity for the FISIBA polymer.

The immediate development objective of CTA spinning group is delivering some batches, around 6 Kg/month, of the CTA polymer, to be spun at FISIBA plant to achieve better properties. These precursors then, will be sent back to CTA, for heat and surface treatments.

PROPERTIES	CTA POLYMER SPUN AT CTA PLANT	FISIBA POLYMER SPUN AT CTA PLANT	FISIBA POLYMER SPUN AT FISIBA PLANT
TENSILE STRENGTH (GPa)	0,32	0,4	0,42
MODULUS (GPa)	8,14	6,0	7.0
TENACITY (GPa)	3,18	4,2	4,5

TABLE 2 - RESULTS ON SPINNING AT CTA LABORATORY AND AT FISIBA

6.3 The State of the Stabilization furnace built by Máquinas Santa Clara Ltda

This investment for the pilot-line at CTA is covered by additional brazilian budget input, only. The furnace has been demonstrated before the last Tripartite Meeting at São José, in Feb 86, but turned out to be unacceptable because of insufficient thermal insulation. It was brought back to the factory at São Paulo, redesigned and rebuilt by the delivery company. It was tested in Oct 86, by the CTA Commission and was classified as still unacceptable because of the remaining heat losses to the environment.

It is finally decided that the aid of an expert is needed to solve the problems and to allow the installation of the furnace at CTA, carbon fibre plant again.

Carefull estimations let expect the opperation readiness of this oven earliest in april 86 and latest end 86.

It seems possible that the amount of 300 Kg multifilament carbon fibres can be fabricated from the imported stabilized yarn. Furthermore 3-6K carbon fibres can be prepared in the laboratory line or eventually also in the Santa Clara furnace (if availabie in time) from imported PAN SAF precursor material (again 300Kg) before the end of the present course of cooperation with COPENE.

6.4 The Carbonization Furnace, designed and built by SIGRI/RUHSTRAT

This investment for the pilot line at CTA is covered by UNFSST budget part, only.

The last demonstration of successful opperation with this furnace was given recently in cooperation with the expert Josef Steinhart (october and november 86), and during consecutive runs by the team after the departure of the expert.

The table3 shows the achieved carbon fibers properties as function of various process parameters. Maximum strength values around 3 GPa have been achieved with a final HTT of 1400^{o}C and allowed carbonization shrinkage of 5 to 7 percent. The Young modulus for these high strength fibers is around 210 GPa. A small increase of Young modulus up to 220 GPa was measured after maximum HTT of 1500^{o}C. However, strength dropped to 2.2 GPa under these condition. A reduction of HTT decreases the Young modulus to values below 220 GPa.

Nº	RESIDENCE TIME (min)	SHRINKAGE %	TEMPERATURE 1º FURNACE °C	TEMPERATURE 2º FURNACE °C	DENSITY g/cm³	GPa	GPa
1717	4	5	700	1350	1,79	2,82	197
1718	5	5	700	1350	1,79	2,47	193
1719	6	5	700	1350	1,79	2,33	192
1720	12	5	700	1350	1,81	1,48	177
1721	4	5	700	1200	1,83	1,62	167
1722	4	5	700	1300	1,80	2,43	185
1723	4	5	700	1400	1,78	3,08	211
1724	4	5	700	1500	1,76	2,21	220
1725	4	0	700	1400	1,79	2,38	203
1726	4	7	700	1400	1,78	2,88	209
1727	4	10	700	1400	1,78	2,43	215

TABLE 3 - RESULTS ON OXIDATION AND CARBONIZATION

The figures 1 and 2, below, show two aspects of the SIGRI/RUHSTRAT carbonization furnace, in opperation, during the stay of the expert Mr Steinhart. The material processed is the multi-filament tow (320K) oxidized PAN fibers, delivered from SIGRI. The results are shown on table 3.

FIG 1 : PARTIAL VIEWS OF THE SIGRI/RUHSTRAT CARBONIZATION FURNACE, IN OPERATION.

There is justified expectation for improving mechanical properties of the resulting carbon fibres as soon as the apparative improvements proposed by the expert during his stay will have been finalized. Additionally graphite parts for the channels with reduced cross section are in preparation (from Brazilian origin).

With such a supplement a small number of low filament tows will become processable.

5.5 Summary of the activities in 1986/1987

The work performed during this last (fifth) year has shown the absolute need for extension of the programme as proposed by CTA and accepted by the Tripartite Review Meeting in 1984 and 1985.

a. Only during this last year a breakthrough was achieved in the polymerization development under the cooperation of the Polymer Chemist of COPENE.

b. Based on this result on polymerization a variety of modified PAN precursor polymers became available for spinning experience at CTA. For former spinning studies only imported precursor was used as well as the official commercial FISIBA polymer, not optimum as precursor for carbon-fibres.

c. Thanks to the cooperation with COPENE the pilot spinning equipment set up at FISIBA plant (an investment covered by UNFSSTD budget only) is, for the first time, running for systematic experiments.

d. Although the stabilization oven from SANTA CLARA is not ready for successful operation, the basic for the final solution for the heat losses has been elaborated during this last year of the project only.

e. The initial problem with the carbonization furnace (which was set up at CTA) has been successfully solved during this last year of the programme.

f. Most satisfying is the fact that all these improvements in the last year of the programme have been achieved by the Brazilian team with only minor contributions from UNIDO experts. This fact demonstrates capability of the team to perform creative technical work on its own.

7. OVERVIEW OF THE RESULTS FROM THE FIVE YEARS' PROGRAMME AND FINAL CONCLUSIONS

The early eighties, the period when the UNFSSTD supported programme started at CTA, were exactly the years when the US FOR Company developped the prototype of a personnel streetcar mainly made from carbon-fibre composites.

From today's viewpoint, the judgement of all international experts at that time on the possibility of a very near broad industrialization in production of carbon fibres and in general use of such advanced composites in fields besides aerospace was too optimistic. It was assumed that all technical problems were nearly solved already.

As a consequence, the aim of the overall programme planned at that time was too optimistic, and first of all too broad to be fullfilled within three years only, namely:

starting from polymer chemistry, spinning technology, carbon fibre fabrication and surface treatment and ending with application of the fibres and finally with transfer of all results from these fundamental steps to industrialization.

Nevertheless, with the understanding and practical support of the CTA direction, Governmental representatives, UNDP, UNFSSTD and UNIDO, it was possible to extend the working programme from three to five years in the course of the project.

Furthermore, with an additional budget input from CTA, inputs from industry and the enthusiasm of the team members, it was possible to achieve many benefits for Brazilian technoloy, in the field of carbon fibres, as can be seen from the information and results given in this report before.

7.1 The team

First of all, a well trained team could reach a high technological level from precursor development up to the final product.

The CTA team is able to enlarge the group, educate people and to successfully cooperate internally and externally and to transfer the results from laboratory to industrial scale.

The design and construction of a pilot-scale stabilization oven, even with some technical problems, shows that the Brazilian industry is becoming able to develop and fabricate equipment for advanced materials technology.

7.2 Industrialization

The first step towards industrialization was achieved by the cooperation programme between CTA and COPENE, bringing in the near future the capability for industrial production of commercial carbon fibres, showing that the real objectives were achieved within the project plans.

7.3 The properties of the Carbon Fibres achieved in the programme:

In the laboratory line, after optimization of all parameters, carbon fibre tows, with 6000 filaments were obtained from COURTAULDS precursor, with the following properties:

Density (g/cm^3)	1,77
Tensile strength (GPa)	3,0
Elasticity Modulus (GPa)	220

Oxidized PAN fibres from CTA laboratory line, carbonized in the SIGRI/RUHSTRAT furnace, showed the same properties as written overleaf.

Carbon fibres from the multifilament oxidized material delivered by SIGRI, after the carbonization in the SIGRI/RUHSTRAT furnace showed the following properties:

Density (g/cm^3)	1,39
Tensile strength (GPa)	3,0
Elasticity Modulus (GPa)	210

Concerning the surface treatment:

Some modifications in the electrolytic cell were introduced, to allow a better current distribution within the whole cell. Those modifications will be introduced in the pilot-plant cell too.

In both, laboratory and pilot scales, the team is able to conduct surface treatment work and to match different degrees of surface oxidation as needed for the various matrix resins.

Quality control:

The team is able to perform quality control from the raw material to the finished product.

7.4 Future aspects

One has to be aware however that the cost for running the pilot plant are extremely high for CTA, especially as far as the nitrogen consumption but also the labour costs are concerned.

It is proposed that CTA has to run the pilot plant to produce carbon fibers, at least until the following up programme has resulted in further improved carbon fiber qualites.

The, the pilot plant should be transferred to an industrial partner with the obligation to supply carbon fibers materials to CTA in quantities, needed for the further research development work on composite materials at CTA.

In any case, the carbon fiber laboratory line and basic equipments for laboratory work & tests have to remain at CTA for further technological improvements in general and for use in the follow up programmes.

JOÃO RENATO SANTOS MARTINS - Eng
Carbon Fibers Project Leader, at CTA

PAULO REMI GUIMARÃES SANTOS-Eng
Head of Materials Division IPD/CTA

ENCLOSURE 1

(Written by Dr. Nagabushanam, Dec. 1984)

2.0 - DEVELOPMENTAL ACTIVITIES IN THE PRECURSOR WORK

2.1 - Activites in 1982

i - Polymerization Studies

For the first time, the group was trained in the polymerization of acrylonitrile in the presence of comonomers like methylacrylate in aqueous medium. Free radical polymerization methods were introduced. Initiator system such as potassium persulfate-bisulfite was used to polymerize the vinylmonomers. The polymers synthesized were purified and characterized by viscometric methods outside PMR/CTA as there were no facilities at that time in CTA.

Table 1 gives some of the results of polymerization. Meanwhile, in August 1982, the lab. model wet spinning assembly arrived (supplied by UNIDO) at the Project site. As the spinning experiments require larger quantity of the polymers, and as CTA group had only a small polymer-

ization vessals, ie 100 to 200 grams capacity and had no comonomers, it is felt important to standardize the spinning experiments using Fibras Sintéticas da Bahia S.A. (FISIBA) supplied commercial acrylic polymers. The polymerization experiments were postponed to a later date. The activities were concentrated on spinning of acrylic fibers, in order to standardize the spinning aparameters.

Table 1 - Results of polymerization

POLYMER Nº	REDUCED VISCOSITY
1	4.46
2	2.45
3	2.21
4	2.89
5	2.84
6	3.19
7	6.06

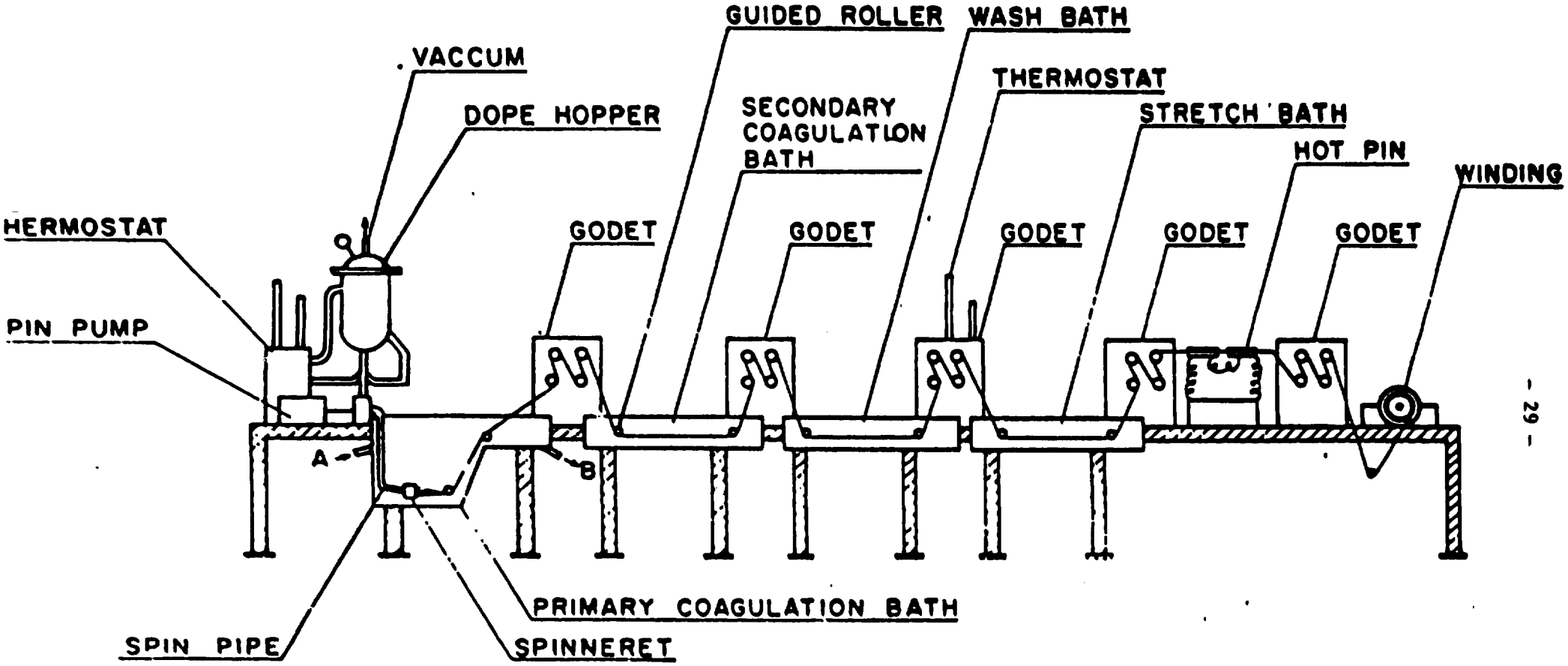
Monomers: acrylonitrile: 94%
Methylacrylate: 6%

ii - Studies in Spinning

With the arrival of Lab. Model Wet Spinning Assemply supplied by UNIDO, the activities started in spinning acrylic fibers using the commercial acrylic polymer supplied by FISIBA. The line diagram of the spinning equipment is given in Figure 1. In order to standardize the working condition of this equipment, preliminary spinning experiments were commenced using 23% polymer in N N dimethylformamide (DMF). The results of initial fiber spinning were presented in Table 2. Later, several experiments were made in spinning using variations in the spin pump speed and successive coagulation, etc.

iii - DSC Studies of the Spun Fibers

With the availability of UNIDO supplied differential scanning calorimeter, it was possible to carry out preliminary studies on CTA spun fibers. The results would through light on the cyclization and stabilization parameters. The DSC results are presented in Table 3.



A,B: COOLING IN-LET AND OUT-LET

FIG. 1 = SPINNIG ASSEMBLEY

TABLE 2 - PRELIMINARY SPINNING RESULTS

SPINNING N°	STRETCH RATIO	TENSILE STH Kg/mm^2	MODULUS Kg/mm^2	DENSITY G/m^3
1	2.35	7.6	236	1.17
2	2.35	19.4	545	1.17
3	2.25	17.7	600	1.18
7	3.3	14.3	393	1.18
8	3.3	43.3	1297	1.16
9	3.3	35.7	990	1.17
10	3.6	39.3	960	1.16
11	3.6	17.6	408	1.15
12	3.6	20.95	426	1.15
13	3.6	17.4	376	1.16
14	3.5	33.7	937	1.15
15	3.5	33.7	937	1.15
16	5	32.2	415	1.18
17	4	21.4	354	1.19
18	4	22.5	320	1.19
19	4	21.8	466	1.18
20	4	22.1	325	1.17
21	4	21.6	335	1.17
22	4	21.9	362	1.17
23	4	20.2	335	1.17

TABLE 3 - DSC RESULTS OF CTA SPUN ACRYLIC FIBERS

SAMPLE	ORDER REACTION (n)	FREQUENCY FACTOR (min^{-1})	ACTIVATION ENERGY (KJ/MOL)	CORRELATION (%)
1	1,05	6,0 x 10	101,3	99,79
2	1,09	3,0 x 10	99,2	99,53
3	1,04	1,9 x 10	96,7	99,50
7	1,04	8,3 x 10	104,2	99,92
8	1,02	5,4 x 10	102,2	99,75
9	1,06	3,9 x 10	100,5	99,84
10	0,96	3,8 x 10	100,5	99,85
11	1,02	4,6 x 10	100,9	99,92
12	1,01	2,3 x 10	108,7	99,71
13	1,05	1,6 x 10	106,9	99,89
14	1,08	9,7 x 10	104,5	99,80
15	1,05	1,9 x 10	107,8	99,84
16	1,08	2,4 x 10	108,9	99,80
17	1,13	2,8 x 10	109,4	99,58
17A	1,08	8,8 x 10	102,4	99,92
18	1,08	1,2 x 10	105,7	99,87
19	1,12	3,7 x 10	99,8	99,89
20	1,13	1,3 x 10	94,1	99,95
21	1,13	6,5 x 10	102,5	99,92
22	1,12	5,9 x 10	101,9	99,76
22A	1,15	4,3 x 10	100,3	99,84
23	1,15	4,3 x 10	100,3	99,84

2.2- Activities in 1983

i - Activities in Spinning at CTA

Numerous spinning experiments were conducted using Lab. Model Wet Spinning Assembly shown in Figure 1. For example, a few studies are mentioned here.

CASE I

Polymer concentration	: 23% in DMF
Stretch ratio	: 5
Composition of primary coagulation bath	: 50/50 DMF H_2O
Composition of second coagulation bath	: 0-4% DMF in water
Composition of stretch bath	: 6% DMF in water
Composition of wash bath	: water
Temperature coagulation bath	: $1^{o}C$
Temperature of second coagulation bath	: $28^{o}C$
Temperature of hot plate	: $143^{o}C$

CASE II

The temperature of coagulation bath was varied from 0-$8^{o}C$ and the composition of coagulation bath was fixed at 40% DMF in water, stretch ratio was 4. All other conditions were same as in Case I.

In view of the above systematic experiments, Case I and II, the following observations were made:

1- Second coagulation bath (Figure 1) had an observable effect on the physical properties of final fibers.

2- Tensile strength of the final fibers found to increase up to a 10% DMF concentration in the 2^{nd} bath (figure 2).

3- Over and above 10% DMF concentration in the 2^{nd} coagulation bath the tensile strength of the fibers was not effected or had minimum effect (Figure 2).

4- Young's modulus found to increase up to about 30% DMF concentration in 2^{nd} coagulation bath (Figure 2).

5- Young's modulus found to decrease when (DMF) was increased above 30% (Figure 2).

6- The increase in the coagulation temperature had decreasing effect on the physical properties of the fiber (Figure 3).

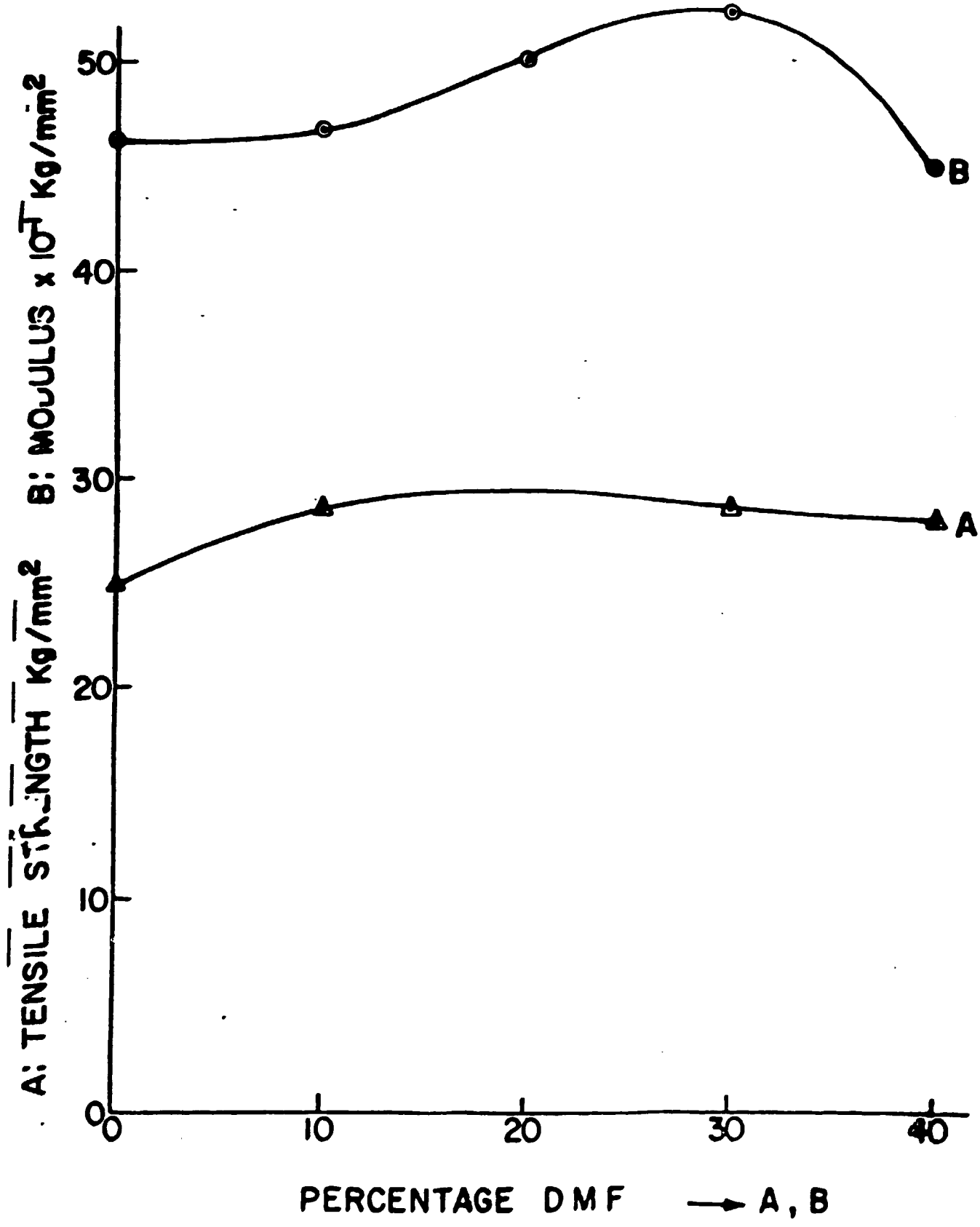

A: TENSILE STRENGTH Kg/mm²
B: MODULUS x 10⁷ Kg/mm²
50
40
30
20
10
0
0
10
20
30
40
B
A
PERCENTAGE DMF → A, B

FIGURE -2

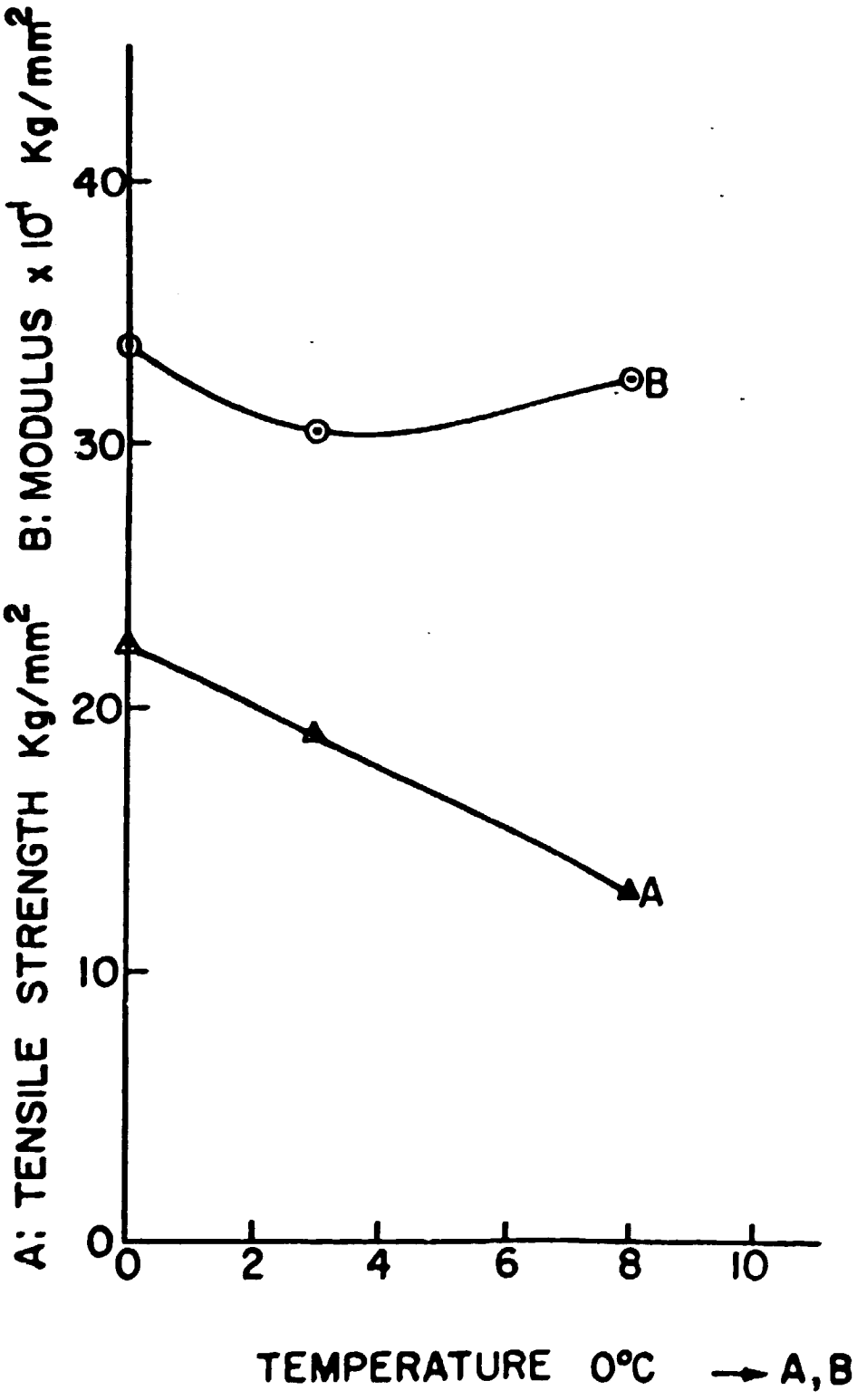

A: TENSILE STRENGTH Kg/mm²
B: MODULUS x 10¹ Kg/mm²
40
30
20
10
0
0
2
4
6
8
10
B
A
TEMPERATURE 0°C → A, B

FIGURE - 3

From these observations, it may be concluded that slow coagulation would yield final fibers with favourable physical properties when the DMF concentration of the 2nd coagulation bath is less than 30% which could be due to the further slow diffision of solvent into the 2nd coagulation bath which would have resulted in the increase of proto fibrile density which in turn would reflect in physical properties of the final fibers. Also it was found lower temperature in the coagulation bath, would also result in high density fibers.

CASE III

Effect of pH of the coagulation bath on physical properties of the acrylic fibers.

Spinning conditions :
Polymer concentration: 24% in DMF
Coagulation bath : 50/50 DMF: H_2O
Spinnerette hole dia.: 0,08mm
Nº of holes : 50
Spin pump temperature: 60°C
Draw ratio : 5.6
Hot spin temperature : 143°C
Composition of stretch bath: 6% DMF, temp.: 97°C
Coagulation bath temperature: Varied
pH of the coagulation bath : Varied

In each spinning experiment, the polymer dope was filtered before introducing into the dope hopper. The dope hopper containing the polymer solution was devaccuated before spinning.

The following observations were made:

- Under the same pH and at different temperatures, the cross section of the final fibers found to change from kidney shape at lower pH values, ie, pHs 2.8, 3.8, 6.6 to circular at higher pH values, ie, pHs 9.1, 10.8.
- However, under the same temperature and in different pH values, there was not much effect on the cross section, showing that pH may not effect on the structural aspects of the fibers. However, in certain cases at high pHs voids are noticed in the optical microscopy.
- Density decreased with an increase in the pH of the coagulation

bath, thereby effecting the mechanical properties of the final fibers.

- The increase in pH values tend to have diminishing effect in general on tensile strength values of the fibers. At coagulation temperatures of 4°C, 15°C, 20°C, 25°C a decreasing trend in general was observed. However, there are some discrepancies in some places. Overall picture is that there is a decreasing effect.
- Modulus values are also in general decreased with increasing pH, however, a decrease and increase and decreasing tendencies were observed. The general trend, however, is of decreasing order. These decreasing trends in tensile strength and modulus would have resulted due to decreasing values of density with increasing pH.

CASE IV

Effect of spin pump speed, size and speed of take-up godet on physical properties of acrylic fibers

In wet spinning, the denier of the fiber depends on several spinning parameters such as, spin pump speed, spin pump size (that controle the pumping of polymer dope into the coagulation bath), spinnerette hole diameter, number of spinning holes, take-up speed and hot stretch conditions. While keeping all conditions constant, the fineness of the fiber could be improved by increasing the number of holes of the spinnerette. In cases where there are no spinnerettes with a higher number of holes (in our cases we have only 100 holes spinnerette), the fineness can be improved by reducing the spin pump speed there by controlling the polymer pumping into the coagulation bath. When this is also achieved maximum the next parameter that can be used to get the fine fibers is by reducing the spin pump size. However, when the minimum size pump has already been used, then the take-up speed of the first godet could be increased which facilitates to increase the speed of the subsequent godet. This will not only give fine fibers, but also would increase the speed of production. However, when doing so, one may sacrifice the density of the fiber unless the length of coagulation path is increased. Eventhough various reports are available in literature systematic studies on these parameters are lacking and also most of the results are in patent form. In view of this, a systematic study is conducted using different spin pumps, spin pump speeds, take up roller speeds under identical conditions.

Spinning conditions in Case IV were:

Polymer concentration	: 23% in DMF
Viscosity of spinning solution at 50°C by ball fall method	: time: 23
Coagulation bath composition	: 50/50 DMF H_2O
Spinnerette holes	: 100
Spinnerette dia.	: 0,1 mm
Composition of wash bath	: Baths 1 and 3 water
Composition of stretch bath	: 6% DMF
Temperature of coagulation bath	: 2-3°C
Temperature of hot pin	: 170°C

Maintaing the above spinning conditions, in general, the other variables were changed as given in Table 4.

TABLE 4 - SPINNING RESULTS

SPIN PUMP SPEED METERS/MINUTE		SPEED OF TAKE UP GODET 1 METERS/MINUTE	MAXIMUM STRETCH OBTAINED	DENIER OF THE FIBER
Spin pump size .6cm³/Rev.	3.0	5	7.0	3.990
	2.0	5	7.0	2.470
	1.4	5	6.4	1.828
	1.4	7	6.7	1.560
Spin pump size .4cm³/Rev.	1.4	5	6.2	1.430
	1.4	6	5.4	1.370
	1.4	7	5.7	1.009
	1.4	7	6.0	1.020
	1.4	7	6.3	0.970
	1.4	8	5.6	0.960

Using spin pump of size 0,6 cm^3/Rev when the speed of the spin pump is 3M/m a stretch ratio of 7 could be obtained which resulted in a denier of 3.99. When the spin pump is further reduced to 2M/m a stretch ratio of 7 is achieved (difficult), but the denier of the fiber reduced. A further reduction resulted in a decrease of stretch ratio but denier of the fiber reduced to 1.828. This shows that a decrease in rate of

TABLE 5 - BEST SPINNING RESULTS OF 1983 (LAB. MODEL)

	STRETCH RATIO	DENIER	TENSILE STRENGTH GPa	MODULUS GPa
EARLY 1983	5.6	3.79	0.36	5.8
	5.6	8.20	0.38	5.4
	5.6	1.92	0.34	7.8
2nd HALF OF 1983	4.9	1.35	0.28	7.72
	5.7	1.00	0.34	9.24
	6.0	1.02	0.28	8.04
	6.3	0.97	0.421	7.73
	5.6	0.94	0.349	9.86

pumping of polymer into the coagulation would yield finer fiber keeping al other spinning conditions constant. However, the reduction in the speed of the pump will impose a constrain in the maximum obtainable stretch ratio keeping stretch bath conditions constant. Beyond these limits the fibers were breaking in the stretch bath. However, by increasing the take-up godet to 5m/m to 7m/m a slight raise in stretch ratio and denier could be achieved.

When the pump size was further decreased from 0.6 to 0.4 cm^3/Rev. still finer fibers could be obtained. As shown in Table 4, when the take-up godet speed is changed, very fine fibers could be obtained.

However, the rise in the speed of take-up godet would impose some restriction in spinning. A quicker removal of the fiber from the coagulation bath might effect the density of the fiber which may in turn result in weaker fibers. In such case, one should compensate by increasin the coagulation path.

On the basis of these experiments, the following conclusions were made:

- A decrease in size of the spin pump would yield fine fiber due to the reduction in the pumping of polymer into the coagulation bath.
- Decrease in spin pump speed would also yield finer fibers due to the above reason.
- Care should be taken to compensate the residence time of proto fiber in the coagulation bath by increasing spinning path.
- The reduction in spin pump size and spin pump speed would impose restrictions on obtainable draw ratio.

Later on hundreds of experiments were conducted. The variations in spinning parameters included spin pump speeds, no of holes in the spinnerette, size of the spinnerette hole, dope composition, etc. The best spinning results of 1983 are represented in Table 5. The results during the later half of the year are comparable with some of commercial fibers.

ii - Spinning Activities at FISIBA (Fibras Sintéticas da Bahia S.A., Camaçari, Bahia)

Meanwhile the pilot plant spinning assembly supplied by UNIDO has arrived. This was assembled at the previously agreed site FISIBA. The

visit of Prof. Falkai was planned at the final stages of the commissioning of this equipment. Myself and Dr Falkai visited again the FISIBA, and the pilot plant spinning assembly site and rectified the small defec and started the initial spinning experiments. The FISIBA scientists were trained in several of the spinning experiments. FISIBA, though a fiber producing industry had no previous wet spinning experience They were trained in understanding the spinning conditions and crucial points. The preliminary spinning results at FISIBA towards the end of 1983 are presented in Table 6. After the preliminary testing in FISIBA at the plant site remaining tests like density measurements were performed at CTA. In view of the fact that the density of the fiber was less it was adviced to them to perform a set experiments consisting the variations in polymer composition. The experiences in the bench scale experiments at FISIBA enabled to identity and to improve the properties of fibers in the pilot plant. Also, the scientists trained at CTA by me and Falkai further helped the FISIBA people in commissioning the preliminary spinning experiments. In view of mutual contacts between CTA scientists and FISIBA people, the properties of the fibers at the pilot plant were improved. These contacts and the interest shown by FISIBA were slowly growing and FISIBA and its parent organization COPENE - Petroquímica do Nordeste S.A. were understanding the potentials of carbon fibers. This is very good for a project of this type for further industrialization of this technology in the country.

TABLE 6 - PRELIMINARY SPINNING RESULTS AT PILOT PLANT IN FISIBA

Spinning nº	Stretch	Final Denier	TS GPa	Modulus GPa	Density
1	4	5.77	2.22	-	-
2	2.99	3.1	1.616×10^{-1}	4.31	1.43
3	3	2.2	2.449×10^{-1}	5.292	1.14
4	4.11	1.9	2.711×10^{-1}	5.542	1.14
5	4.47	1.9	3.163×10^{-1}	6.119	1.13
6	4.94	1.84	3.21×10^{-1}	5.36	1.18

TABLE 7 - SPINNING RESULTS AT FISIBA IN 1984

SPINNING Nº	FINAL DENIER	TS GPa x 10^{-1}	MODULUS GPa	DENSITY
7	1.64	3.53	6.258	1.19
	1.71	8.19	5.75	1.15

iii - Studies in Polymerizations

Meanwhile the UNIDO supplied polymerization reactors chemical reagents, initiators and monomers arrived at CTA, polymerization experiments were conducted in smaller scale initially using two monomers, ie acrylonitrile and methylacrylate, and acrylonitrile, methylacrylate and itaconic acid. The smaller scale polymerizations were of 1 litre capacity. These polymerizations were conducted in aquous medium. The polymeris were filtered, dried and characterized. The results are given in Tables 8 and 9.

TABLE 8 - RESULTS OF POLYMERIZATION CONDUCTED IN 1 LITER CAPACITY USING TWO MONOMERS, ie ACRYLONITRILE AND METHYLACRYLATE

EXPERIMENTS	AN (%)	MA (%)	TEMPER. (°C)	TIME (h)	QUANT. (g)	YIELD (%)
A - 1	97	3	40	5	104,70	52,35
2	97	3	35	5	84,91	42,455
3	97	3	40	5	171,52	85,76
4	97	3	50	5	171,50	85,75
5	97	3	60	5	173,94	86,97
6	97	3	70	5	164,71	82,355
7	97	3	80	5	172,00	86,00
B - 8	96	4	40	5	71,71	35,855
9	96	4	60	5	109,77	54,885
10	96	4	50	5	157,72	78,86
11	96	4	70	5	185,24	92,62
12	96	4	80	5	179,11	89,555
C- 13	95	5	40	5	29,95	14,975
14	95	5	40	5	58,73	29,365
15	95	5	50	5	26,84	13,42
16	95	5	70	5	142,40	71,20
17	95	5	80	5	165,10	82,55
18	95	5	60	5	83,56	41,78
D- 19	98	2	40	5	53,57	26,785
20	98	2	50	5		
21	98	2	60	5		
22	98	2	70	5		
23	98	2	80	5		
E- 24	99	1	50	5		
25	99	1	70	5		
26	99	1	40	5		
27	99	1	60	5		
28	99	1	80	5		

TABLE 9 - RESULTS OF POLYMERIZATION CONDUCTED IN 1 LITER CAPACITY USING THREE MONOMERS - ACRYLONITRILA (AN), METHYL ACRYLATE (MA) AND ITACONIC ACID (ITA)

EXPERIMENTS	AN (%)	MA (%)	ITA (%)	TEMPER. (°C)	TIME (h)	QUANT. (g)	YIELD (%)
A - 29	96	3	1	40	5		
30	96	3	1	60	5		
31	96	3	1	70	5		
32	96	3	1	50	5		
33	96	3	1	80	5		
B - 34	95	4	1	50	5		
35	95	4	1	60	5		
36	95	4	1	70	5		
37	95	4	1	40	5		
38	95	4	1	80	5		
39	95	4	1	80	5		
C - 40	94	5	1	70	5		
41	94	5	1	60	5		
42	94	5	1	80	5		
43	94	5	1	40	5		
44	94	5	1	50	5		
D - 45	94	4	2	50	5		
46	94	4	2	40	5		
47	94	4	2	60	5		
48	94	4	2	70	5		
49	94	4	2	80	5		
E - 50	94	3	2	40	5		
51	94	3	2	60	5		
52	94	3	2	50	5		
53	94	3	2	70	5		
54	94	3	2	80	5		
F - 55	95	3	2	40	5		
56	95	3	2	50	5		
57	95	3	2	60			
58	95	3	2	70	5		
59	95	3	2	80	5		

iv - Planning in Polymerizations

Also several of the polymerizations were planned and the following plan was given to the precursor group:

Planned Polymerization Experiments:

- Polymerization in one liter capacity - variation in temperature
- Polymerization in one liter capacity - constant temperature
- Polymerization of acrylonitrile in the presence of two comonomers - variation in temperature (third monomer)
- Polymerization of acrylonitrile in the presence of two comonomers - constant temperature
- Polymerization of acrylonitrile in the presence of two comonomers - variations in temperature (third monomer)
- Polymerization of acrylonitrile in the presence of two comonomers - constant temperature (third monomer)
- Characterization of these copolymers

v - Scaling up of Polymerization to Higher Capacity

A - Scale up of acrylic polymerizations (using monomers, acrylonitrile and methylacrylate) to 5 liter capacity should be continued.

B - Scale up of acrylic polymerizations (using monomers, acrylonitrile, methylacrylate and itaconic acid) should be continued after the analysis of the preliminary results.

2.4- Additional Spinning Studies

i - Spinning of CTA Acrylic Polymers

In future, the best of CTA polymers have to be spun using the previous and modified spinning parameters. The group was advised by me on this. I have also advised the group to prepare polymers of type B in 10 liter capacity after looking at the initially spun A and B CTA polymers. These polymers have to spun using the previously developed spinning conditions.

ii - Planning in New Spinning Methods

Spinning of acrylics polymers using inorganic spinning solvents:

I have advised and gave the planned sheets of the type enclosed to spin

the acrylic fibers using inorganic solvents. Inorganic solvents woul permit in using high spinning temperature in the coagulation bath which would result in circularity in cross section of spun fibers. These inorganic solvents could be sodium thiocynate and zinc chlosid Representative planned sheets are enclosed as Tables 10 and 11.

3.0 - Development Activities in Heat Treatment

3.1- Activities in 1982

i - Position at the Time of my Arrival

Just before my arrival, the previous Chief Technical Adviser, Dr left the Project. At Centro Técnico Aeroespacial, the heat treatment activities were abandoned on FISIBA commercial grade fibers, the researd and developmental activities started already using imported special grade acrylic fibers supplied by Courtaulds, England. At this time, the developmental activities on heat treatment were conducted using the heat treatment system of the type shown in Figure 4. The best results on FISIBA fibers at the end of 1981 are shown in Table 12.

ii - Activities After my Arrival

Several studies were conducted in 1982. Several of the parameters in heat treatments were changed due to the advices of other experts who visited the project site. The studies were concentrated mainly using Courtauld's SAF precursor. Several of experiments were conducted in heat treatment.

Tables 13 and 14 and figures 5 and 6 show some of the initial studies on Courtauld's fibers on the effect of heat treatment temperature on tensile strength and modulus. The best results of heat treatment studies in 1982 are represented in Table 14A (continuous process) and table 14B (discontinuous process). Also, in order to find out the effect of air flux during oxidation stage, several experiments were conducted both in the presence and absecne of moved air. The results are presented in Table 15.

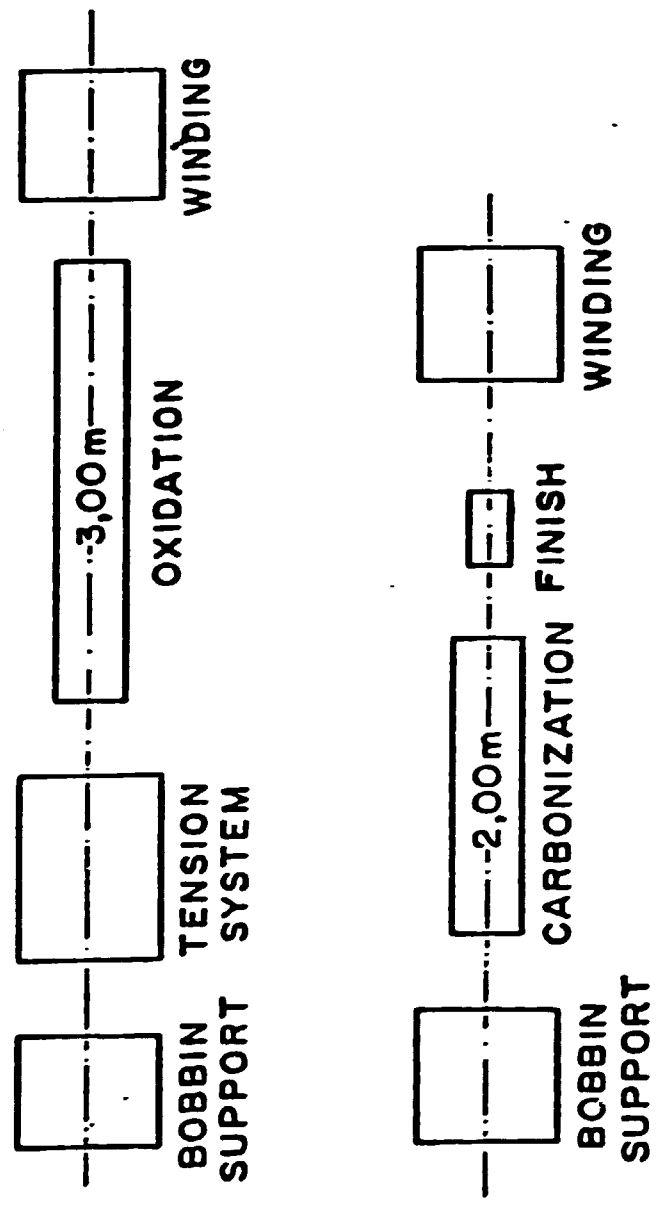


FIGURE 4 - I OLD SYSTEM

TABLE 12 - BEST RESULTS OF 1981 - ONE STEP OXIDATION (FISIBA PRECURSOR)

	OXIDATION				CARBONIZATION			CARBON FIBERS PROPERTIES	
	ELONGATION %	TEMPERATURE °C	RES.TIME MIN.	ATMOSPHERE	TEMPERATURE °C	RES.TIME MIN.	ATMOSPHERE	T.S.	MODULUS
CONTINUOUS PROCESS	+7	230	180	AIR	1000	120	ARGON	200×10^3 PSI 1,38 GPa	20×10^6 PSI 138 GPa
DISCONT. PROCESS.	+6	220	220	FORCED AIR	1000	120	ARGON	345×10^3 PSI 2,30 GPa	26×10^6 PSI 180 GPa

TABLE 13 - EFFECT OF CARBONIZATION TEMPERATURE

CARBON TEMP. °C	DENSITY g/cm^3	CROSS AREA 10^{-5} mm^2	TENSILE STRENGTH (GPa)	TENSILE MODULUS (GPa)
1000	1,80	37,3	1,7 ± 0,5	180 ± 27
1100	1,76	36,9	2,1 ± 0,6	190 ± 22
1200	1,76	37,1	2,2 ± 0,5	180 ± 23
1300	1,75	36,3	2,6 ± 0,7	200 ± 25
1400	1,75	35,4	2,7 ± 0,6	212 ± 31
1500	1,75	34,8	2,1 ± 0,6	215 ± 29
1600	1,77	35,3	1,6 ± 0,4	215 ± 23
1800	1,77	35,5	1,6 ± 0,5	216 ± 23
2000	1,79	34,5	1,5 ± 0,4	245 ± 29
2250	1,81	34,8	1,8 ± 0,4	222 ± 36
2500	1,86	35,5	1,9 ± 0,5	279 ± 36

TABLE 14 - EFFECT OF STRETCH DURING CARBONIZATION

CARBON TEMP. °C	STRETCH %	DENSITY g/cm^3	CROSS AREA 10^{-5} mm^2	TENSILE STRENGTH (GPa)	TENSILE MODULUS (GPa)
1000	0	1,80	38,4	2,1 $\pm$ 0,4	176 $\pm$ 30
1000	5	1,78	35,4	2,2 $\pm$ 0,4	199 $\pm$ 35
1000	10	1,77	35,1	2,5 $\pm$ 0,3	203 $\pm$ 19
1000	15	1,78	32,9	2,8 $\pm$ 0,4	210 $\pm$ 25

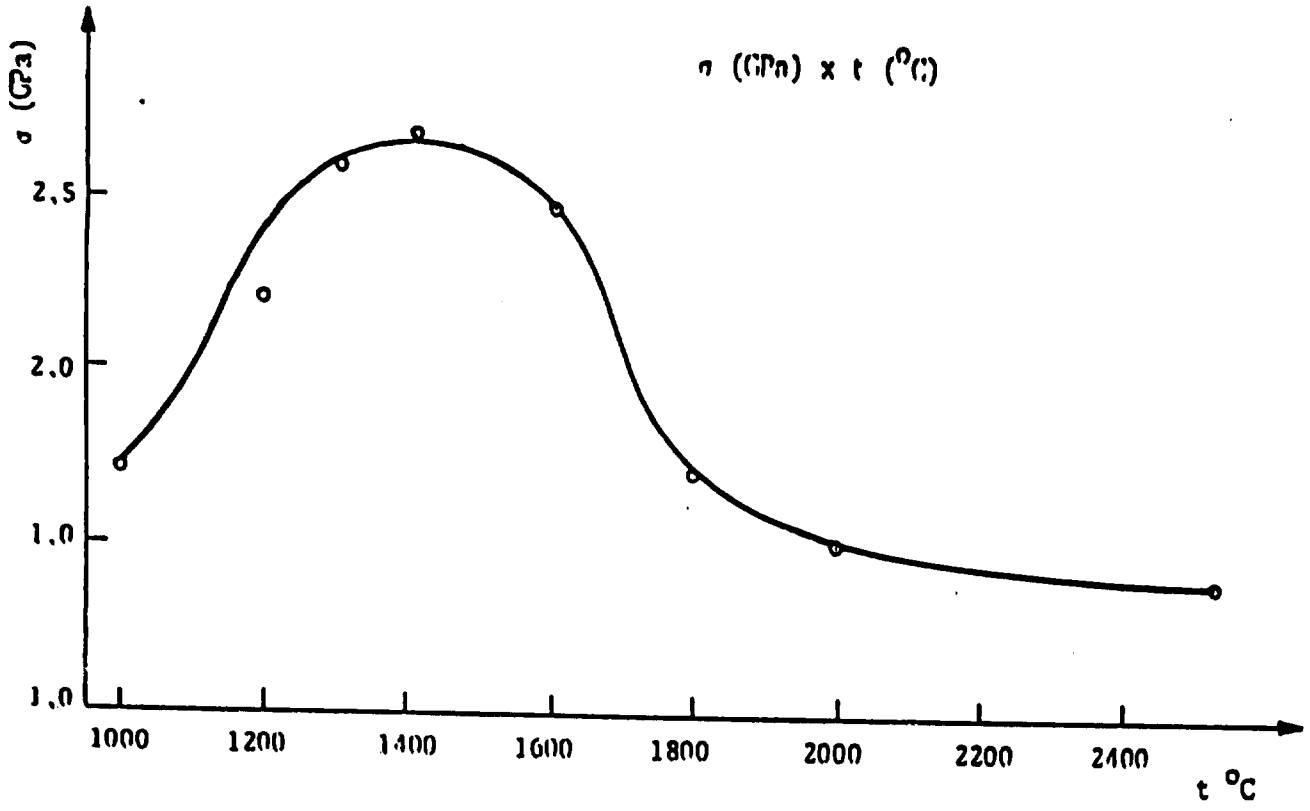

σ (GPa)
σ (GPa) x t (°C)
2,5
2,0
1,0
1,0
1000
1200
1400
1600
1800
2000
2200
2400
t °C

FIGURA 5 -

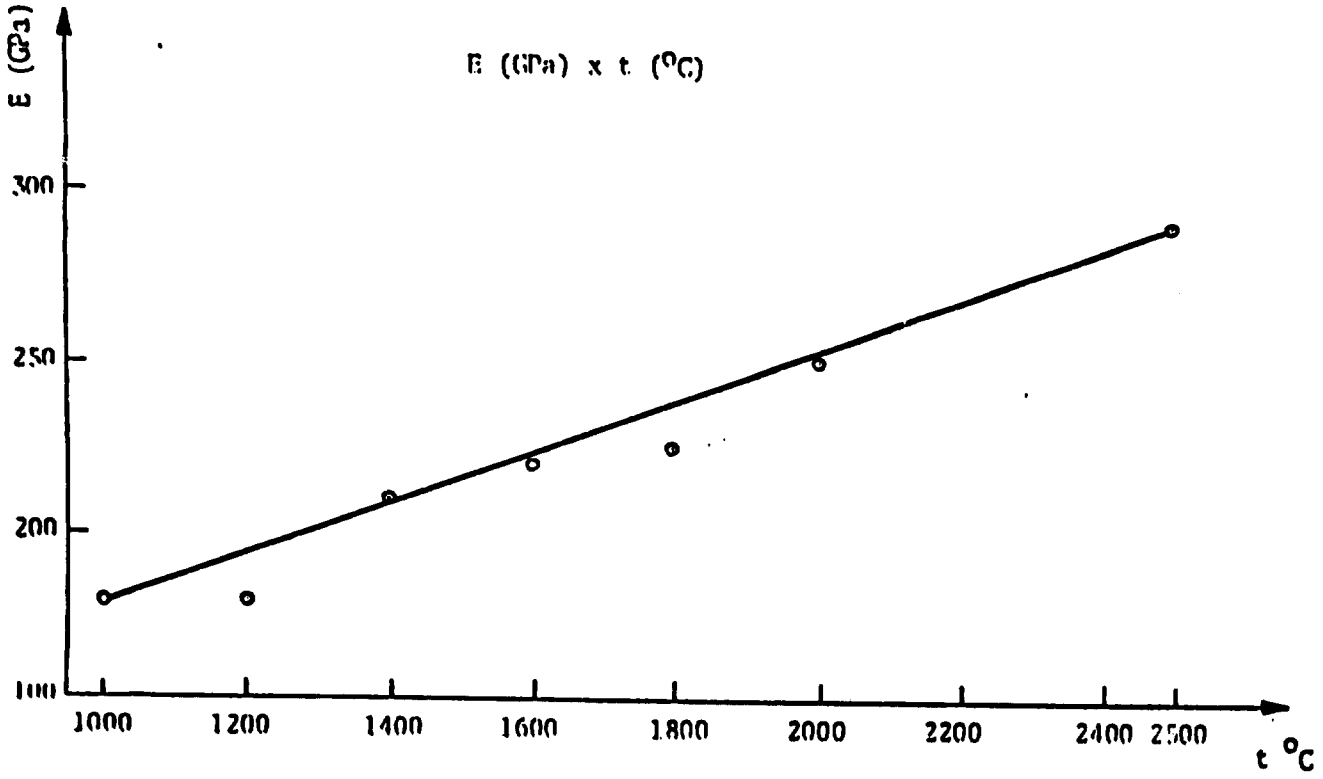

E (GPa) x t. (°C)
E (GPa)
300
250
200
100
1000
1200
1400
1600
1800
2000
2200
2400
2500
t °C

FIGURA 6 -

TABLE 14A- BEST RESULTS OF 1982 (COURTAULDS SAF PAN)

CONTINUOUS PROCESS

ELONGATION PRE-STRETCH %	TEMPERATURE PRE-STRETCH °C	PRE-OXID. TEMP. °C	OXIDATION TEMP. °C	RES.TIME PRE-OXID. MIN.	RES.TIME OXID. MIN.	ATM.	TEMP. CARB. * °C	RES.TIME CARB. MIN.	ATM. CARB.	T.S.	MODULUS
+6	190	220	230	60	120	AIR	1100	120	ARGON	275×10^3 PSI 1,90 GPa	21×10^6 PSI 145 GPa

* SHRINKAGE = (8-9)%

TABLE 14B - BEST RESULTS OF 1982 (COURTAULDS SAF PAN)

DISCONTINUOUS PROCESS

ELONGATION OXID. %	TEMPERATURE OXID. °C	RES.TIME MIN.	ATMOSPHERE OXID.	TEMPERATURE CARB. * °C	RES.TIME MIN.	ATMOSPHERE CARB.	T.S.	MODULUS
+6	220	200	FORCED AIR	1100	120	ARGON	350×10^3 PSI 240 GPa	$2,8 \times 10^6$ PSI 193 GPa

* SHRINKAGE = (8-9)%

TABLE 15 - EFFECT OF AIR FLUX ON THE PHYSICAL PROPERTIES OF CARBON FIBERS

Stretching Ratio (%)	190°C		230°C		265°C		1000°C	1000°C	1000°C	1000°C	1000°C
	Density (g/cm^3)	Weight/m (mg)	Density (g/cm^3)	Weight/m (mg)	Density (g/cm^3)	Weight/m (mg)	Density (g/cm^3)	Weight/m (mg)	Cross Area (μm^2)	Tensile Strength (GPa)	Tensile Modulus (GPa)
WITHOUT AIR FLUX											
-5	1,21	779	1,35	806	1,43	795	1,77	451	42,5	2,4 ± 0,7	199 ± 32
0	1,21	711	1,35	749	1,43	755	1,77	422	39,7	2,0 ± 0,6	204 ± 28
+5	1,21	690	1,35	698	1,43	725	1,77	404	38,0	2,2 ± 0,7	214 ± 52
+10	1,21	668	1,35	693	1,43	707	1,77	400	37,7	2,8 ± 0,4	220 ± 30
WITH FLUX OF 35L AIR/MIN.											
-5	1,21	765	1,32	816	1,46	793	1,75	450	42,8	2,1 ± 0,4	166 ± 16
0	1,21	740	1,30	758	1,46	780	1,75	438	41,7	1,8 ± 0,5	156 ± 25
+5	1,21	714	1,30	714	1,46	727	1,75	413	39,3	2,0 ± 0,6	188 ± 28
+10	1,21	673	1,30	674	1,46	693	1,75	405	38,6	2,7 ± 0,5	197 ± 19

3.2- Activities in 1983

In view of the so-far gained experience, a few modifications were effected in the design of the existing lab. model processing equipment. For easy handling and temperature control, the existing stabilization furnace was cut into two. UNIDO supplied trios were introduced in between the furnaces for easy controlling of the movement of the fiber during processing. The modified versions are shown in Fig.7 and 7A which also include the winding equipment supplied by UNIDO.

Meanwhile CTA/PMR has built a new building for the carbon fiber group, the oxidation and carbonization processing equipment was assembled in line for the continuous processing in the new building.

In view of the several of the experiments conducted by the group and due to availability of useful results, I inspired the group to present the results in the American Carbon Society in 1983 in San Diego. The group and myself identified the subject and more vigorous studies were conducted on these lines. Also the expert Th.Mueller was very much helpful in this venture. Prof. Fitzer had also encouraged the group. This is for the first time the CTA/PMR Carbon Fiber Group presenting results in an outside Conference. In view of these effects, a paper was presented. The results were appreciated by the participants in the Conference.

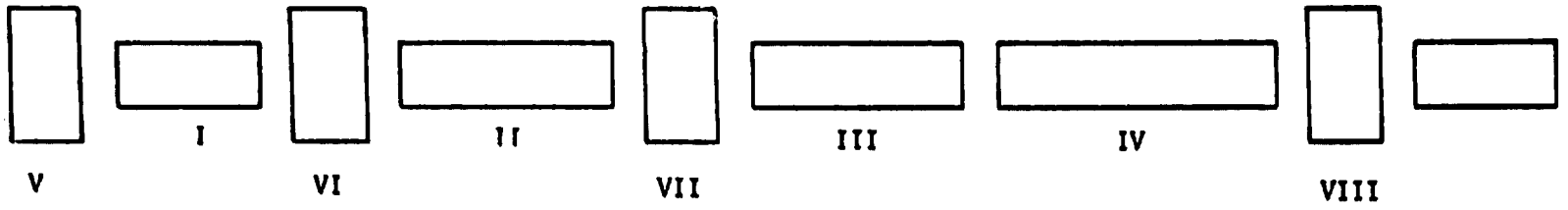
3.3- Activities in 1984

i - Studies in Heat Treatment

As per the advice of the expert Dr Kalnin, experiments were conducted by modifying the processing conditions. The main aspect of these studies were modified stabilization temperatures. Stabilization studies were conducted at three stabilization temperatures, ie, 220-230°C, 250-270°C and 270-300°C. From these studies it was observed that closer the individual furnaces, better properties were obtained. DSC experiments were conducted at every stage of heat treatment. Some of the results using three stabilization experiments are presented in Table 16 and Figures 8 and 9.

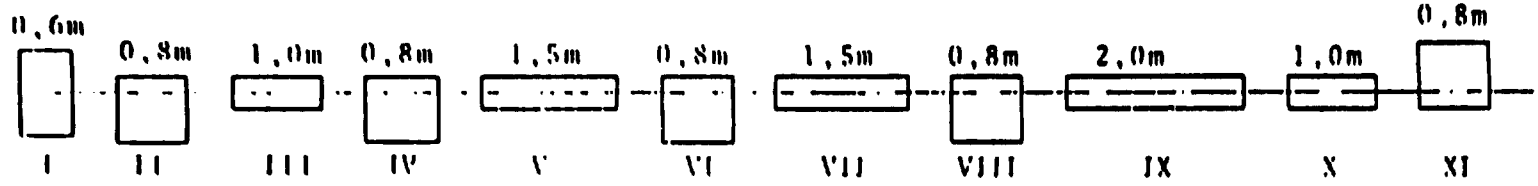
In order to explore the additional oxidants, studies were conducted

FIGURE 7 - LINE DIAGRAM OF PROCESSING EQUIPMENT USED FOR RESULTS IN TABLE 16, FIGURES 8, 9.



I, II, III - Stabilization furnaces
IV - Carbonization furnaces
V, VI, VII, VIII - Trios
IX - Bobbin

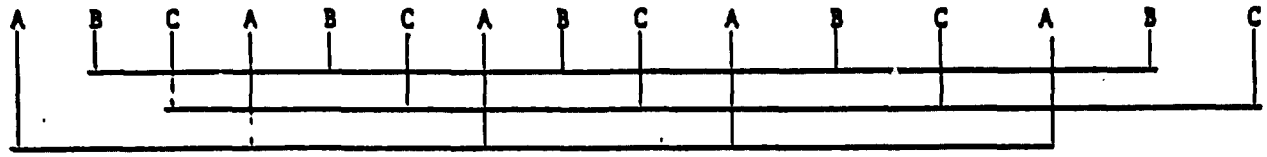
FIGURE 7A - NEW INSTALLATION OF CARBON FIBER PROCESSING EQUIPMENT



I - P.A.N.
II - Trio nº 1
III - pre-stretching
IV - trio nº 2
V - stabilization furnace nº 1
VI - trio nº 3
VII - stabilization furnace nº 2
VIII- trio nº 4
IX - pre-carbonization furnace
X - carbonization furnace
XI - winding

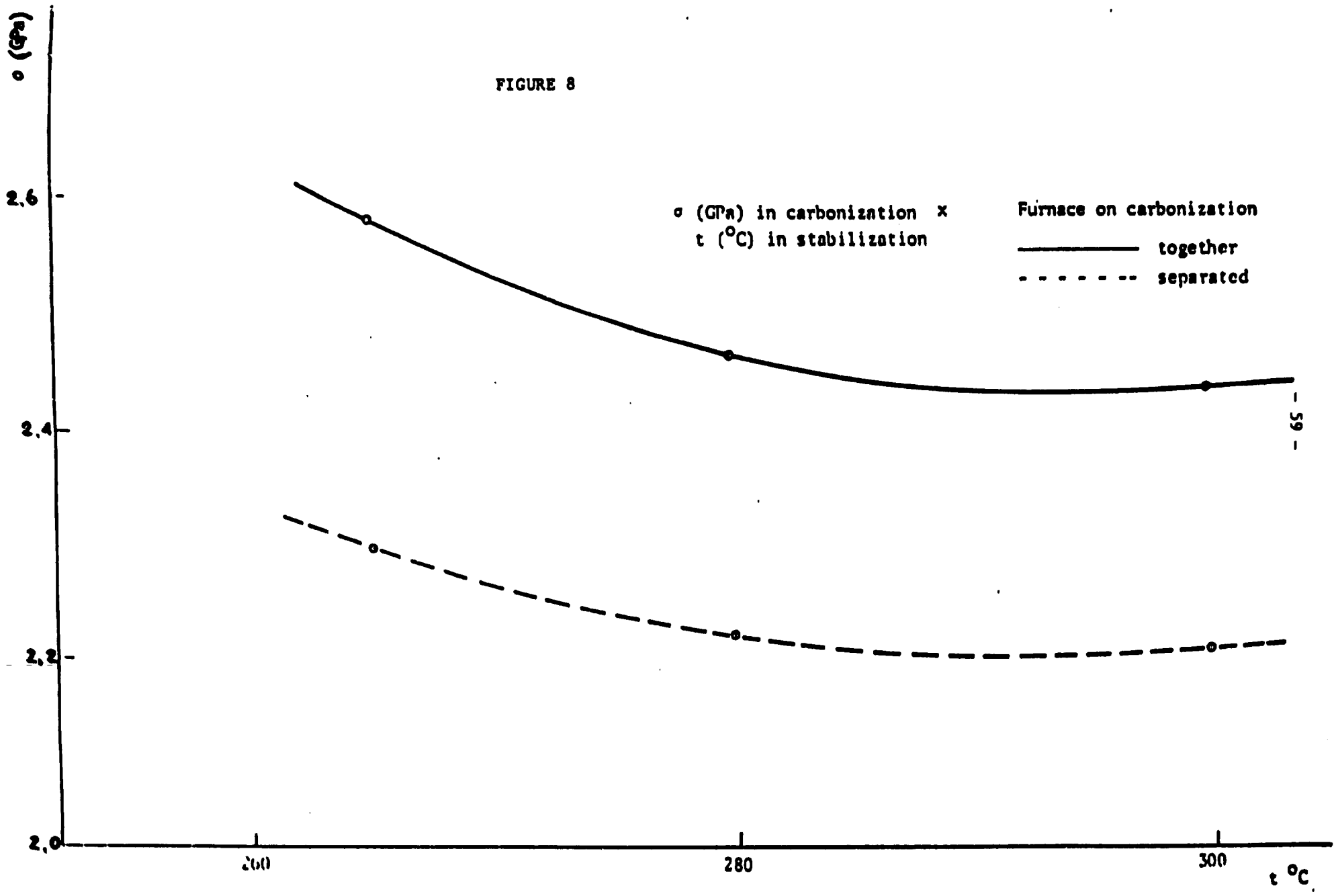
TABLE 16 - RESULTS OF CARBONIZATION USING 3 STAGES STABILIZATION

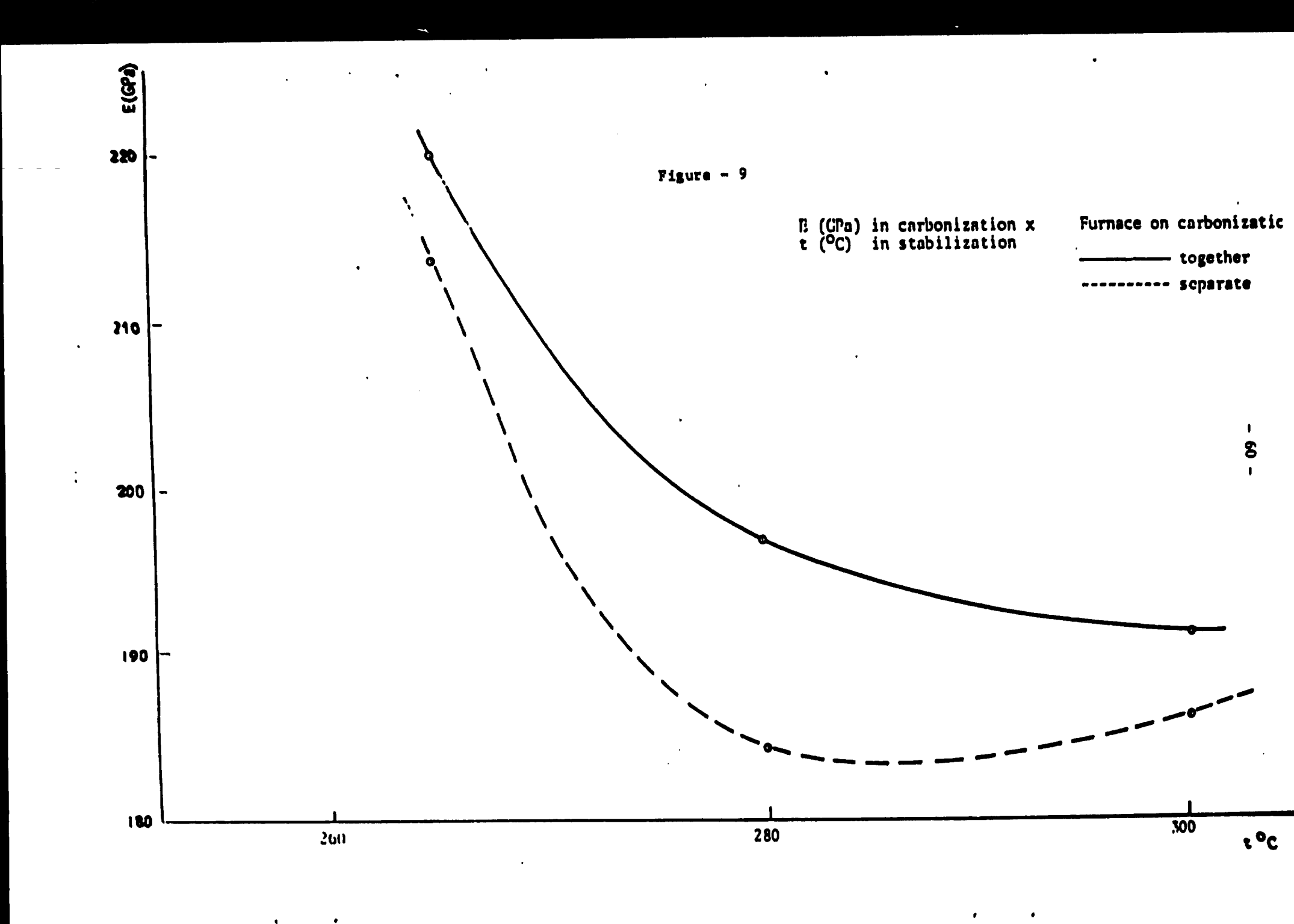
	STEP I			STEP II			STEP III			STEP IV					
										TOGETHER			SEPARETED		
Temperature °C	200_A	200_B	240_C	230_A	230_B	280_C	265_A	280_B	300_C	1.100_A	1.100_B	1.100_C	1.100_A	1.100_B	1.100_C
Linear density (mg/m)	676	676	723	708	708	732	718	704	697	382	351	350	371	344	356
Volume density (g/cm^3)	1,22	1,22	1,36	1,38	1,38	1,46	1,45	1,48	1,51	1,14	1,72	1,72	1,72	1,70	1,76
JSC Test (°C)	217	217	245	255	255	310	*	*	*	-	-	-	-	-	-
tm (°C)	308	308	328	343	343	350	*	*	*	-	-	-	-	-	-
Δh (°C)	2,79	2,79	0,763	0,550	0,550	0,210	*	*	*	-	-	-	-	-	-
Young's modulus (GPa)	10,6	10,6	7,2	8,34	8,34	6,47	9,32	9,12	9,05	220	197	192	214	184	187
Tensile strength (GPa)	0,58	0,58	0,31	0,35	0,35	0,21	0,24	0,22	0,21	2,58	2,47	2,39	2,30	2,22	2,31



* Complete

FIGURE 8


σ (GPa)
2,6
2,4
2,2
2,0
σ (GPa) in carbonization ×
t (°C) in stabilization
Furnace on carbonization
together
separated
280
300
t °C


E(GPa)
220
210
200
190
180
280
300
t °C
Figure - 9
E (GPa) in carbonization x
t (°C) in stabilization
Furnace on carbonizatic
together
separate

using NO_2 as the oxidants. It was observed that NO_2 stabilization did not improve the physical properties. These results were presented in Carbon 84 Conference in France

ii - Activities in Oxidized Polyacrylonitrile (PAN-Ox)

PAN-Ox is a good substitute for Asbestos. It is a heat resistant material and has several of industrial applications. Some of the companies which participated in the Conference at CTA were interested to use oxidized polyacrylonitrile fiber as thermally resistant materials. A company ASBERIT has tested CTA PAN-Ox material and were pleased to inform us that it can be used and they have a demand of 60 ton per year. The physical properties of this PAN-Ox are given in Table 17. As per the requirement of the ASBERIT company about 3.0 Kg of the processed PAN-Ox fiber were sent for testing at ASBERIT Co.

TABLE 17 - PHYSICAL PROPERTIES OF CTA OXIDIZED FIBER

Fiber nº	: CTA PAN OX-1
Tensile strength	: 0.175 GPa
Modulus	: 6.577 GPa
Density	: 1.498 g/cm^3
Denier	: 1.0888
Elongation	: 10%
Nº of filaments	: 18000
Tenacity	: 1.3 gm/denier
	1.29 gm/dtex
Breaking strength	: 1.57 gm
Filament dtex	: 1.2088
Heating temp.final	: 300°C, (first 230)
Residence time	: 120 minutes

4.0 - Developmental Activities in Surface Treatment

Surface treatment of carbon fibers is very important to form good composite with resin. The bonding of resin to the fiber depends mainly on the groups present on the surface of the carbon fibers. Poor bonding results, poor properties in final composites. The surface treatment to carbon fiber is done by different methods. For example, electrolytic oxidation, acid treatment alkali electrolysis, thermal oxidation, etc. In our group we have initiated surface treatment by electrolytic process .

4.1 - Activities in 1982

At the time of my arrival, a few experiments were already conducted using nitric acid for the surface treatment of the carbon fibers. Due to non availability of uniformly processed carbon fiber, the developmental activities were postponed. However, attempts were made to acquire the materials and personnel for this development.

4.2 - Activities in 1983

With the formation of a group in surface treatment, the activities restarted. Anodic oxidation equipment was assembled by the CTA group in view of the information and assistance given by UNIDO experts, a few surface treatment experiments were conducted using CTA processed carbon fibers. A 20% surphuric acid was used as the electrolyte. About 125 meters of the fiber was surface treated. Unidirectional composites were made using epoxy resin DER 383 (Dow) and curing agent DEH 50 (Dow These composites were tested. In the subsequent experiments, the graphite electrode used earlier was replaced. Modifications were made using glassy carbon tube made out of polyperfural alcohol resin in CTA. Also subsequently several other modifications were made in the electrolytic cell. Also the experimental conditions such as currant density, electrolyte were changed and several of the experiments were conducted. Meanwhile, it is felt that we should get untreated carbon fibers from a commercial firm and surface treat them in order to standardize the surface treatment work. In view of our latest contacts with RK Textiles UK, sample of the untreated carbon fiber was obtained and surface treated with improved parameters. The Tables 18, 19, 20, 21 and 22 show some of the results of surface treatment.

TABLE 18 - TYPES OF FIBERS USED FOR SURFACE TREATMENT

SAMPLE	TYPE OF FIBERS
1	PMR 428
2	PMR 429
3	PMR 432
4	SIGRAFIL
5	RK

TABLE 19 - DENSITIES OF SURFACE TREATED AND UNTREATED FIBERS

SAMPLE	NON SURFACE TREATED g/cm^3	SURFACE TREATED g/cm^3
1	1,75	1,78
2	1,75	1,76
3	1,75	1,79
4		1,78
5	1,74	1,74

TABLE 20 - PROPERTIES OF SINGLE FILAMENTS

SAMPLE	TREATMENT	TENSILE STRENGTH (GPa)	MODULUS E (GPa)
1	NT	2,4	190
	T	2,19	171
2	NT	2,4	190
	T	3,1	186
3	NT	2,7	190
	T	2,56	188
4	T	2,34	196
5	NT	3,25	222
	T	2,20	212

NT = Non-surface treated

T = Surface treated

TABLE 21 - PROPERTIES OF CARBON FIBERS/EPOXY RESIN COMPOSITES (VOLUME FRACTION: AROUND 60%)

SAMPLE	TREATMENT	FLEXURAL STRENGTH FS (MPa)	MODULUS E (GPa)
1	NT	1121	70
	T	988	80,5
2	T	973	79,5
3	NT	1614	117,5
	T	1100	81,2
4	[illegible]	1520	123,7

Table 22- INTERLAMINAR SHEAR STRENGTH - ILSS

SAMPLE AND TREATMENT	ILSS (MPa)
2 T	45,3
3 T	42,0
4 T	54,1
5 NT	41,1
5 T (step 1)	4[illegible],8
5 T (step 2)	46,3
5 T (step 3)	40,6
5 T (step 4)	50,5

(Steps 1 to 4 = different current densities)

4.3 - Activities in 1984

i - Pilot Plant Surface Treatment Apparatus

Eventhough currantly batch scale surface treatment work is going on in order to fix the surface treatment parameters, the final objective is to introduce a surface treatment equipment in line with the carbonizatic processing equipment. Such as equipment should be able to process 6 K tow at the rate of 1 to 30 m/h. After a detail analysis a cell was designed. Contacts were also made with local companies for the construction of this cell. This cell after completion will look like figure 10.

ii - Sizing

An equipment has been fabricated for the sizing of the surface treated carbon fibers. This will also go on line in the total carbonization equipment. A few batch scale experiments were already performed for sizing using 2% epoxy resin DER 757 (Dow) dissolved in acetone.

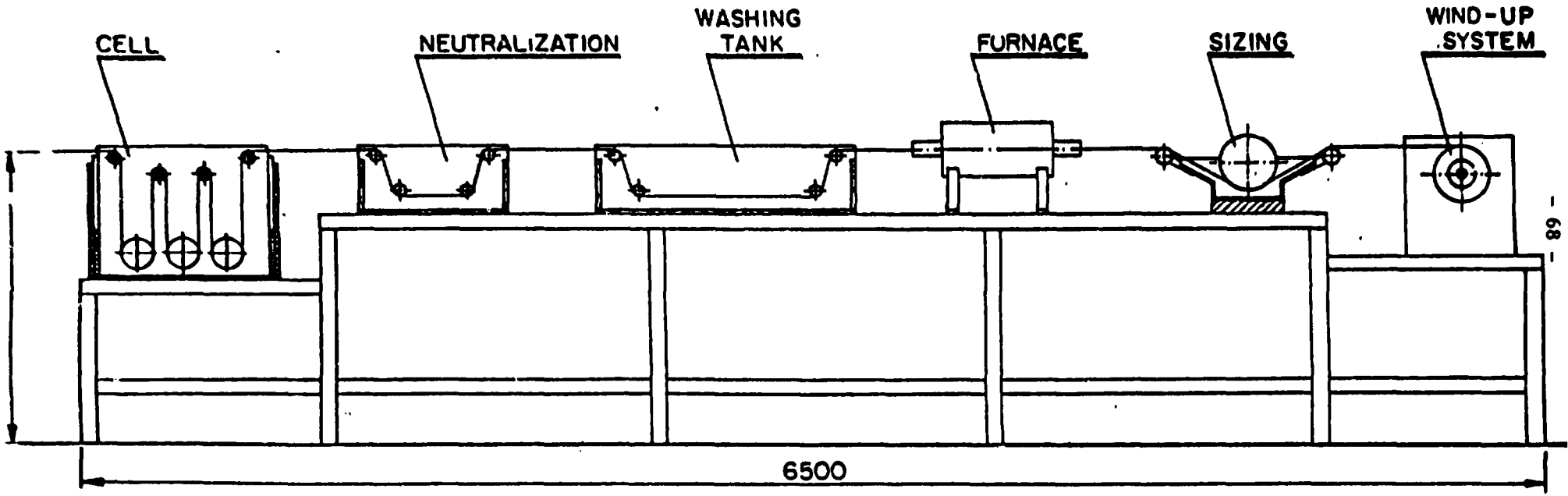


Figure 10- LAY-OUT OF THE CARBON FIBRE PILOT PLANT SURFACE TREATMENT UNIT

ENCLOSURE 2

Drive shafts, wheels, brakes, rear axel housing, gears, rear axel transmission housing, for chasis and suspension such as leaf and coil spring, frames torsion bars, upper and lower arms, for the engine connection rods, push rods, pump housing, cover plates in take manffold cylinder block, fly wheels and for the body sheet and structure, panels, pillars, stressed skin design, etc. Weight reduction in automotive industries will save fuel consumption. In case of substituing steel up to 50%, in case of aluminum 40%, in USA, a total gasoline savings of 7 billion gallons is forecasted for 1990.

Carbon fibers also find application in acoustic instruments, such as loud speackers and in musical instruments. Loud speakers with CFRP cone are available in Japanese market. Violins and guitars built bu using CF epoxy sound board, are found to be superior over conventional ones.

Further applications are portable bridges, which could be used in case of devastation by floods, storms, etc., wind channels, windmills and air compressor, in transportation and as substitute for asbestos, bicycle frames, ski poles, down hill skis, endurance car, economy cars, etc. Activated carbon fibers are also finding applications in filters, substituing the powdered or granulated activated carbon.

CTA EXPERIENCES IN CARBON FIBERS

Centro Técnico Aeroespacial (CTA) started the developmental activities in carbon fibers in 1976 on laboratory scale with the objectives of developing self-reliance in this fast developing and industrially potential technology. After a period of 4 years, CTA achieved the following :

Evaluated the locally available precursor fibers.
Developed a continuous process to oxidize and carbonize the precursor fibers.
Designed and produced critical parts of the furnaces.
Developed carbon fibers with reasonable properties though not equal to those of imported.
Characterized precursor fibers and carbon fibers.
Above all, created a nucleus for the development of this technology.

There was a necessity of a comprehensive program, which sould include :

Modifying procedures for stabilization and carbonization.
Purchasing new equipment for heat treatment and precursor spinning.
Acquiring expertise to guide the group.
Training the counterpart scientists in this technology elsewhere in the world.
Exchanging views with the experts in this field.
Redesigning the existing furnaces.
Training the counterparts in the characterization of the fibers.

Hence, a project on "OPTIMIZATION AND DEVELOPMENT OF CARBON FIBERS TECHNOLOGY" was drafted and was approved and signed by CTA/UNIDO/UNFSSTD on 18/05/81 with a duration of 3 years. The main objectives of this project were :

To create a scientific nucleus to produce fiber precursors, carbon fibers, CFRP composites and to develop the technologies involved.
To optimize the continuous process of carbon fiber making and to extend to the pilot plant scale.
To generate information to produce precursor fiber and to transfer it to production line.
To complete the minimum infra-structure required for the projetc.
Special considerations : To cooperate in exchanging views in this field liberally with others developing countries.

The proposed outputs for the project were as follows :

AR & D team capable of understanding, absorbing and adapting this technology used in other countries and to further improve this technology, and to conduct R & D work in similar other areas.
Technology to produce carbon fibers, using national raw materials and the transfer of this technology to Brazilian industry.
Techniques and scientific capabilities to test the raw materials as well as final products.
Infra-structure facilities for PAN spinning, carbon fibers surface treatment, surfaces for carbonization, equipment to characterize fibers, DTA, X-ray, microscope, etc.

After a period of 2 1/2 years, most of the outputs were achieved as

discussed in the Tripartite meeting of this project held on 2nd Dec 1983. A summary of the achievements are outlined below:

In view of the excellent experts who consulted the project from the start of project till now, a gradual growth in a steady thinking and development in R & D aspects of this technology was achieved.

At the start of the project, the CTA group was using one step oxidation and one step carbonization (Figure 1). The best results of carbon fiber processing using such a system are presented in table 1. However, the fibers used were poor grade textile fiber of FISIBA - FIBRAS SINTÉTICAS DA BAHIA S/A.

As the technical competence of the counterpart scientists was improving in view of their study tours to outside travel and continued advises of the UNIDO experts, the Figure 1 was further modified. The modified versic is represented in Figure 2 which has two steps oxidation processing. This modified version was further modified into 3 steps oxidation (including pre-stretch, pre-oxidation and oxidation steps) (Figure 3).

Also Figure 3 represents additional modifications in carbonization stage Hitherto one step carbonization was used, but the temperature was only 1100°C. In order to get carbon fibers with commercially comparable high strength fibers as temperature of 1400°C is advised. Hence, attempts are being made to use two stage carbonization, ie 900°C and 1400°C.

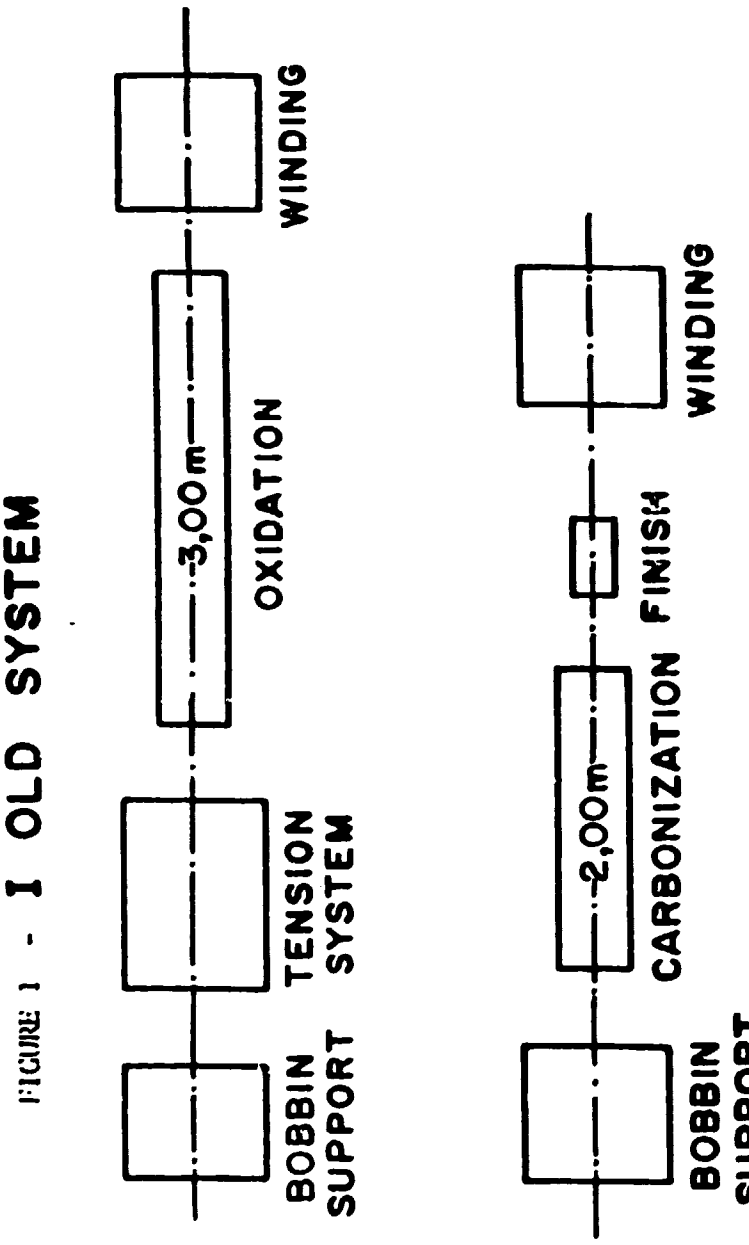


FIGURE 1 - I OLD SYSTEM

FIG. 2 - II MODIFIED OLD SYSTEM

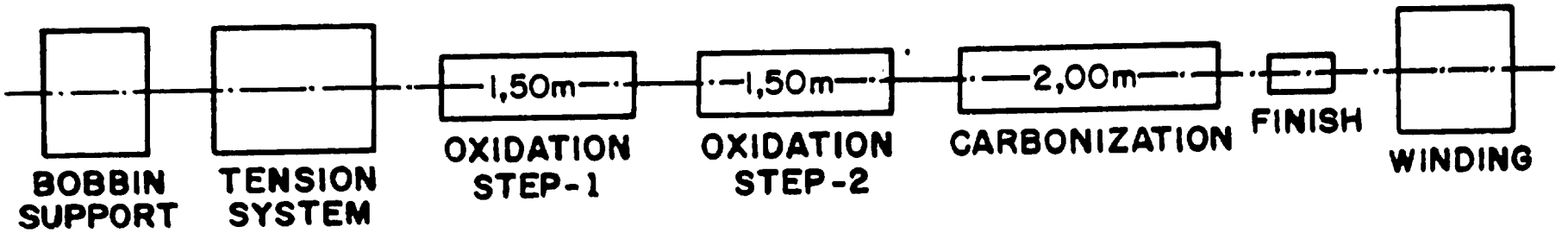
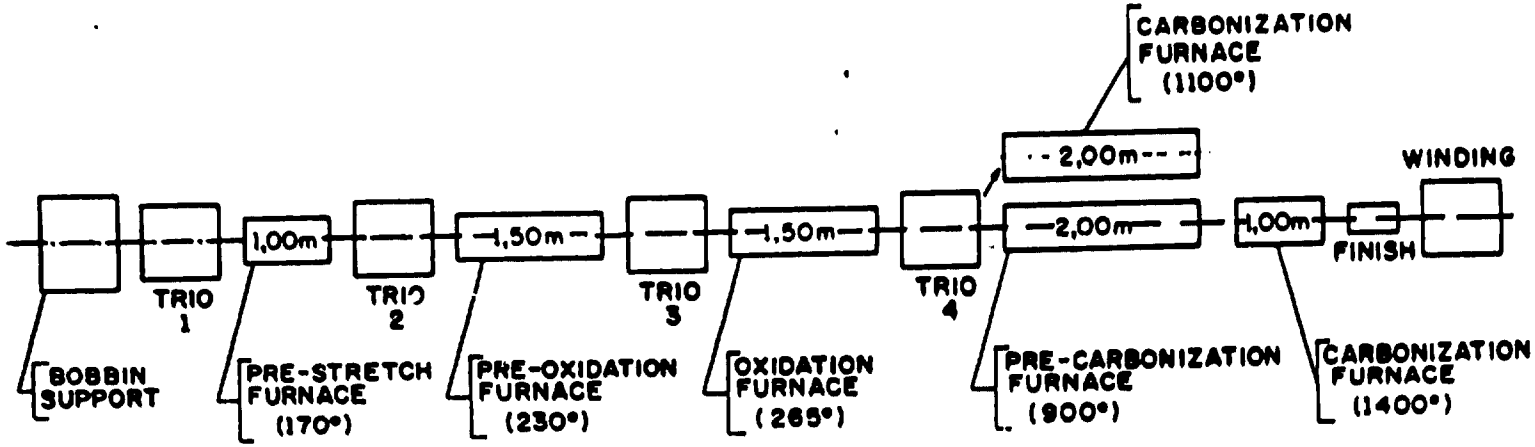


FIGURE 3 - THE PRESENT SYSTEM



ENCLOSURE 3

ACTIVITIES CONDUCTED IN 1985

This section describes, in detail, the activities conducted in the whole Project, in 85.

Project Item iii.a

POLYMERIZATION

Polymerization experiments were conducted under the following processing conditions:

pH, monomers concentration and quantity, dilution in aqueous media, temperature, reaction time, stirring velocity and monomer addition velocity.

The first tentatives were performed in a reactor with the capacity of 1 l. Further experiments were conducted in reactor with the capacity of 10 l.

Redox system: Amonium persulfate and sodium bissulfite.

Monomers: Acrylonitrile, Methyl acrylate and Itaconic acid.

A view of the polymerization laboratory is shown on photo 1.

Photo 1. VIEW OF THE POLYMERIZATION LABORATORY

SPINNING

Some modifications were inserted in the process, to improve the deviations of properties average values, and a better controle upon the filaments.

The dispersion preparation was also improved, with an accurate control of viscosity.

Better results, however, must be achieved.

Photos 2, 3 and 4 show aspects of this work.

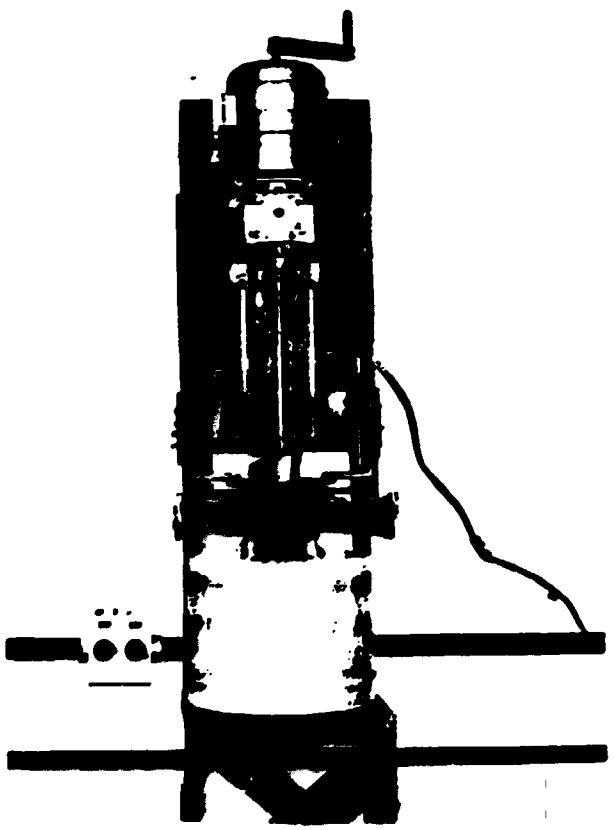


Photo 2. DISPERSION MIXER

HEAT TREATMENTS

Laboratory-scale line.

The following opperation were conducted :

a. Obtention of carbon fibres, delivered to the ORTHOPAEDICAL DEPARTMENT of the MEDICAL SCHOOL - UNICAMP.

b. Obtention of carbon fibres to be used as reinforcement in carbon-carbon composites.

c. Obtention of carbon fibres for surface treatment experiments.

d. Obtention of PAN-OX (oxidized fibres) to be used in the opperation of the pilot-plant RUHSTRAT carbonization furnace.

e. PAN oxidation and carbonization using hydrogen peroxide as oxidizing agent. In determined conditions, the characteristics of the fibres were improved. These results will be presented in the CARBON INTERNATIONAL CONFERENCE - 1986.

Photo 5 shows a view of the lab scale line.

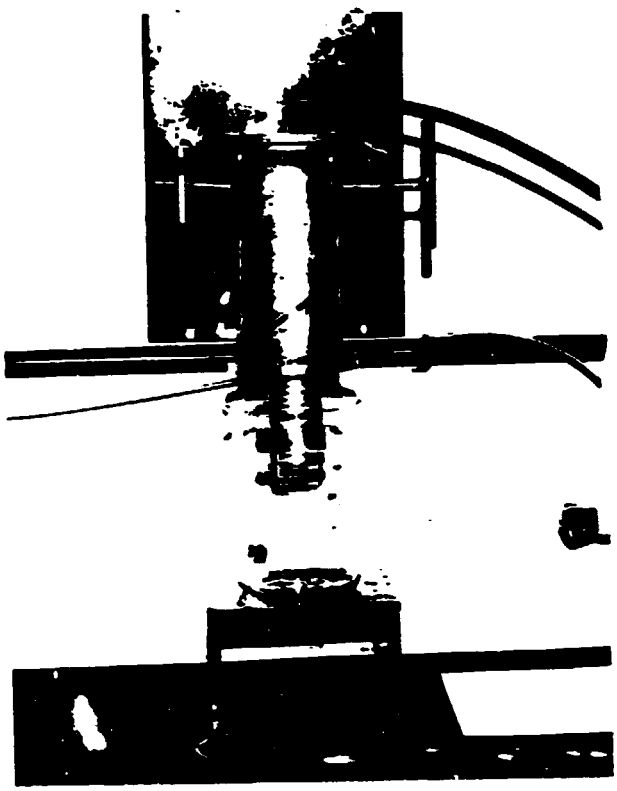


Photo 3. PNEUMATIC FILTER

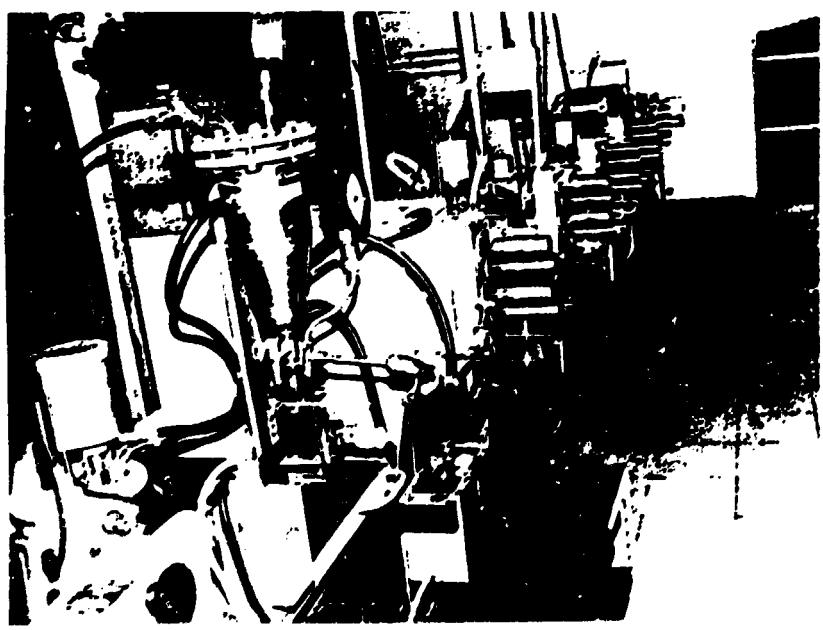


Photo 4. LABORATORY UNIT FOR SPINNING

Photo 5. LABORATORY SCALE LINE, FOR CARBON FIBRES OBTENTION.

PILOT-PLANT

THE SANTA CLARA STABILIZATION OVEN

The company MAQUINAS TEXTEIS SANTA CLARA LTDA, S. Paulo, concluded a stabilization three zones oven, for continuous oxidation of PAN. This oven is able to opperate 80 (eighty) 6K tows simultaneously.

During the testing procedures this oven has shown a great heat lost through the external structure.

Efforts has been done by SANTA CLARA and the Project staff, to solve this problem; with the introduction of some modifications.

Photo 6 shows the aspect of this equipment.

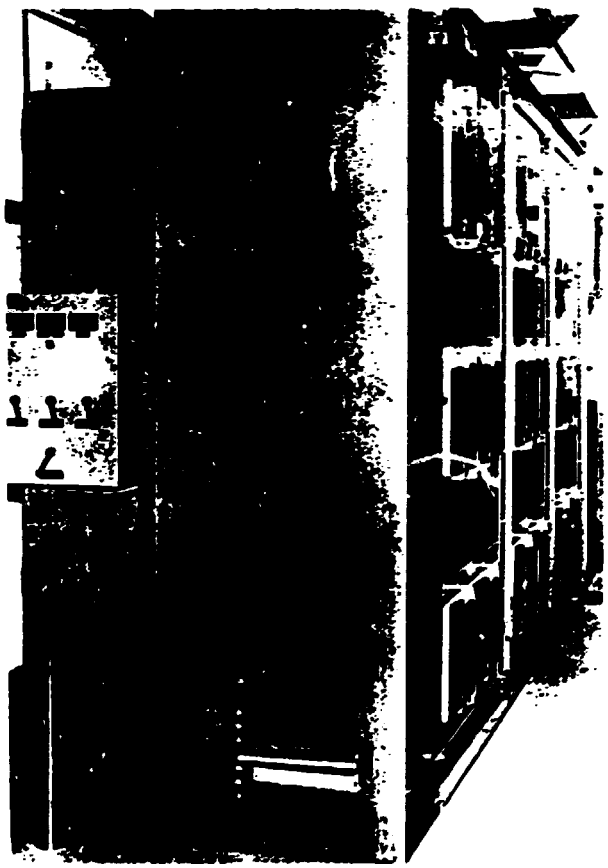


Photo 6. FRONT VIEW OF SANTA CLARA STABILIZATION OVEN.

THE RUHSTRAT CARBONIZATION FURNACE

Two experiments were performed, as follows :

a. Carbonization of tows oxidezed in the laboratory scale line.

b. Carbonization of PAN-OX heavy tow, from SIGRI ELEKTROGRAPHIT GMBH.

The experiments, however, were stopped, due to the occurrence of problems with the furnace (see the next item).

Problems and resolutions :

Since the opperation was started, a strong and quick oxidation of heating elements and overheating of the second transformer were detected.

During his STUDY-TOUR, Eng JOÃO RENATO has discussed such troubles with the experts, at Karlsruhe University. A visit to SIGRI ELEKTROGRAPHIT GMBH, Meitingen, Germany, was also arranged for the discussion of these problems with the furnace builders.

On Sept 26, 1985, a meeting at SIGRI ELEKTROGRAPHIT GMBH was carried out, with the following persons :

Mr. YOGELSANG, Mr. GROSS, Dr. BODER (SIGRI), Mr. HARTMANN (RUHSTRAT) and Mr. HEINE (University of Karlsruhe).

Decisions and Recomendations :

During this meeting, a schedule for the furnace maintenance was decided, to be conducted by the Project staff as follows :

Furnace body :

a. Open the top, taking out all graphite wool (thermal insulators) carefully, looking for corrosion inside.

b. Look for any hole in the cooling boxes.

c. Check all connections along the water cooling system, looking for any leakage, through a slight air pressure in the water cooling line.

d. After these procedures, clean the furnace inside carefully.

e. When assembled again, use only original heating elements from SIGRI.

f. Start the heating slowly, with nitrogen, up to 200°C and keep it heated.

REMARK : SIGRI has already delivered the new heating elements.

Transformer :

a. The internal temperature is 120°C.

b. Measure the temperature on the secondray output wires, It must not be over 100°C.

c. Check the diodes and thyristor.

d. Contact EUROTHERM, in Brazil, if necessary.

REMARKS :

a. SIGRI will send a complete INSTRUCTION MANUAL of the RUHSTRAT furnace.

b. SIGRI will send. also, a quotation for the furnace maintenance, int the worst case.

NOTE.: This quotation was not requested yet.

MAINTENANCE OF THE RUHSTRAT FURNACE

According to the recomendations given during the meeting at SIGRI, the Carbon Fibre staff has performed the furnace maintenance.

The following parts were found with damage :

. Rubber syphons with holes (photo 7)

. Broken ceramic tubes (photo 8)

. Graphite wool insulators with severe oxidation (photo 9)

Letters were sent to UNIDO office (Brasília) and to SIGRI (Germany) requesting these spare parts , for replacement. (UNIDO refused to order the parts) because of budget reasons.

However, as the spare parts were not received yet, the maintenance was completed with materials available at PMR-IPD-CTA.

The following photos shows aspects of the furnace, under maintenance work.

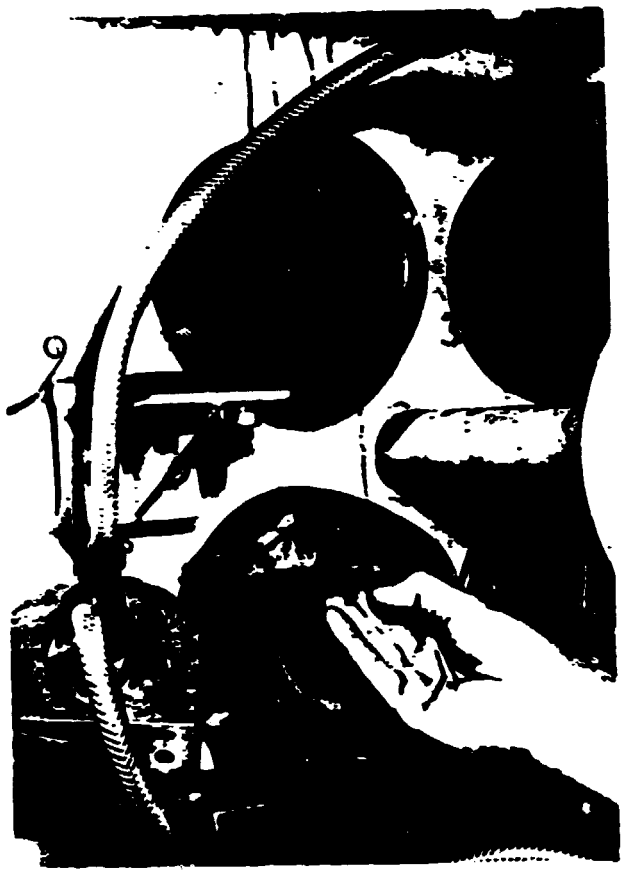


Photo 7. SYPHONS V6-643 WITH HOLES

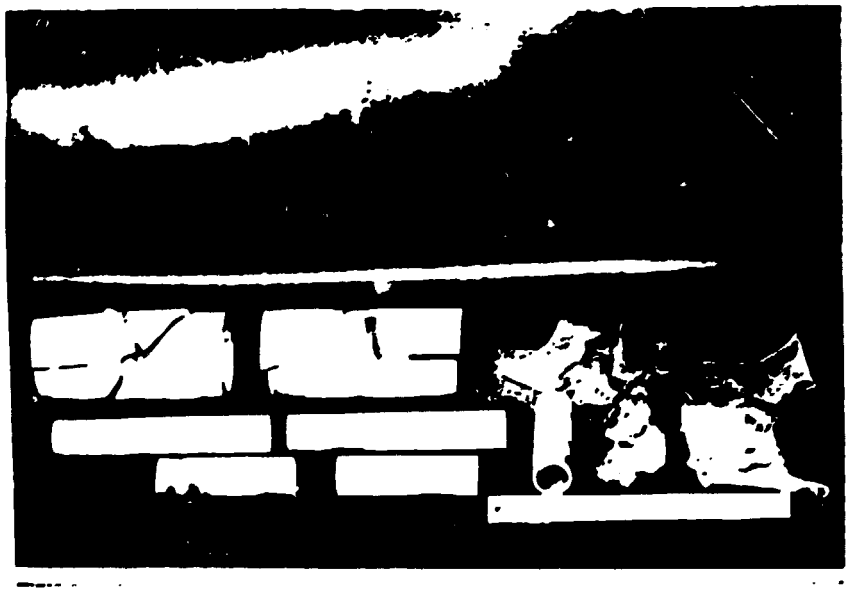


Photo 8. BROKEN CERAMIC TUBES

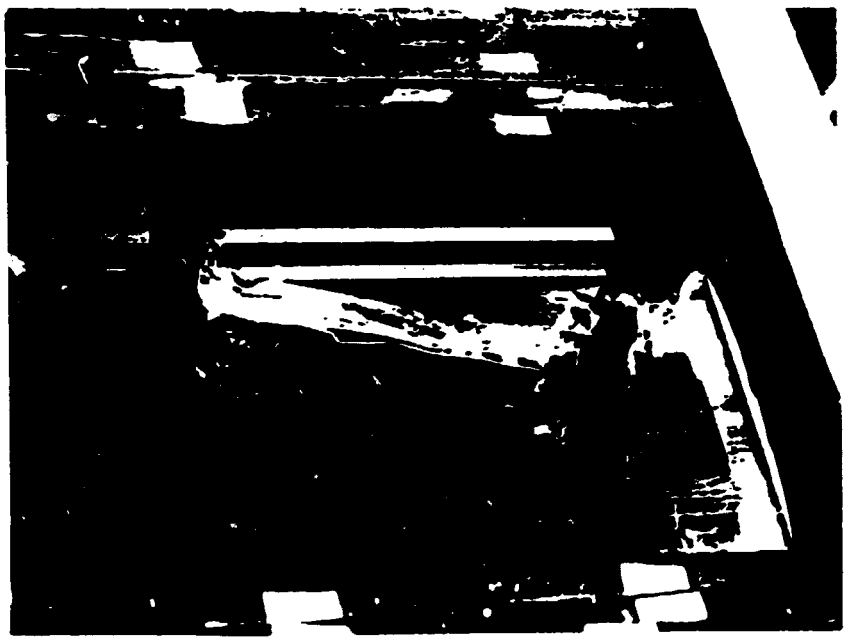


Photo 9. DETAIL OF A GRAPHITE WOOL PART, SHOWING SEVERE OXIDATION.

WIND-UP SYSTEM

A brazilian company was contacted, for supplying the wind-up system, for 20 (twenty) bobbins.

SURFACE TREATMENT

Laboratory Scale

A new lab scale surface treatment was made, to improve the experimental conditions. A PMMA cell (photo 10) and a washing tank with stirrer (photo 11) were constructed, able to opperate at higher velocity (30 m/h). The whole unit is shown on photo 12 .

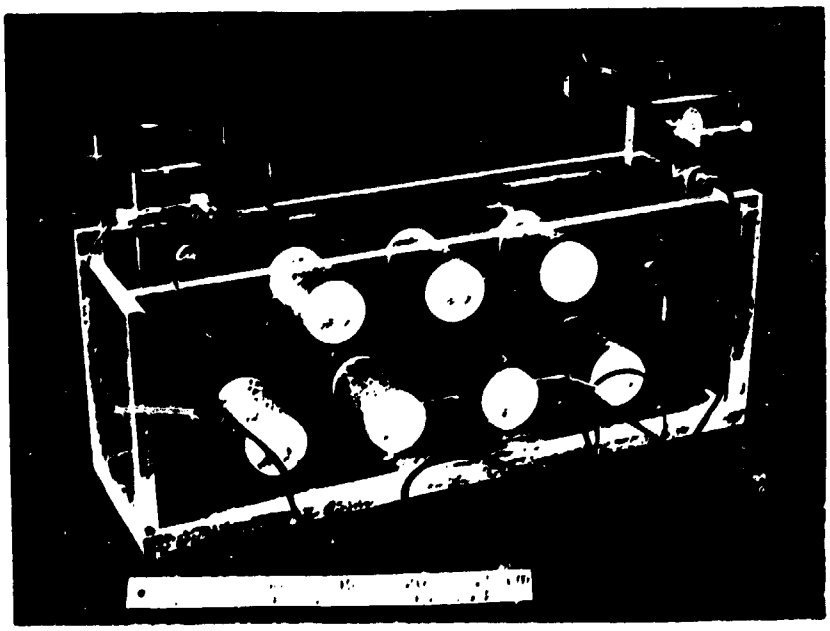


Photo 10. THE NEW LABORATORY ELECTROLYTHIC CELL, FOR ANODE OXIDATION.

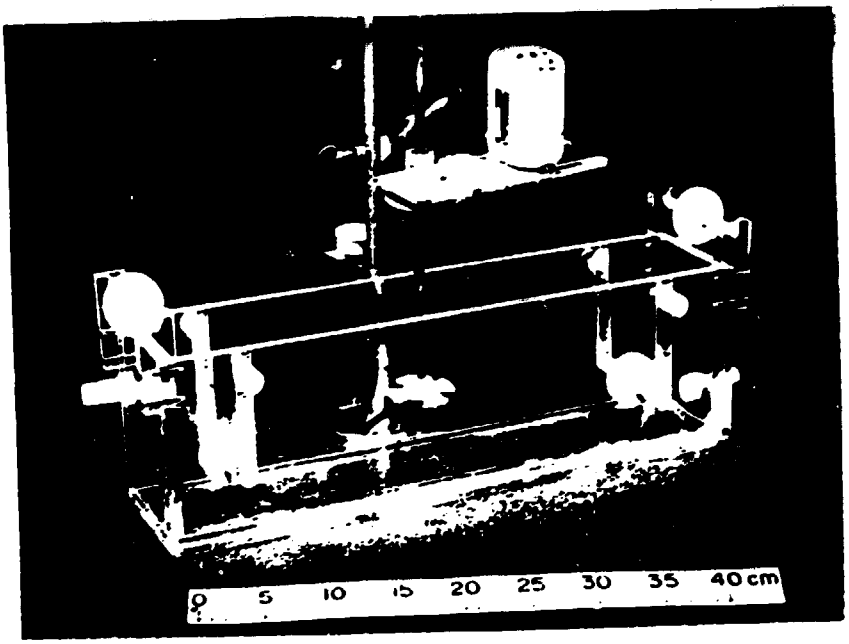


Photo 11 . THE WASHING TANK WITH STIRRER

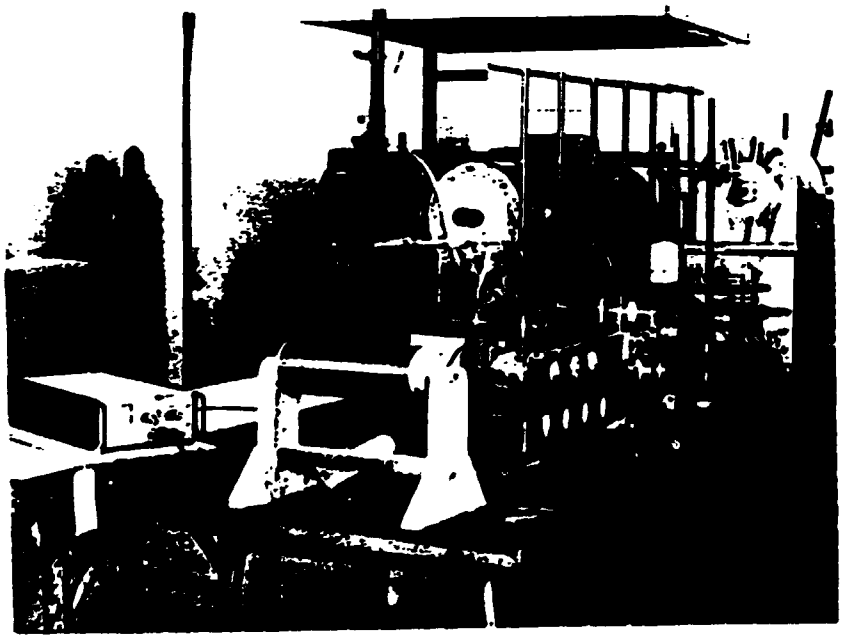


Photo 12 . GENERAL VIEW OF THE SURFACE TREATMENT LABORATORY.

SURFACE TREATMENT EXPERIMENTS

Surface treatments in lab scale line (photo 12) has been performed, in the conditions as follows :

Carbon fibres	:	PMR 18K
		HITEO MAT. DIV. 3K
Method	:	Anodic oxidation
Electrolyte	:	Water solution of $(NH_4)_2 SO_4$, 8,0%
Velocity	:	30 m/h
Residence time	:	2 min.
Current density	:	0,0275 mA/cm^2
Washing	:	Water, at room temperature
Drying	:	Furnace at 200^oC

A new dispensing device for untreated carbon fibre was made, to replace the existing one, allowing a continuous and smooth displacement of the carbon bobbin (photo 13).

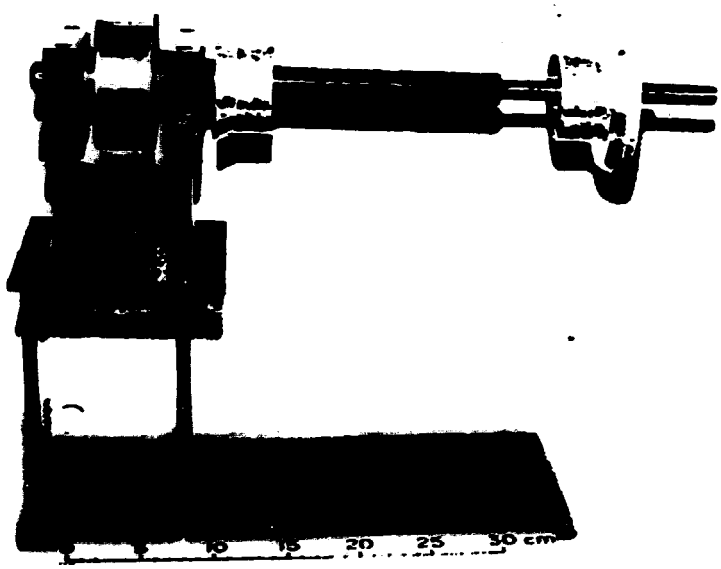


Photo 13 . THE TENSION CONTROLED REEL FOR DISPENSING UNTREATED FIBERS.

Helpful discussions were conducted with Dr. J. HARVEY (Royal Aircraft Establishment-England) and Mr. H. JAGER (University of Karlsruhe-Germany) concerning the surface treatment of carbon fibres, during Eng JOÃO RENATO's study-tour . These discussions brought a great benefit to the development of this task.

THE PILOT-PLANT SURFACE TREATMENT UNIT

The pilot-plant surface treatment is completed. This system consists of the following equipment :

a. Electrolythic cell, able to opperate in the velocity from 1 m/h, up to 60 m/h. 80 (eighty) carbon fibres tows may be treated in such all (photo 14).

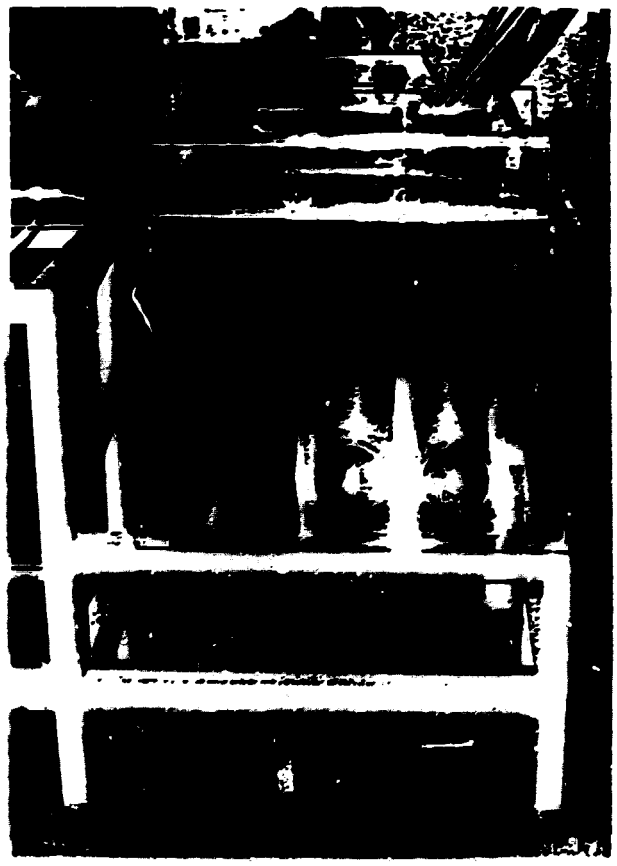


Photo 14. THE PILOT-PLANT SURFACE TREATMENT CELL.

b. Pre-washing tank (photo 15).

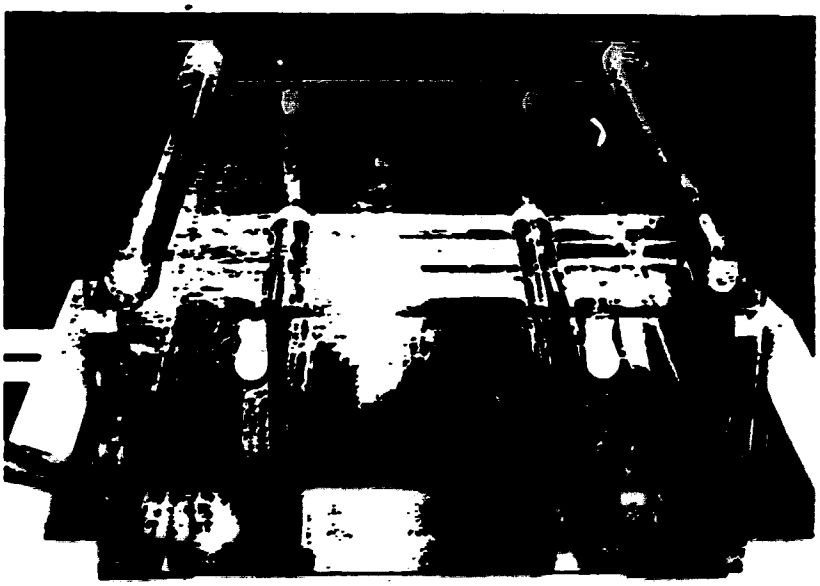


Photo 15 . PRE-WASHING TANK.

c. Washing tank with stirrers (photo 16).

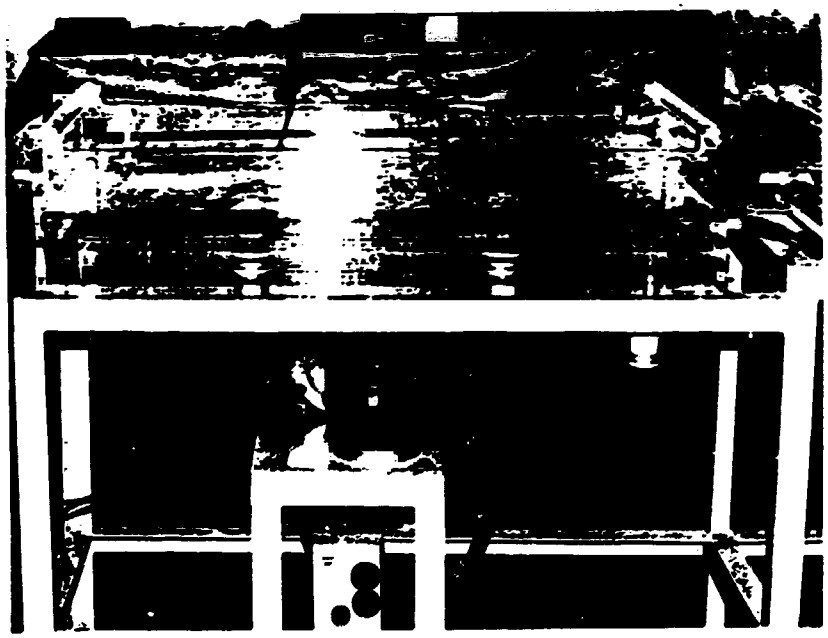


Photo 16 . WASHING TANK WITH STIRRERS

The vessels a, b and c were made with PMMA plates 16mm tick, all machined at PMR-IPD workshop. The soldering of PMMA pieces was made by IMAKE-INDUSTRIA E COMERCIO DE PRODUTOS PLASTICOS LTDA - São Paulo.

d. Drying Oven

The dryer oven uses 20 (twenty) PHILIPS infrared lamps (250W each one) as heating source. Sandwich structure (polyurethane foam and fiber-glass reenforced polyester) was used in main body (photo 17).

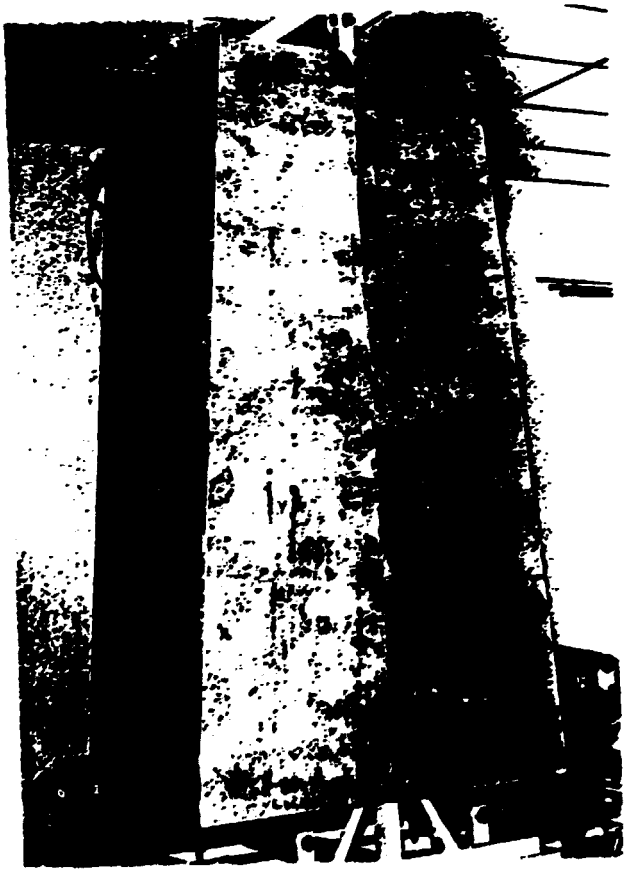


Photo 17 . . DRYING OVEN

e. Sizing Tank

A fiberglass reinforced polyester vessel was built for this purpose (photo 18).

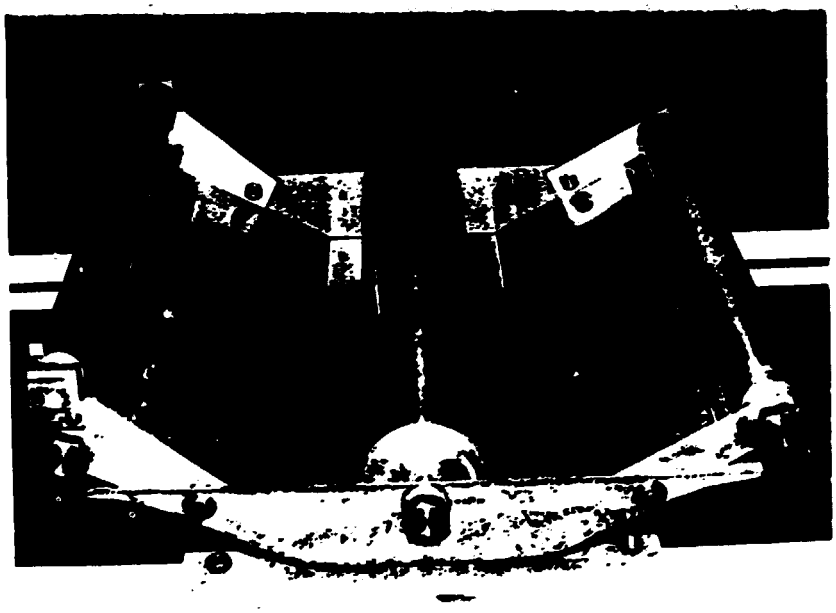


Photo 18. SIZING TANK.

f. Final Dryer

This last unit, basically similar to the dryer oven, employs 5 (five) infra-red lamps (250W) (photo 19). Its function is to eleminate the sizing solvent.

Photo 19 . FINAL DRYER

The equipments under items d, e and f were made by PMR's Composite Materials staff.

Photo 20. GENERAL VIEW OF PILOT-PLANT SURFACE TREATMENT UNIT.

EVALUATION OF SURFACE TREATMENT

The evaluation of surface treatment, up to date, has been carried out through the interlaminar shear strength (ILSS) determination, in carbon fibres reinforced epoxy composites.

The following epoxy systems has been used :

Dow DER 331/DEH 12

DER 331/DEH 14

DER 331/DEH 50

During his study-tour, Eng JOÃO RENATO could discuss these procedures with the experts, in detail. New resin systems, according to the expert's quidance, are being used. The systems under experiments are :

CIBA GEIGY MY 720/DDM

MY 720/DDS

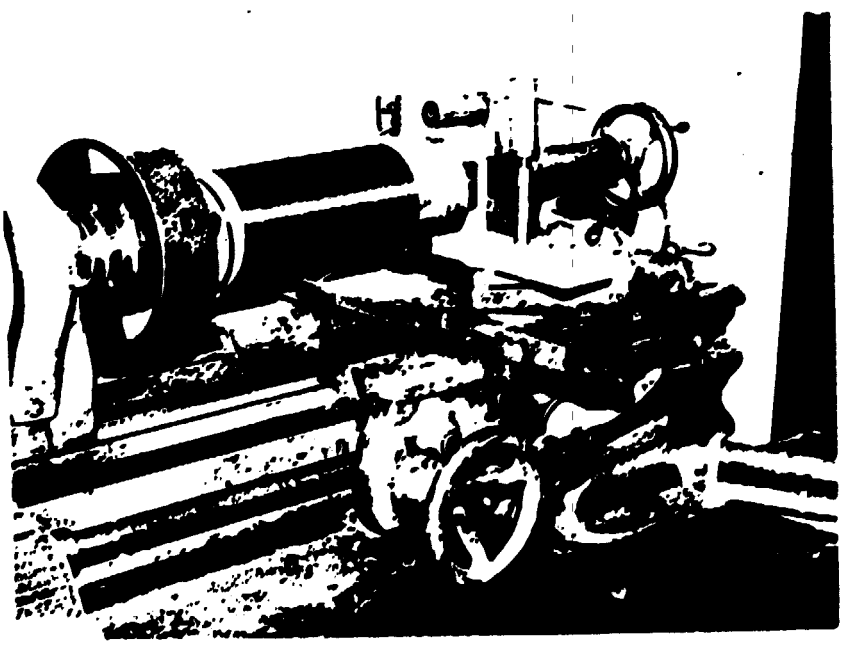


Photo 21. PREPEG MANUFACTURE

OUTPUTS

This section discribes the results obtainedin 1985.

POLYMERIZATION

The tables below shrw the results of a polymerization experiment.

Synthesis No 58

Acrylonitrile : 95%

Methyl acrylate : 3%

Itaconic acid : 2%

Capacity of the reactor : 1ℓ

EFFLUX TIME			VISCOSITY		
c%	No	Ns	Nr	Nsp	Nsp/c
0,2	11,0	15,6	1,418	0,418	0,209
0,3	11,0	16,6	1,509	0,509	0,169
0,4	11,0	17,5	1,609	0,609	0,127
0,5	11,0	19,5	1,772	0,772	0,154
0,6	11,0	26,2	2,381	1,381	0,230
M.w. 56.599,614					

e : concentration

No : efflux time of the solvent

Ns : efflux time of the solution

Nr : relative viscosity

Nsp : specific viscosity

Nsp/c : reduced viscosity

ELEMENTAL ANALYSIS		DSC				
C%	S%	HEATING RATE	PEAK TEMP.	DATA CORRELATION	N	ρ
68,87	0,545	8,7 13,6 19,6 24,0	547,50 558,00 567,00 570,00	99,38%	1,0170	1,210

C% : carbon content

S% : sulphur content

N : reaction order

ρ : density

SPINNING EXPERIMENTAL RESULTS

POLYMER	TENSILE STRENGTH (GPa)	MODULUS (GPa)	ELONGATION %	TENACITY (g/den)	DENSITY (g/cm^3)	VISCOSITY (cp)	FILAMENT DIAMETER (μm)
FISIBA	0,25-0,30	7,5 -8,25	3,0 -3,9	2,41-2,73	1,15-1,17	15.500-17.250	9,85 -17,20
PMR/CTA	0,17-0,18	4,31-4,86	3,44-4,28	1,58-1,77	1,17-1,19	1075-17.000	11,00 -20,07
COURTAULDS	0,70	9,93	7,19	6,70	1,19	-	11,72

HEAT TREATMENT

LABORATORY SCALE LINE

CARBON FIBRES PROPERTIES

OPPERATION	a	b	c
K	6	36	6
TENSILE STRENGTH (GPa)	2,8	3,0	3,0
MODULUS (GPa)	210	210	210
DENSITY (g/cm^3)	1,76	1,77	1,77
FILAMENT DIAMETER (µm)	7 - 8	7 - 8	7 - 8

K = No of filaments per tow x 1000

PROPERTIES OF PAN-OX

K	108
DENSITY (g/cm^3)	1,39

THE RUHSTRAT CARBONIZATION FURNACE

PROPERTIES OF CARBON FIBRES

OPPERATION	PAN FROM PMR/CTA	PAN FROM SIGRI
K	108	320
TENSILE STRENGTH (GPa)	3,0	3,0
MODULUS (GPa)	210	210
DENSITY (g/cm^3)	1,77	1,76
FILAMENT DIAMETER (µm)	7 - 8	7 - 8

SURFACE TREATMENT

The following table shows a result of ILSS, in a laminate manufactured with the resin system DER 331/DDM and carbon fibres from HITEO MATERIALS DIVISION (3K). These fibres were treated in the lab. scale unit, under conditions mentioned in this report.

SPECIMEN NUMBER	DENSITY (g/cm^3)	ILSS Kgf/mm^2
1	1,54	7,62
2	1,60	7,16
3	1,44	6,32
4	1,51	9,53
5	1,50	7,68
6	1,48	9,13
7	1,44	8,25
8	1,54	7,54
9	1,55	7,76
10	1,65	8,11

FIBRE VOLUME FRACTION : 60%

MAINTENANCE OF THE RUHSTRAT FURNACE

Photos 24, 25 and 26 show some aspects of the furnace, during maintenance. Right now this job is completed. Testing procedures are being imitiated.

Photo 24. INSIDE VIEW OF THE RUHSTRAT FURNACE. ALL PARTS WERE IDENTIFIED, TO BE PLACED AT THE SAME POSITION.

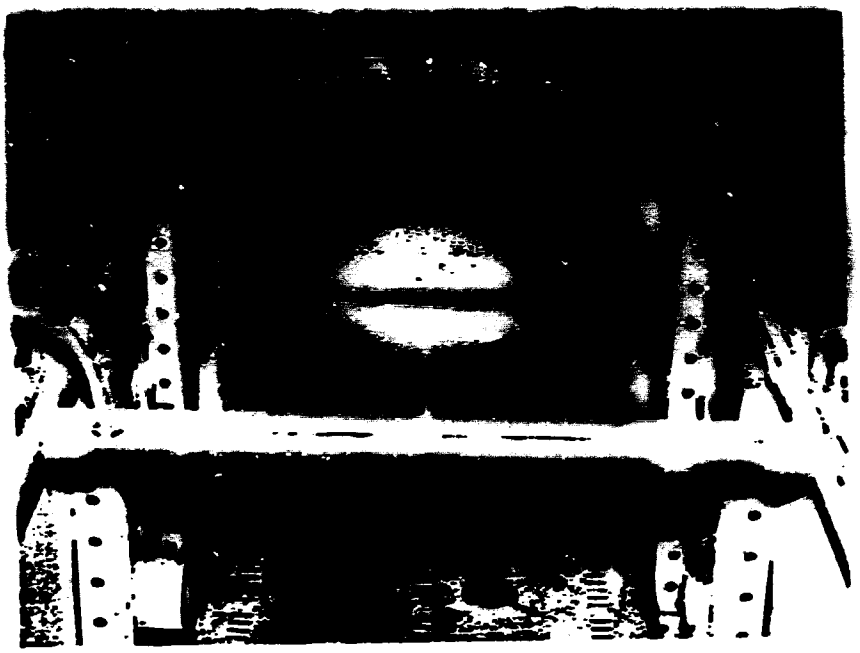


Photo 25. PARTIAL VIEW OF THE FURNACE BOTTOM.

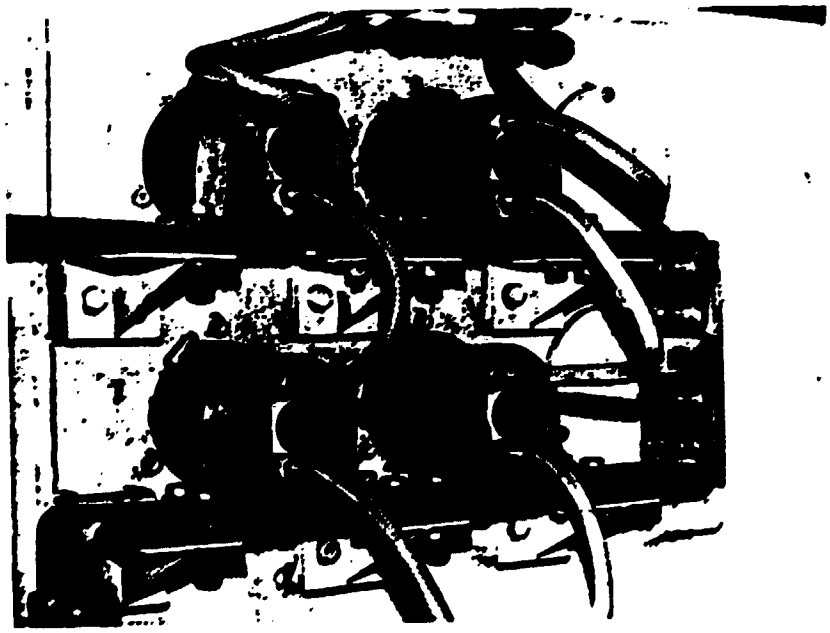
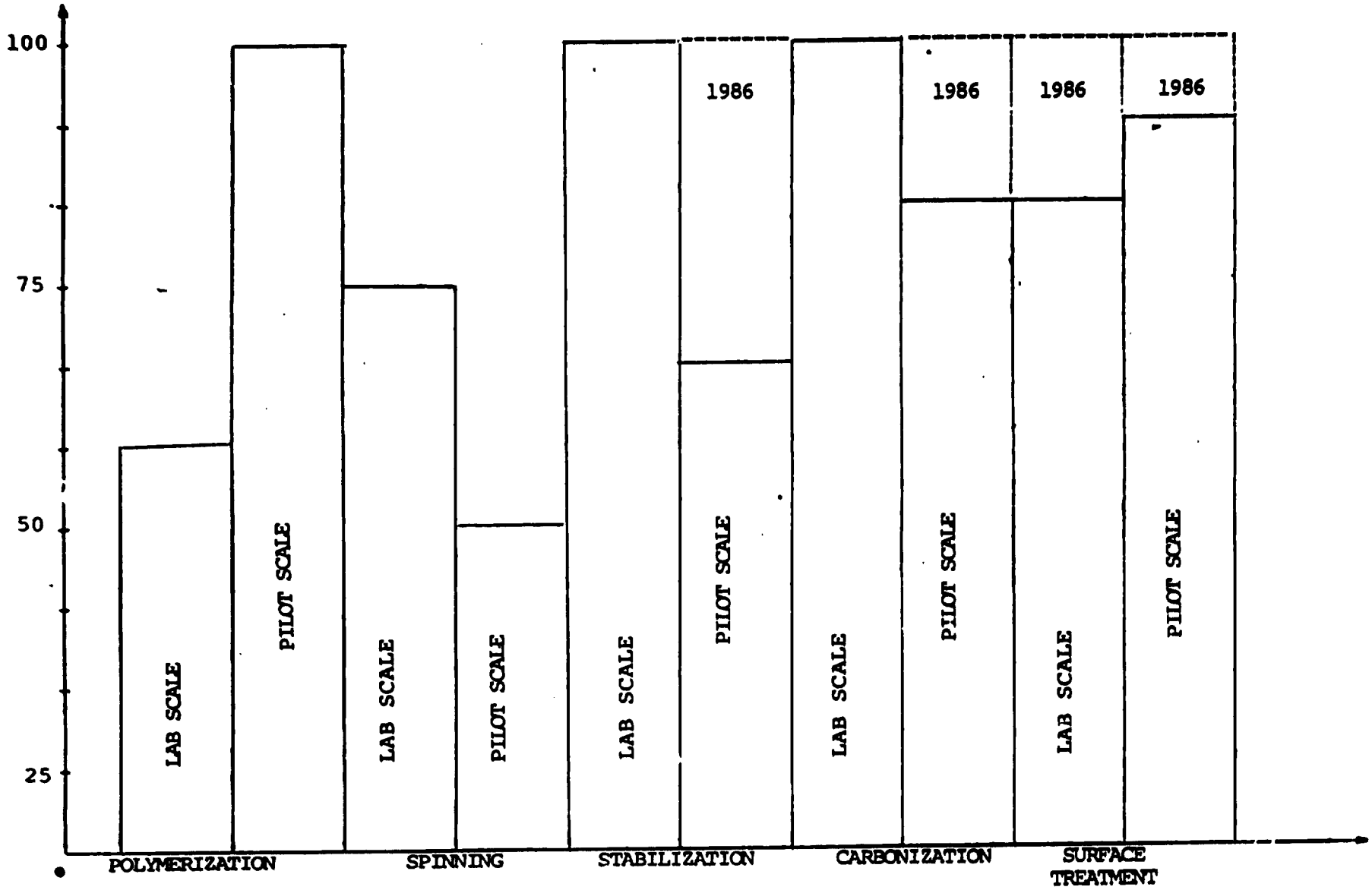


Photo 26. THE SYPHONS WITH DEFECTS (PHOTO 21) WERE REPLACED BY RUBBER AVAILABLE AT PMR.


100
75
50
25
LAB SCALE
PILOT SCALE
LAB SCALE
PILOT SCALE
LAB SCALE
PILOT SCALE
1986
LAB SCALE
PILOT SCALE
1986
LAB SCALE
1986
PILOT SCALE
POLYMERIZATION
SPINNING
STABILIZATION
CARBONIZATION
SURFACE TREATMENT

CONCLUSIONS

In December 1985 the project status was :

i. A trained team with capacity of technical scientific self decisions, able to absorb and adapt the technology used in other countries to produce general purpose high tensile strength carbon fibers, to conduct R & D work related to other similar materials as high performance carbon fiber, from the laboratory scale to the industrial scale.

Necessary improvments in the polymerization team will take place within CTA-COPENE cooperation work by bringing some more people from COPENE and a cooperation agreement with the Macromoleculas Institute in Rio de Janeiro.

ii. Achieved the technology for producing general purpose high strength carbon fiber of the appropriate quality from imported precursor. This technology is ready to be transferred to the industrial partner COPENE. The remaining problems existing in polymerization and sppining will be solved within the CTA-COPENE cooperation programme as above mentioned stabilization, carbonization process have to be optimized for all new precursor types.

Knowledge and techniques to characterize the raw materials as well as the final products for the production of the precursor and carbon fiber has already achieved in 1983 and is being widelly used by the team and even transferred to industries with similar problems.

iii. During the 4 years long research & development on c-fibre fabrication, it turned out that type and quality of the PAN precursor fibre are most important parameters to achieve high performance c-fibre qualities comprehensive knowledge on polymerization was elaborated in as new polymerization laboratory. Experience in spinning was

acquired, in laboratory and pilot scale both subjects need further improvement, which only can be elaborated in close cooperation with experience macromoleculas scientist and with industry of synthetic fibers.

iv. One of the best research laboratory and pilot plant in the world for carbon fiber, in the final setting up, (mentioned problems with the pilot line furnaces) ready for the continuation of the research and development programme.

The needed equipment for analytical control are available.

FUTURE WORK

The existing cooperation program between CTA and COPENE will cover the quality improvment and especially the necessary work to finalize the development of optimum PAN precursor. It will result in necessary process optimization for final cost reduction of general purpose H. T. carbon fibers.

The technology transfer will also be supported by the industrial partner, as well as the market development.

As known, intensive research has been carried out every where in the world in the development of the new generation of high performance carbon fibers and results such as young modulus up to 500 GN/m^2 and tensile strength up to 6 GN/m^2 were achieved in some developed countries.

A second phase project will be necessary to support the development of high performance Carbon Fibers and to develop the applications of the already achieved technology, by means of a intensive composite materials programme.

ENCLOSURE 4

UNFSST/UNIDO CONTRIBUTION

A. VISITS OF EXPERTS, DURING THE PROJECT DEVELOPMENT

1. Dr. Kawamura
2. Dr. Davies
3. Dr. Johnson
4. Dr. Falkai
5. Dr. Nagabhushanam
6. Dr. Böder
7. Dr. Müller
8. Dr. Jacobsen
9. Dipl. Chem. Mr Heine
10. Mr. Steinhart
11. Prof. Dr Fitzer (Special Technical Adviser)
    (One visit per year)

B. VISITS OF EXPERTS, DURING THE CONFERENCE ON CARBON FIBERS AND THEIR APPLICATIONS

(Dec 5th, 9th - 1983 - at CTA)

1. Dr Brunsch (GERMANY)
2. Dr Adams (USA)
3. Dr Bergmann (GERMANY)
4. Dr Hayes (UK)
5. Dr Kalnin (USA)
6. Dr. Diefendorf (USA)
7. Dr. Hastings (UK)
8. Dr. Stenzenberger (GERMANY)
9. Dr. Zen (CHINA)
10. Dr. Kim (KOREA)

C. STUDY-TOURS FOR THE CARBON FIBERS STAFF, OF CTA, SPONSORED BY UNFSST/UNIDO

1. Mr. Simionato
2. Mr. Polidoro
3. Mr. Otani
4. Mr. Maciel
5. Mr. Gomes da Silva
6. Mr. Gomes
7. Mr. Scyllas
8. Mr. Renato

D. EQUIPMENT FROM UNSFD FUNDS.

(see the following 6 pages).

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Project Title OPTIMIZATION AND DEVELOPMENT OF CARBON FIBER TECHNOLOGY Period ending

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

NON-EXPENDABLE PROPERTY CONTROL RECORD

HQ Req. Ref.	Item No.	Qty.	Unit	Description	US Dollar Equivalent	P.O./Shipping Advice Ref.	Received Qty.	Received M	Received Y	Condition	Qty. on hand	Remarks
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
82/6	1.2	1	EA	BLOCK OF THE SPINNING PUMP, MOTOR AND A CONTINOUSLY CONTROLLABLE TRANSMISSION, WITH ADJUSTABLE HEATING SYSTEM	1,633.-	15-2-00362	1	7	82			
	1.3	1	EA	SPINNING PIPE WITH A CANDLE-SHAPED FILTER STAINLESS STEEL	449.-	- " -	1	"	"			
	1.4	1	EA	COAGULATION BATH OF STAINLESS STEEL	408.-	- " -	1	"	"			
	1.5	1	EA	TAKE-UP GODET WITH IDLER AND INFINITELY ADJUSTABLE DRIVE FOR 0-20M/MIN AND SUPPORT	1,429.-	- " -	1	"	"			
	1.6	2	EA	HORIZONTAL INSULADET WASHING BATHS OF STAINLESS STEEL	326.-	- " -	2	"	"			
	1.7	1	EA	TAKE-UP GODET WITH IDLER AND INFINITELY ADUSTABLE DRIVE FOR 0 - 20 M/MIN	1,510.-	- " -	1	"	"			
	1.10	4	EA	SPINNING PUMPS OF HIGH-GRADE STELL	1,306.-	- " -	4	"	"			
	2			LABORATORY WET STRETCHING UNIT:								
	2.1	1	EA	FEEDING DEVICE WITH TREAD TENSION REGULATOR	163,-	- " -	1	"	"			
	2.2	2	EA	DRAW GODETS IDLER AND INFINITELY ADJUSTABLE DRIVE FOR 0 -100 M/MIN AND SUPPORT	3,020.-	- " -	2	"	"			
	2.3	1	EA	HORIZONTAL DRAW BATH OF STAINLESS STEEL	327.-	- " -	1	"	"			
	2.4	1	EA	HORIZONTAL WASHING BATH OF STAINLESS STEEL	327.-	- " -	1	"	"			
	2.5	1	EA	DRYER, CONSISTING OF TWO TAKE-UP GODETS AND TWO ELECTRICALLY HEATING PLATES, WITH INFINITELY ADUSTABLE DRIVE FOR 0 - 100 M/MIN	1,059.-	- " -	1	"	"			
	2.7	1	EA	COMPLETE FINISHING EQUIPMENT, WITH INFINITELY ADUSTABLE DRIVE FOR 0 - 20 REVOLUTION MINUTE	571.-	- " -	1	"	"			
	2.10	1	EA	THERMOSTAT FOR HEATING THE STRETCHING BATH (item 2.3)	980.-	- " -	1	"	"			
	2.11	1	EA	PRECISION TORSION BALANCE, UP TO 50 MG	1,714.-	- " -	1	"	"			

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Project Title: OPTIMIZATION AND DEVELOPMENT OF CARBON FIBER TECHNOLOGY Period ending

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

NON - EXPENDABLE PROPERTY CONTROL RECORD

HQ Req. Ref.	Item No.	Qty.	Unit	Description	US Dollar Equivalent	P.O./Shipping Advice Ref.	Received Qty.	Received M	Received Y	Condition	Qty. on hand	Remarks
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
87/6	1.2	1	EA	BLOCK OF THE SPINNING PUMP, MOTOR AND A CONTINOUSLY CONTROLLABLE TRANSMISSION, WITH ADJUSTABLE HEATING SYSTEM	1,633.-	15-2-00362	1	7	82			
	1.3	1	EA	SPINNING PIPE WITH A CANDLE-SHAPED FILTER STAINLESS STEEL	449.-	- " -	1	"	"			
	1.4	1	EA	COAGULATION BATH OF STAINLESS STEEL	408.-	- " -	1	"	"			
	1.5	1	EA	TAKE-UP GODET WITH IDLER AND INFINITELY ADJUSTABLE DRIVE FOR 0-20M/MIN AND SUPPORT	1,429.-	- " -	1	"	"			
	1.6	2	EA	HORIZONTAL INSULADET WASHING BATHS OF STAINLESS STEEL	326.-	- " -	2	"	"			
	1.7	1	EA	TAKE-UP GODET WITH IDLER AND INFINITELY ADUSTABLE DRIVE FOR 0 - 20 M/MIN	1,510.-	- " -	1	"	"			
	1.10	4	EA	SPINNING PUMPS OF HIGH-GRADE STELL	1,306.-	- " -	4	"	"			
	2			LABORATORY WET STRETCHING UNIT:								
	2.1	1	EA	FEEDING DEVICE WITH TREAD TENSION REGULATOR	163.-	- " -	1	"	"			
	2.2	2	EA	DRAW GODETS IDLER AND INFINITELY ADJUSTABLE DRIVE FOR 0 -100 M/MIN AND SUPPORT	3,020.-	- " -	2	"	"			
	2.3	1	EA	HORIZONTAL DRAW BATH OF STAINLESS STEEL	327.-	- " -	1	"	"			
	2.4	1	EA	HORIZONTAL WASHING BATH OF STAINLESS STEEL	327.-	- " -	1	"	"			
	2.6	1	EA	DRYER, CONSISTING OF TWO TAKE-UP GODETS AND TWO ELECTRICALLY HEATING PLATES, WITH INFINITELY ADUSTABLE DRIVE FOR 0 - 100 M/MIN	1,959.-	- " -	1	"	"			
	2.7	1	EA	COMPLETE FINISHING EQUIPMENT, WITH INFINITELY ADUSTABLE DRIVE FOR 0 - 20 REVOLUTION MINUTE	571.-	- " -	1	"	"			
	2.10	1	EA	THERMOSTAT FOR HEA ? THE STRETCHING BATH (item 2.3)	980.-	- " -	1	"	"			
	2.11	1	EA	PRECISION TORSION BALANCE, UP TO 50 MG	1,714.-	- " -	1	"	"			

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Project Title OPTIMIZATION AND DEVLOPMENT OF CARBON FIBER TECHNOLOGY Period ending ...

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

NON – EXPENDABLE PROPERTY CONTROL RECORD

HQ Req. Ref.	Item No.	Qty.	Unit	Description	US Dollar Equivalent	P.O./Shipping Advice Ref.	Received Qty.	Received M	Received Y	Condition	Qty. on hand	Remarks
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
82/6	2.3	1	EA	TRANSFORMATOR, ADJUSTABLE FROM 0 - 220V	878.-	15-2-00362	1	7	82			
	3.1	1	EA	TRESTLE FOR THE SEVERAL FACILITES	694.-	- " -	1	"	"			
81/1	1-20	1	EA	SOLUTION WET SPINNING MACHINE, SUITABLE FOR ACRYLIC WET SPINNING AND DRAWING FOR CARBON FIBRES, FOR OPARTION ON 220 V/3 PHASE 60 Hz A.C. SUPPLY, COMPLETE WITH SELECTED EQUIPMENT AND SPARE PARTS	176,653.-	15-1-01114	1	"	"			
		2	EA	TIMER TYPE ZSC 1820 - Magdeburg	955.-	FPO. 001889						
		1	EA	LEVER ACTION GRIPS FOR FIBRE SPECIMENTS LOAD CAPACITY 50gms	230.-	FPO. 001890	1	"	"			
8/11	1-8	2	EA	HOT PLATE	290.-	FPO. 00188	2	"	"			Other items or are expendable
82/1				WINDING/ROLLING EQUIPMENT:								
	1	1		FIBRE DRAWING SYSTEM, FOR STABILIZATION AND CARBONIZATION FURNACES, CONSISTING OF:				7	83			
	1.1	4	EA	TRIPLE ROLLER SYSTEMS, HORIZONTALLY SUITABLE FOR PAN TOWS COMPLETE WITH ALL ATTACHMENTS	35,276.-	15-2-00372	4	7	83			
	1.2	1	EA	CROSS BOBBIN WINDER, FOR 1 MULTIFILAMENT SPEED RANGE CORRESPONDING TO 1.1.	5,055.-	- " -	1	"	"			
	1.3	1	EA	- DITTO - FOR UP TO 40,000 DEN	9,488.-	- " -	1	"	"			
	1.4	10	EA	THREAD COMBS, EACH FOR UP TO 10 MULTIFILAMENTS	4,094.-	- " -	10	"	"			
82/2	1	1	EA	CARBONIZATION FURNACE FOR SYNTHETIC FIBRES PROCESSING	172,075.-	15-2-0765						

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Project Title OPTIMIZATION AND DEVELOPMENT OF CARBON FIBER TECHNOLOGY Period ending

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

NON – EXPENDABLE PROPERTY CONTROL RECORD

HQ Req. Ref.	Item No.	Qty.	Unit	Description	US Dollar Equivalent	P.O./Shipping Advice Ref.	Received			Condition	Qty. on hand	Remarks
							Qty.	M	Y			
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
83/1		1	EA	LVT BROOKFIELD VISCOMETER WITH ACCESSORIES	880.-	15-3-1543						
83/1		1	EA	DSC TOP SECTION #900611905	2,131.-	15-3-1544						
		1	EA	EXPANSION PROBE ASSEMBLY #941086000	633.-	- " -						
		1	EA	FIBER PROBE ASSEMBLY #941140000	719.-	- " -						
		1	EA	FIBER PROBE SAMPLE HOLDER ASS. #941144000	644.-	- " -						
83/1		1	EA	ULTRA STY 100 7MMX30CM CO	890.-	15-3-01546						
		1	EA	ULTRA STY 500 7MMX30CM CO	890.-	- " -						
		2	EA	ULT STY 10-3 7MMX30CM COL	1,780.-	- " -						
83/1		2	EA	PRECISION 10163 VACUUM PUMP	15,130.-	15-3-01553						
83/1		1	EA	ROTARY EVAPORATOR MIKADO COMPLETE WITH MOTOR 10-220 R.P.M., DRIVE AND STAND	804.-	15-3-01555						
		2	EA	FLAT FLANGE REACTION VESSEL CAP. 6000 ML	1,277.-	- " -						
		2	EA	FLAT FLANGE REACTION VESSEL CAP. 10.000ML	1,583.-	- " -						
83/1		1	EA	EVACUABLE DIE KBR 1860025	565.-	15-3-1545						
83/1		1	EA	STEAM GENERAT 6KW 240V3PH	1,104.-	15-3-01549						
		1	EA	PUMP GEAR 1.2 GPM PED	476.-	- " -						
		1	EA	MOTOR 1/3-HP 115/208-230V	104.-	- " -						
		1	EA	PUMP POS DISP TE 115V	575.-	- " -						
		1	EA	PUMP GEAR EXPRF 115/230V	480.-	- " -						
83/1		1	EA	CIRCULATOR MODEL A82 FISHER SCIENTIFIC	2,344.-	15-3-1547						
		1	EA	CIRCULATING SYSTEM " "	1,720.-	- " -						

UNITED NATIONS

UNIDO NATIONAL INDUSTRIAL DEVELOPMENT ORGANIZATION

Country BRAZIL Project No. ST/BRA/81/001 Page 2 of

Project Title OPTIMIZATION AND DEVELOPMENT OF CARBON FIBER TECHNOLOGY Period ending

NON – EXPENDABLE PROPERTY CONTROL RECORD

HQ Req. Ref.	Item No.	Qty.	Unit	Description	US Dollar Equivalent	P.O./Shipping Advice Ref.	Received Qty.	Received M	Received Y	Condition	Qty. on hand	Remarks
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
84/1		1	EA	ISOMET SAW NO. 11-1180-160	1,950.-	15-4-0375						
		1	EA	MINIMET POLISHER NO. 69-1000-160	1,040.-	- " -						
84/1		1	EA	AUTOMATIC KARL FISCHER TITRATOR, BASIC INSTRUMENT WITH STIRRER + ACC.	1,637.-	15-4-0376						
		1	EA	ULTRASTYRAGEL COLUMN NO. 85503	950.-	15-4-0368						
		1	EA	" " NO. 85504	950.-	- " -						
		1	EA	" " NO. 85505	950.-	- " -						
83/1		1	EA	BALANCE PC4400 MFG NO RC4400	1,670.-	15-3-01568						
		1	EA	IMMERSION COOLER	613.-	- " -						
		2	EA	VISCOSIMETER SIZE 2 MFG NO V-2200	141.-	- " -						
		2	EA	SPECIAL MAKE-UP CIRCULATOR MODEL KS-20D	3,922.-	- " -						
		3	EA	ZZMFG SPECIAL MAKE-UP RELAY ELECTRONIC BRINKMANN	1,375.-	- " -						
		3	EA	SPECIAL MAKE-UP THERMOMETER BRINKMANN	251.-	- " -						
		2	EA	SPECIAL MAKE-UP STIRRER, CON-TORQUE	1,283.-	- " -						
83/1	1	1	EA	MODEL P1-C PYRO PHOTO II AUTOMATIC OPTICAL PYROMETER	7,200.-	15-4-0378						
		1	EA	MODEL 95E4C PYRO MICRO OPTICAL PYROMETER SET	1,810.-	- " -						
84/1		1	EA	451 L LABORATORY MICRO GRINDER INCL. SPARE PARTS	3,522.-	15-4-0381						

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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANISATION

Country BRAZIL Project No. ST/BRA/81/001 Page 6 of

Project Title OPTIMIZATION AND DEVELOPMENT OF CARBON FIBER TECHNOLOGY Period ending

NON-EXPENDABLE PROPERTY CONTROL RECORD

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(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
85/4	1	1	EA	FULLY ELECTRONIC MACRO ANALYTICAL BALANCE METTLER AE 160	1,549.-	15-5-1170						
85/3	1	1	EA	MODEL 240C ELEMENTAL ANALYZER 0240-0814	24,190.-	15-5-01015						
	2	1	EA	MODEL 240DS ELEMENTAL ANALYSIS DATA STATION 0240-0825	13,200.-	- " -						
	3	1	EA	MODEL AD-6 AUTOBALANCE ELECTRONIC ULTRAMICROBALANCE 0655-0000	7,230.-	- " -						
		1	EA	PAPER 12 ROLLS 650 PRINTER	310.-	- " -						
		1	EA	SULFUR ANALYSIS KIT	2,470.-	- " -						
		1	EA	OXYGEN ANALYSIS KIT	2,470.-	- " -						
		1	EA	SAMPLE HANDLING ACCY KIT	1,030.-	- " -						
85/4	1	2	EA	THERMOCOUPLES TK 10 FOR FURNACE TYPE A689601	1,237.-	15-5-1358						

ENCLOSURE 5

CTA CARBON FIBRE TEAM (STATE FEB 87)

RESEARCHES

João Renato Santos Martins

Francisco José Xavier de Carvalho

Gilton Esperidião Ferreira

Jurandir Pereira

Angelo Eduardo Simionato

José Luiz Gomes da Silva

Heitor Aguiar Polidoro

José Gustavo Freitas Coelho

Clara Leal Nogueira

Luis Claudio Pardini

TECHNICIANS

Ana Maria Tofolleto

Valter Gorgulho

Miriam Eiko Iemanich

José Benedito da Silva

Pedro Macário Rosa

João Batista Rodrigues

Rogério Gonçalves Duque

Marcos Alves

Rosangela Barbosa

Roseli de Fátima Cardoso Souza

João Batista Damasceno

Oladir Pires de Lima

Scilas Pereira

Vicente Ferreira Pinto

Napoleão Fares Cavalcante

Julio Kenji Noguti

ENCLOSURE 6

STUDY TOUR (10 days, two participants)

COUNTRY : P.R. China

PLACES TO BE VISITED :1 - BICT, Beijing Institute of Chemical Technology
2 - BIAM, Beijing Institute for Aeronautical Materials
3 - Textil Academy in Beijing

NAMES OF THE PARTICIPANTS : 1 - Col. Roberto Kessel, Vice-Director of the Institute for Research & Development at CTA (Centro Técnico Aeroespacial)
2 - Mr. Paulo Remi Guimarães Santos, Head of the Materials Division (PMR) at CTA (Centro Técnico Aeroespacial)

SCHEDULE : Start of the tour in the beginning of July 1986
3 working days at BICT
1 working day at Textil Academy
3 working days at BIAM

ALTERNATIVES : If possible, the following additional visites are recommended:
1 - carbon fiber plant at JILIN Province
2 - Polymer Institute at Gouangzhou University (Prof. Zen)

ENCLOSURE 6

PURPOSE OF THE VISITES : P.R.China, Ministry of Chemical Industry is working on a 3 years programme on carbon fibers and composites for one year already. This project is supported by UNDP and partly executed by UNIDO.

Five members of the Chinese research team have visited CTA in 1986 and invited CTA members to visit the research facilities in Beijing.

The present study tour of both leading CTA (IPD&PHR) members has the objective of exploring possibilities of future cooperation in the respective UNIDO supported programmes on C-fibers&composites in both countries.

RELATÓRIO DE VIAGEM AO EXTERIOR

JULHO/AGOSTO 1987

Engº PAULO REMI GUIMARÃES SANTOS

Engº FRANCISCO JOSÉ XAVIER DE CARVALHO

Í N D I C E

RELATÓRIO DE VIAGEM AO EXTERIOR

PARTICIPANTES : Engº PAULO REMI GUIMARÃES SANTOS
Engº FRANCISCO JOSÉ XAVIER DE CARVALHO

1. PROGRAMA CUMPRIDO

22/07/87 : Viagem SÃO PAULO - LOS ANGELES
23/07/87 : Contacto preliminar com a NARMCO em Anaheim
24/07/87 : Viagem LOS ANGELES - TOKYO
25/07/87 : Recebidos em Tokyo pelo Prof. KIMURA
26/07/87 : DOMINGO Acompanhados pelo Prof. Kawamura da Nihon University
27/07/87 : Visita à UNIVERSIDADE GUNMA em Kyriu
28/07/87 : Visita à TORAY e INSTITUTO DE TECNOLOGIA DE TOKYO.
29/07/87 : Engº REMI visitou a NIHON UNIVERSITY em Tokyo e o Engº FRANCISCO visitou a UNIVERSIDADE de KYUSHO em Fukuoka.
30/07/87 : Engº REMI continuou visitando a NIHON UNIVERSITY em Tokyo enquanto o Engº FRANCISCO visitava o INSTITUTO GOVERNAMENTAL INDUSTRIAL de PESQUISAS DE KYUSHU.
31/07/87 : Viagem de TOKYO a PEQUIM recebidos pelo Dr LI FENGSHAN.
01/08/87 : Sábado acompanhados pelo Engº XIONG JU
02/08/87 : Domingo
03/08/87 : Visita ao INSTITUTO DE TECNOLOGIA QUÍMICA DE PEQUIM (BICT).
04/08/87 : Continuação da visita ao BICT.
05/08/87 : Visita ao INSTITUTO DE MATERIAIS AERONÁUTICOS DE PEQUIM.
06/08/87 : Visita ao INSTITUTO DE TECNOLOGIA TEXTIL DE PEQUIM.
07/08/87 : Reunião final com o Dr LI FENGSHAN
08/08/87 : Viagem PEQUIM - TOKYO - SEOUL.
09/08/87 : DOMINGO
10/08/87 : Visita ao KOREA ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY e à fábrica de fibra de carbono COSCO em SEOUL.
11/08/87 : Visita à UNIVERSIDADE NACIONAL CHUNGNAM em DAEJON e INSTITUTO DE TECNOLOGIA QUÍMICA

12/08/87 : Visita a KYONGJU
13/08/87 : Dia reservado para a visita a KOREA FIBRE COMPANY.
14/08/87 : Viagem PUSAM - TOKYO - LOS ANGELES
18/08/87 : Visita à BASF STRUCTURAL MATERIALS (NARMCO)
20/08/87 : Regresso ao Brasil.
21/08/87 : Desembarque no Aeroporto de Guarulhos.

2. DETALHAMENTO DAS VISITAS

2.1 - JAPÃO

Dia 27/07/87 - KIRYU
Visita à UNIVERSIDADE DE GUNMA
KIRYU GUNMA 376
Tel: 0277 - 223181 - JAPÃO

Fomos recebidos pelos Prof Dr SUGIU OTANI; Dr ASAO OYA e Prof. Dr YASUAKI NAKAIDO, do Departamento de Química da Faculdade de Tecnologia.

Dentre os assuntos discutidos destacaram-se os seguintes:

RESINA COPNA : Trata-se de uma resina termofixa, cuja característica principal é a boa aderência às fibras de carbono e aos materiais carbonosos.

Corpos de prova de grafite colados com esta resina mantiveram as propriedades mecânicas da colagem, mesmo após a carbonização. No ensaio de tração, a ruptura ocorreu fora da região da colagem. No caso de colagem de eletrodos, as propriedades elétricas ficam inalteradas mesmo após a carbonização.

Esta resina foi desenvolvida principalmente para servir como precursora da matriz nos compósitos carbono-carbono, graças à retenção das propriedades mecânicas após a carbonização.

Perguntamos se havia reação química entre a mesma e os grupos reativos da superfície da fibra de carbono. Responderam não poder explicar se a natureza da ligação é física ou química. A cura da resina COPNA é de 3 minutos à temperatura de 70 a 80 graus Celsius.

Fibras de Carbono à Base de Piche : Desenvolveram este material, não tendo nunca trabalhado com fibras de carbono

à base de PAN, uma vez que a TORAY já tem grande competência nesta área. A KUREHA CHEMICAL IND. é a única produtora das fibras à base de piche no Japão, comercializando fibras com as seguintes propriedades : resistência à tração : 2,87 GPa e módulo de elasticidade : 55 GPa para as fibras de alta resistência, e módulo de elasticidade de 620 GPa, para as fibras de alto módulo, com peso específico de 2,16 g/cm³ e elongação de 0,48.

Não responderam a nossa pergunta sobre como controlar a regularidade das propriedades mecânicas ao longo das fibras de carbono à base de piche.

Cimento Reforçado com Fibras de Carbono : (CFRC) Tem sido uma das grandes aplicações das fibras de carbono no Japão. Consiste de barras de CFRC que substituem as barras de aço no concreto armado. A principal vantagem está na resistência à corrosão do material e na possibilidade de estruturas mais leves, fator importante na construção de edifícios à prova de terremotos. Há uma economia de 60% no peso das paredes quando se utiliza este material. Um compósito CFRC com 4% de fibras de carbono, quando submetido à compressão, tem um comportamento plástico. As fibras de carbono para este fim não recebem tratamento superficial e a fração volumétrica utilizada é de 20%. Comentamos que o ideal seria produzir estas barras pelo processo de "PULTRUSION" ao que responderam não terem tentado.

Capacitores : As fibras de carbono têm sido utilizadas também na produção de capacitores. Os japoneses ganharam o prêmio de 1984 da invenção do ano nos USA, com a apresentação de um bateria solar que consiste de duas placas à base de fibra de carbono ativada, separadas por um composto orgânico à base de Lítio. Estas baterias solares têm a vantagem de funcionar também à noite e a demanda de produção é da ordem de 200.000.000 de unidades.

Fibras de Carbono à Base de Lignina : A partir de 1973 , durante a crise do petróleo desenvolveram fibras de carbono a partir de lignina, tendo posteriormente abandonado por ser economicamente inviável para o Japão. A NIPPON

KAYAKU chegou a iniciar a produção destas fibras.

Se houver interesse do Brasil em desenvolver a tecnologia de fibras de carbono a partir da lignina, o Prof Otani sugere que se contrate o Mr Fukuoka que foi quem fez o desenvolvimento para a Nippon Kayaku, está na iminência de aposentar-se e é a maior autoridade em fibras de carbono a partir de lignina no Japão.

Carbono Vítreo : Desenvolveram carbono vítreo a partir de resina composta de cloreto de polivinila e resina furânica, com adição de grafite para densificação. Conseguiram módulo de elasticidade de 200 GPa e acreditam que com outra resina não se consiga valores acima de 20 GPa. Mostraram-nos uma mola espiral feita com carbono vítreo, com grande resistência à fadiga.

Célula de combustível : Apresentaram um modelo de placa para célula de combustível em que as bordas são feitas de carbono vítreo e as placas de um compósito carbono-carbono poroso.

Dia 28/07/87 - VISITA À TORAY TOKYO
2-1 Nihonbashi muromachi 2 chome
Chuo-Ku, Tokyo 103 JAPAN
Telex J22623 TORAYINC

Fomos recebidos por : Mr Ken Tanaka, Gerente Geral do Departamento de Fibras de Carbono; Mr Akira Koyama, Mr Junishi Matsui, Mr Keishiro Saito e Mr Katsunori Mori, da MITSUI & CO. O Mr Koyama fez uma apresentação dos últimos desenvolvimentos tecnológicos no campo de fibras de carbono, destacando a fibra de carbono T-1000, com resistência à tração de: 7 GPa e módulo de elasticidade 300 GPa. Perguntamos ao Mr Tanaka se existia alguma restrição no fornecimento de fibras de carbono para o Brasil. Mr Tanaka respondeu que já existem restrições para a India e acredita que existirão para o Brasil.

Dia 28/07/87 - VISITA AO TOKYO INSTITUTE OF TECHNOLGOGY.
Faculty of Engineering Department of Inorganic Mat.
2-12-1 Ookayma Meguro-Ku Tokyo Japan

Fomos recebidos pelo Prof Dr Shiushichi Kimura e Prof Dr Akira Takaku.

Carbono reforçado com fibras de carbono : Ressaltaram a sua preferência por matrizes termofixas, pelas vantagens que estas apresentam. Em termos de processos disse preferir o C.V.D. (Carbon Vapor Deposition).

Para caracterização da estrutura destes materiais utilizam técnicas de difração de raios-x, incluindo baixo ângulo Utilizam muito a técnica de ressonância magnética na caracterização da estrutura do carbono-carbono, ressaltando que em alguns casos é impossível detectar variações significativas na estrutura destes materiais, à temperatura ambiente, sendo necessário utilizar ressonância magnética a temperaturas extremamente baixas, como a do hélio liquefeito.

Fibras de Carbono à base de PAN : O Prof Takaku produz fibras de carbono em escala de laboratório, com a finalidade exclusiva de desenvolver técnicas de caracterização. O sistema de produção consiste em um processo contínuo em escala de laboratório, bastante simples, constituído de um pequeno forno de estabilização com fluxo de ar aquecido e de um forno de carbonização.

A matéria prima utilizada é a poliacrilonitrila, provavelmente fornecida por algum produtor japonês de fibras de carbono. O que mais nos chamou a atenção foram as técnicas de caracterização utilizadas. Para o controle de estabilização, construíram um dispositivo que simula as condições do forno de oxidação, medindo as tensões, estiramentos e/ou contrações que ocorrem, podendo ainda utilizar o mesmo corpo de prova para estudo da estrutura e medida de propriedades mecânicas. Também para o controle da carbonização desenvolveram dispositivo semelhante que permite simular as condições reais do processo e analisar todos os fenômenos físicos que ocorrem, de uma maneira mais real que uma análise por TMA. Vimos ainda outro dispositi

vn que permite fazer difração de raios-x enquanto as fibras são tensionadas.

Para verificação da aderência entre a fibra e a matriz polimérica, aplicam sobre monofilamentos de fibras de carbono, gotas de resina epoxy. Após a cura é feito um ensaio de tração no qual a fibra deslisa dentro da gota, permitindo medir a força de cizalhamento, bem como verificar, por microscopia, a superfície da fibra, para avaliar a aderência.

Dia 29/07/87 - NIHON UNIVERSITY TOKYO

O Engº Remi visitou a Nihon University, levado pelo Dr. Kyoshi Kawamura.

Durante esta visita o Dr Kawamura, que já esteve por duas vezes no CTA e é conhecedor do nosso trabalho, bem como do nosso pessoal, traçou considerações sobre o progresso dos trabalhos da PMR, nas áreas de Fibras de Carbono e Grafite, avaliando os resultados e orientando sobre caminhos, alternativas e principalmente sobre a formação do pessoal existente, analisando a capacidade e o potencial de cada elemento.

Como continuação desta análise, recomendou as linhas básicas para a formação e aperfeiçoamento de cada elemento da equipe. Durante a visita aos laboratórios, mostrou os trabalhos de caracterização de materiais carbonosos, utilizando susceptibilidade magnética. O equipamento utilizado é uma Bobina de Lewis e faz medidas da temperatura desde o He líquido até a temperatura ambiente.

Mostrou também os métodos de medidas de condutividade elétrica a baixas temperaturas.

Forneceu ainda farto material bibliográfico dentro dos assuntos de nosso interesse e colocou-se à nossa disposição para colaborar com o Projeto Materiais Carbonosos, via JICA.

Dia 29/07/87 - UNIVERSIDADE DE KYUSHU
RESEARCH INSTITUTE OF INDUSTRIAL SCIENCE
KASUGA 816 FUKUOKA - JAPÃO

Fomos recebidos pelo Dr Yozo Korai, pois o Prof Mochida, que deveria nos receber, estava nos EUA.

Reativamos através da entrega de correspondência atualizada, as negociações sobre a vinda do Prof Mochida ao Brasil, pelo Convênio com a JICA.

Estão desenvolvendo fibras de carbono a partir do piche. Para a produção da fibra precursora, têm um dispositivo muito simples, que consiste em um pequeno recipiente metálico, onde o piche é fundido e pressurizado por nitrogênio, sendo forçado a passar por um orifício extrusor, produzindo um monofilamento de piche, que é estirado, ao ser bobinado, em uma polia lisa.

O estudo mais importante que pudemos notar foi o da formação da mesofase do piche. Utilizam uma filmadora de vídeo acoplada a um microscópio com câmara aquecida, que permite filmar e controlar toda a formação da mesofase, que é o ponto mais importante na obtenção destas fibras de carbono. Estão mais preocupados com estudos de caracterização das fibras obtidas do que da otimização dos processos.

Informaram-nos, sem fornecer detalhes, que estão produzindo carbono reforçado com fibras de carbono pelo processo de deposição em fase gasosa.

Dia 30/07/87 - GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE
Shuku Tosu Saga Kyushu Japan 841

Fomos recebidos pelo Dr Kasuo Bobaiashi, Diretor do Instituto, Dr Sumio Nagata e Dr Kazuhico Jinnai.

Compósito Carbono Cerâmica : Apresentaram de início, um material novo para nós : um compósito carbono cerâmica , que alia a resitência a altas temperaturas, com grande resistência à oxidação térmica, bem como boas proprieda - des mecânicas. O material é obtido a partir da dispersão de partículas cerâmicas em uma matriz carbonosa.

O exemplo que nos foi apresentado e do qual conseguimos um pequeno corpo de prova, foi o resultado da dispersão de SiC e B_4C em uma matriz carbonosa.

A matriz carbonosa utilizada foi coque de petróleo não calcinado e tratado à temperatura não superior a 600°C. O Si/C.e o B_4C, conferem ao material a resistência à oxidação. Após feita a homogeinização da mistura, o produto é moldado e sinterizado a 1000°C. Este material é empregado em mancais resistentes a altas temperaturas e outras apli-

cações que envolvam temperaturas elevadas, inclusive tubeiras de foguete.

Fibras de Carbono à base de Piche : Obtiveram os melhores resultados já conseguidos para este material :resistência à tração entre 2 e 4 GPa e módulo de elasticidade até 500 Gpa. O processo para a produção destas fibras de carbono de alto desempenho, à base de piche é o seguinte :

PICHE CRU → HIDROTRATAMENTO 380°C a 500°C → PICHE → HIDRO TRATADO → TRATAMENTO TÉRMICO ACIMA DE 450°C POR TEMPO CURTO → PICHE PRONTO PARA FIAÇÃO → FIAÇÃO → → FIBRAS DE CARBONO.

Maiores informações sobre este processo encontram-se em documentação disponível na Biblioteca da PMR.

Possuem uma unidade piloto para a produção destas fibras , com uma unidade de fiação de piche capaz de fiar à velocidade de 1000m/min.

O processo que empregam permite a utilização de piche de alcatrão ou piche de nafta e permite ainda a fiação a altas velocidades.

Foram ainda mencionados outros trabalhos na área de cerâmicos especiais e metalurgia do pó. Chamou-nos a atenção o aproveitamento das cinzas do "husk" de arroz, para produção de painéis rígidos e isolantes térmicos, sendo que é ótimo substituto para as espumas de poliuretano em construção civil e câmaras frigoríficas.

2.2 - CHINA

Dias 03 e 04/08/87 - VISITA AO BEIJING INSTITUTE OF CHEMICAL TECHNOLOGY
Heping Street Beijing CHINA

Fomos recebidos pela Madame Liu Meizhu, Diretora do Instituto e pelos Professores Wang Zhen Ping, Diretor do Laboratório de Fibras de Carbono, Shen Zengmin, que esteve no CTA em 1986 , Li Pei Ren, Chen Han e Wang Pei Hua que também esteve no Brasil. O BICT é composto de 6 Departamentos : Ciência de Polímeros, Engenharia Química, Engenharia Mecânica, Automação, Engenharia de

Gerenciamento, Química Aplicada e Cursos Elementares.

Estão recebendo suporte da UNIDO para o desenvolvimento de fibras de carbono em escala piloto, em projeto semelhante ao do CTA/UNIDO, não tendo ainda recebido os equipamentos que já encomendaram à FOURNÉ da Alemanha.

O Projeto Fibras de Carbono conta com 31 pesquisadores, divididos em 4 grupos : Polimerização e Fiação, Produção de Fibras de Carbono, Estrutura e Propriedades das Fibras e o Grupo de Compósitos.

Visitamos a unidade laboratorial de produção de fibras de carbono, muito parecido com a nossa : a principal diferença que encontramos foi o fato de lavarem a PAN antes da entrada no forno de oxidação.

Estavam utilizando PAN importada da COURTAULDS e como tivessem nos apresentado resultados de propriedades mecânicas superiores aos que costumamos conseguir no CTA, desconfiamos de que a PAN que utilizam fosse de uma nova geração produzida pela COURTAULDS, uma vez que o lote era de maio de 1987. Deram-nos uma amostra para que pudéssemos ensaiar e comparar com a PAN por nós utilizada.

Na síntese da PAN, utilizam persulfato de amônia, sulfato de sódio, ácido itacônico 1 volume molar e metil metacrilato 1 volume molar.

Estão experimentando a utilização de outros comonômeros para substituir o MMA tais como : metil vinil cetona, metil vinil pirolidona e outros.

O tempo de reação de síntese é de 1 a 2 horas à temperatura de 90°C e com pH 3. O peso molecular é de 80000 a 100000. Controlam o peso molecular pela medida de viscosidade Brookfield , raramente utilizando GPC e quando o fazem, utilizam poliestireno como padrão.

Demonstraram grande interesse em manter intercâmbio científico com o CTA.

Visitamos ainda o Departamento de Ciência dos Polímeros e ficamos impressionados com a quantidade de equipamentos científicos modernos de que dispõem, muitos importados dos USA, JAPÃO e EUROPA, porém muitos, incluindo microscópios eletrônicos, produzidos na CHINA.

Informaram-nos que a China produz resinas epoxy, inclusive a tetrafuncional. No BICT formulam sistemas de resinas.

Dia 04/08/87 - JANTAR FORMAL COM AS AUTORIDADES.

Fomos convidados para um banquete que se realizou no dia 4 à noite, no PEKING ROASTED DUCK, com a presença das seguintes autoridades : Hu Boxiong Deputado, Chefe da Divisão de Cooperação Técnico-Científica do Departamento de Assuntos Estrangeiros do Ministério da Indústria Química; Prof. Zhao Guanqi, Vice Presidente do Instituto de Tecnologia Química, Sr Li Fengsham e outros professores do BICT.

Dia 05/08/87 - VISITA AO INSTITUTO DE MATERIAIS AERONÁUTICOS

Tel. 287556 - CABLE 9138 - BEIJING - CHINA

Fomos recebidos pelo Dr Wang Zufa, Diretor Técnico do Instituto, Dr Yu Dechang, Sr Zhou Hongfang, do Departamento de Assuntos Estrangeiros, Engº Ni Ronggen e Engº Zhang Fengfan. Este Instituto nos impressionou pelo tamanho, pois tem 1200 pessoas trabalhando somente na área de materiais aeronáuticos. Além de pesquisas, dedicam-se também à produção de componentes. Possuem um grande Departamento de Compósitos, o qual vem utilizando fibras de carbono há dez anos , estando inclusive produzindo componentes para a indústria aeronáutica. Vimos duas máquinas para produção de prepregs, com capacidade industrial de pequena escala, uma para prepregs unidirecionais e outra para tecidos e uma terceira máquina com capacidade de produção para escala piloto. Na produção de componentes, possuem uma autoclave com 4m de diâmetro e uma pequena, de laboratório.

Os laboratórios de ensaios e caracterização estão muito bem equipados, com equipamentos dos mais modernos e com todos os recursos e facilidades existentes.

A principal novidade na área de caracterização de compósitos foi a utilização de holografia a lazer para detectar defeitos em laminados.

Quanto aos materiais utilizados, importam fibras de carbono da TORAY. Possuem produção nacional de resina epoxy tetrafuncional, comprometendo-se, inclusive, a enviar-nos amostras. Informaram ainda que a China possui boa capacidade de produção de

fibras de vidro com possibilidade de fornecê-las ao Brasil, ou fornecer know how para empresas brasileiras . Na área de termo plásticos avançados, produzem o PEEK em escala de laboratório. Insistiram no fato de que participam de todos os congressos importantes na área de materiais. Mostraram interesse em manter intercâmbio com o Brasil e de receber nosso pessoal técnico para treinamento.

Dia 06/08/87 - VISITA A ACADEMIA TEXTIL DE BEIJING
Ying Jia Fen - East Suburb Beijing CHINA

Fomos recebidos pela Madame Liu Zhen Zhong, Vice Diretora da Academia, que é constituída de 4 Institutos e 2 Escritórios : Instituto de Tecnologia Textil, Instituto de Fibras Sintéticas, Normalização Textil e Automação Textil e dos Escritórios de Engenharia Elétrica e Mecânica e Técnico/Econômico.

Visitamos o Instituto de Tecnologia Textil e ficamos mais uma vez impressionados com a grande quantidade de equipamentos, sendo a maior parte novos e alguns ainda embalados ou sendo instalados. Dentre os equipamentos para fiação, cerca de 90% são da FOURNÉ.

Informaram-nos que ainda não estão produzindo PAN, principalmente porque não têm como se descartar do DMF.

Durante esta visita, almoçamos junto com o Prof MacIntoshy, da Universidade de Leeds Uk, que estava dando assessoria à Academia Textil. Discutimos com o Prof MacIntoshy aspectos técnicos sobre "jet spinning" e este colocou-se à nossa disposição para futura cooperação.

2.3 - COREIA DO SUL

Dia 10/08/87 - VISITA AO INSTITUTO COREANO DE TECNOLOGIA AVANÇADA - KAIST

39-1, Haweolgog-dong, Seongbuk-gu, Seoul, KOREA.

Fomos recebidos pelo Dr Eng Jang Bo Yung e Dr Tae Won Son. Começaram a trabalhar com fibras de carbono em 1974 na Agência para Desenvolvimento da Defesa. Mantiveram cooperação técnica com a ADD da NASA e SNP, SNIAS e SEP da França.

O Grupo de Fibras conta com 12 Pesquisadores e está trabalhando em cooperação com a KOSKO, que é produtor coreano de

fibras de carbono, no desenvolvimento de FC a partir de piche médio, não tendo ainda iniciado o spinning pois estão tendo dificuldades na formação da mesofase.

Pretendem começar a estudar fibras de carbono e partir de PAN, mas apenas em coopeação com alguma empresa.

Estão produzindo prepregs em escala de laboratório, apenas para caracterização. Utilizam fibras de carbono com tratamento superficial e tratam-nas com CTBN, que é um modificador de epoxy que se liga à superfície tratada da FC e possui radicais reativos que irão ligar-se à resina de reforço.

Contaram-nos ainda que produzem o polímero aramida, bem como fibras curtas obtidas por pulverização.

Estão muito bem equipados em termos de laboratórios e principalmente equipamentos científicos dos mais modernos.

Dia 10/08/87 - VISITA A KOSKO CARBON FIBER
KOREA STEEL CHEMICAL CO, LTD
Daewoo Securities Bldg 9th Floor, 34-3
Youido-Dong, Yongdungpo-Gu Seoul KOREA

Fomos recebidos pelo Dr Jung Ki Park, Diretor de Pesquisa e Desenvolvimento e Engº Jae Sup Lee.

A KOSKO é o único produtor de fibras de carbono da Coréia do Sul. Pertence à Korea Steel Chemical Co e comprou a tecnologia e a unidade industrial de produção de fibras de de carbono da RK, da Inglaterra. Possuem hoje uma capacidade instalada para 100 t/ano de fibras de carbono.

Importam a matéria prima PAN, da COURTAULDS e o seu produto final tem as seguintes características : resistência à tração : 3,5 GPa e módulo de elasticidade : 240 GPa. O preço de venda destas fibras é de US$ 27 kg para rovings de 6000 filamentos.

Estão investindo em pesquisa de fibras de carbono à base de piche. Não nos permitiram visitar a fábrica de fibras de carbono, tendo a visita se limitado aos laboratórios de ensaio e produção de compósitos.

Dia 11/08/87 - VISITA A UNIVERSIDADE NACIONAL DE CHUNGNAM
DEPARTMENT OP CHEMICAL ENGINEERING
300-31 Daejon - KOREA

Fomos recebidos pelo Prof Dr B. Rhee, o qual já conhecíamos, pois visitou-nos no Brasil alguns dias antes de iniciarmos esta viagem e também esteve conosco durante as visitas no Japão. Foi ele quem organizou o nosso programa de visitas na Coréia do Sul.

Receberam também financiamento da UNIDO e desenvolveram processo semi-industrial de produção de fibras de carbono a partir de PAN, utilizando PAN importada da COURTAULDS. Já terminaram este projeto e estão atualmente recebendo novo financiamento da UNIDO para o desenvolvimento de fibras de carbono à base de piche.

Na unidade de produção de FC à base de PAN, observamos o seguinte : utilizam um forno de carbonização RHUSTRAT, parecido com o nosso e tiveram os mesmos problemas que tivemos. Fazem a lavagem da PAN em água quente, antes de entrar no forno de oxidação. No tratamento superficial utilizam uma bateria de cubas eletrolíticas ao invés de apenas uma.

Sugeriram que tentássemos utilizar outros comonômeros na obtenção de nossa PAN, como por exemplo o acetato de vinila. Forneceram-nos um pequeno relatório que mostra esquematicamente tanto a linha de produção à base de piche como a linha para produção à base de PAN.

Atualmente estão dedicando-se somente ao estudo das fibras de piche, estando na fase de obtenção da mesofase.

Dia 11/08/87 - VISITA AO INSTITUTO DE PESQUISA DE TECNOLOGIA QUÍMICA
P.O. Box 9 - Daedeog Danji, 300-31 Chungnam - KOREA.

Fomos recebidos pelo Dr Jong Ho Kim, Diretor e Dr Eng Kyu Wan Lee, Chefe do Laboratório Petroquímico.

Este instituto, como os demais da Coréia do Sul,é bastante novo e compreende as seguintes Divisões : Orgânica; Polímetos; Inorgânica; Engenharia Química; Ciências da Vida; Textil

e Divisão de Suporte Técnico.

Visitamos o Laboratório de Compósitos onde estão estudando o comportamento e caracterização de compósitos, bem como formulação de prepregs.

Estão muito bem equipados, com máquinas de laboratório, para a produção de prepregs, autoclaves para produção de placas para corpos de prova, cromatógrafos, espectrofotômetro de infra-vermelho, analisador térmico diferencial e câmaras de climatização para caracterização de compósitos.

Dia 13/08/87 - VISITA À KOREA FIBRE CO.

Esta visita não se realizou porque não fomos apanhados no hotel, conforme estava previsto.

Não tendo conseguido contacto por telefone com o Prof Rhee, organizador do programa, encaminhamos um telex à empresa solicitando que nos recebessem para uma visita. Como a resposta, recebida via telex, fosse negativa, a visita foi cancelada.

2.4 - ESTADOS UNIDOS

Dia 19/08/87 - VISITA À BASF STRUCTURAL MATERIALS INC
NARMCO MATERIALS
1440 N. Kraemer Boulevard
Anaheim CALIFORNIA USA.

Fomos recebidos pelo Dr Gerald Sauer, Gerente de Marketing, Mr Ron Ornellas, Gerente de Produção, Mr Gregory M. Hart, Supervisor dos Laboratórios.

Foi-nos mostrada, em detalhe, toda a linha de produção de prepregs, bem como os laboratórios de desenvolvimento e de controle dos produtos.

A primeira etapa da fabricação dos prepregs, consiste na preparação das formulações de resina. Neste setor as misturas de catalizadores, cargas, aditivos etc, são feitas em moinhos de rolos e com um controle rigoroso da homogeneidade e viscosidade da mistura. O ambiente é muito limpo e o nível de pó em suspensão no ar é controlado.

O maior segredo industrial, na produção de prepregs está na formulação do sistema de resinas. As formulações de resina

são programadas para serem preparadas momentos antes de sua utilização nas linhas de produção do projeto. As matérias primas utilizadas são resinas epoxy de diversos tipos, modificadas ou não, disponíveis no mercado norte americano e fibras de carbono de várias procedências, apesar de a BASF ter adquirido a CELION, produtora de fibras de carbono nos Estados Unidos.

Para a utilização pela indústria aeronáutica, utilizam somente fibras de carbono da TORAY, porque ainda é a única homologada pelo FAA.

A produção dos prepregs é feita em equipamentos modernos, em ambiente extremamente limpo e com recursos que permitem um perfeito controle das variáveis do processo, garantindo uma qualidade perfeita em termos de homogeneidade e relação volumétrica fibra/resina.

A estocagem do produto acabado é feita em imensas câmaras frigoríficas e a distribuição do estoque é programada para um tempo de armazenagem o menor possível.

No laboratório de moldagem, estão preparados para simular condições de trabalho dos clientes ou mesmo desenvolver para eles os seus produtos finais. Para isto, contam com facilidades de moldagem, incluindo autoclaves de diversos tamanhos.

Os laboratórios de ensaios estão equipados com diversas máquinas universais de ensaios, incluindo máquinas dinâmicas e com facilidades para ensaios a quente.

Para a caracterização das resinas, estão equipados para utilizar as técnicas mais modernas e eficientes em termos de análise instrumental.

Colocaram os seus laboratórios à nossa disposição, para o treinamento de nosso pessoal técnico.

3. CONCLUSÕES

Comparando o desenvolvimento da tecnologia dos materiais, no Japão, China e Coréia do Sul, podemos avaliar o estado em que nos encontramos no IPD e vislumbrar os rumos que deveremos seguir para apoiar o desenvolvimento tecnológico do País. O Japão, com os seus cientistas SENIORS, com um embasamento teórico e vivência prática muito grande, lidera de longe a corrida tecnológica, com materiais e soluções das mais avançadas. Os Centros de Pesquisa, governamentais ou não, estão empenhados em desenvolver tecnologias, processos e produtos, mantendo uma vanguarda sobre as indústrias, futura usuária destas tecnologias.

As Universidades, com sólidos conhecimentos conceituais e teóricos, está apta a ajudar os Centros de Pesquisa a enxergar os problemas tecnológicos, à luz do forte embasamento teórico e conceitual.

Assim, o entrosamento eficiente entre Indústria, Universidade e Centros de Pesquisa garantem a vanguarda tecnológica do Japão.

Na China, não existem pesquisadores muito experientes e os chineses procuram suprir estas deficiências, com equipamentos de laboratório novos e sofisticados. No entanto, estão muito preocupados com a formação de recursos humanos, mandando um grande número de pessoas para treinamento no exterior e recebendo um grande número de consultores estrangeiros.

A Coréia do Sul encontra-se em um estágio de desenvolvimento superior ao da China, mas ainda continua investindo bastante na formação de recursos humanos.

Pôde ser notado que estes países não hesitam em importar tecnologias que os mantenham na vanguarda comercial e tecnológica. A maior preocupação é que suas instituições de pesquisa e universidades tenham capacitação para entender, absorver e aprimorar ou adaptar as tecnologias importadas. Esta é uma política saudável, uma vez que temos o exemplo do Japão que importa muito mais tecnologia do que exporta.

São José dos Campos, 30 de novembro de 1987.

FRANCISCO JOSÉ XAVIER DE CARVALHO - Engº
Chefe da Subdivisão Técnica

PAULO REMI GUIMARÃES SANTOS - Engº
Chefe da Divisão de Materiais do IPD