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14806

Brazil. Carbon fibre technology.

TRIP-REPORT

Ref.: Project ST/BRA/81/TO1
Job description ST/BRA/OO1/11-74/32.1 H

Title: Consultant in stabilization and carbonization treatment

Mission to Brazil, carried out between April 27 and May 26, 1985

Time Schedule

April 27,	1985	Travel day Karlsruhe - Miami
April 28/May 1,	1985	189th International Meeting of ACS in Miami on 'Carbon fibre and other high performance fibres' Presentation of the following paper: 'Optimization of stabilization and carbonization treatment of PAN fibres and structural characterization of the resulting carbon fibres.'
May 1/2,	1985	Travel days Miami - Sao José dos Campos
May 2-7,	1985	Stay at CTA, Sao José dos Campos
May 8,	1985	Stay at SANTA CLARA, Sao Paulo
May 9-24,	1985	Stay at CTA, Sao José dos Campos
May 25/26,	1985	Travel days Sao José dos Campos - Karlsruhe

Content of this report

1. General

According to the Job Description ST/BRA/001/11-74/32.1 H of April 1985 (Consultant in stabilization and carbonization treatment) the subjects have been the following:

(1) Report newest state of carbon fibre technology

(2) Advise carbonization intermediate fibre product (stabilized PAN as multi filament two from SIGRI) in CTA pilot furnace

(3) Advice handling furnace and improvement of it for lower nitrogen consumption

(4) Advice development optimum stabilization conditions by laboratory methods (DTA, TMA and others)

(5) Advice surface treatment of carbon fibres

(6) Advice testing carbon fibres in model composites.

Contacted CTA-members and their responsibilities within the UNIDO-project:

- T.Col. RUNIVAN WELLINGTON SILVA (chief of PMR-division)
- Cap. Scyllas Souza Costa (responsible for the whole carbon material group)
- Mr. Angelos Simionato (carbon fibre group)
- Mr. Heitor A. Polidoro (graphite group)
- Mr. Francisco Xavier Carvalho (composite group)
- Mr. Joao Renato Santos Martins (surface treatment of C-fibres
- Mr. José Louis G. Da Silva (thermoanalytical methods, carbon fibre group)
- Mr. Ruy Rehder (spinning of polyacrylonitrile)

2. Polymerisation of Polyacrylonitrile (PAN)

The group has synthesized about 50 samples of polyacrylonitrile with different comonomer content of methylacrylate and itaconic acid by free radical polymerization. The synthesized polymers were characterized by viscometric and differential scanning calometries.

The new polymerization reactor (see fig.1)[+)] allows the production of large quantities of polymer material which is necessary to perform the planned spinning experiments.

There are still some problems with the humidity content of the produced polymers. It is still too high for to get a good solution of the polymer in N-N-dimethylformamide (DMF).

They now will solve this problem by using a fluidizing bed reactor for drying with heated nitrogen (see fig.2).

+) compare final report Dr. Nagabushanam (1982-1984)

3. Spinning of PAN-Fibres

The laboratory wet spinning assembly (see fig.3) is working well. They have produced about 250 samples with different spinning conditions. All samples are completely characterized by the viscosity of spinning solution, the density and the mechanical of the resulting PAN-fibres and by differential scanning calometry.

It is especially the success of Mr. Ruy Rehder that the spinning activities started last year with an acrylic polymer supplied by FISIBY can now be expanded to the polymer material of own production.

4. Stabilization of PAN

4.1 Determination of temperature/time profiles by thermoanalytical methods

The transformation of the meltable precursor fibre into an unmeltable ladder-polymer is the most difficult step in carbon fibre production because of the complexity of the chemical reactions. The Differential Scanning Calometry (DSC) and the Thermo-mechanical Analysis (TMA)[++)] allow the determination of temperature/time profiles by measuring the heat flow of the reactions and by measuring the resulting shrinkage of the polymer chain. (see fig.4a,b).

++ (supplied by [illegible])

The members of the carbon fibre group were trained by myself to use a special method for determination of the best reactions parameters (T start, T Final, T/min).

This is important because expecially for fibres of own production the thermal characteristic of the stabilization furnace must be adapted for each polymer composition.

4.2 Stabilization Furnace of SANTA CLARA

The furnace produced at SANTA CLARA in Sao Paulo must be able to realize a temperature profile near to that found by thermoanalytical methods.

For decreasing the costs, the furnace has only three horizontal heating zones, which allow a three-step increase of the temperature. Latest results have shown, that it is useful to avoid a decrease of the temperature of the fibre when passing the rollers.

Because of this reason some modifications are useful:

- Possibility for temperature control of the rollers.
- Protection of the roller surface against heat (silicon instead of rubber)
- Exhausting system especially for the part of the furnace where the rollers are installed (to avoid contamination with tarry byproducts).

Furthermore there must be the possibility for a visual control of the fibre during stabilization process.

The first run of the stabilization furnace will be about end of June 85.

5. Carbonization of Stabilized PAN (Multi-filament-Tow from SIGRI

5.1 Handling of Carbonization Furnace from RUHSTRAT

The nitrogen consumption of the furnace is one important part of the costs during production. The amount of nitrogen is now about 6 m^3/h. This value can be decreased by use of special brushes made of carbon fibres at the in- and outlet of the furnace (see fig. 5)+) This will be prepared by the carbon fibre group in the next weeks. Furthermore it is useful not to stop the furnace at the weekend. The temperature should decrease to about 500°C and the total amount of nitrogen can be reduced at that temperature to 2 m^3/h. In this case the furnace can start again very quick on Monday.

The electronic control (see fig.6) has to be optimized to avoid oszillation of the temperature inside of the furnace. The people at CTA, especially Mr. Ruy Rehder are now able to do that by themselves. It has to be controlled after each exchange of the heating elements and after long periods of using the carbonization furnace.

5.2 Construction of a Guide System for Handling of Multi-Filament -Tow from SIGRI

The stabilized intermediated product of SIGRI (multi tow) needs a special treatment of get a parallel spreading of the 220 000 filaments. The use of some different prototypes of guide systems gave the optimal conditions which are necessary for a sufficient spreading of the multi tow (see fig. 8a, b, c).

The guide systems are made of polished alumina tubes. It is planned to complete the system with some banana tubes to guarantee best guiding also at short absences of the technician, who controls the fibres at the guide system.

+) by courtesy of Prof. Fitzer. Compare also the publication FITZER, E., HEINE, M., Offenlegungsschrift Deutsches Patentamt DE 33 25 521 (1983/1985)

5.3 Problems with Carbonization Furnace

5.3.1 Thermocouple Heating Zone 2

The temperature in the second heating zone 2 (see fig.9) is measured by a W/Re-thermocouple. This thermocouple needs some additional protection against oxidation at the high carbonization temperature by installation of a gas in- and outlet for argon.

5.3.2 Oxidation of Heating Elements by Water Contamination inside of the furnace

The watercooled covering of the furnace can cause condensation of humidity inside of the furnace. To remove the water inside of the furnace it is necessary to heat up the furnace to about 200°C with opened top outlets. To avoid a recondensation inside of the furnace, it is necessary to reduce the amount of cooling water. Otherwise it is not sure that all humidity is out of the furnace and remaining water will be cracked into nitrogen and oxygen and causes damages of the heating elements (see fig.10a, b).

5.3.3 Overheating of Transformer (Heating Zone 2)

The transformer of the second heating zone showed after some days of peration an increase of surface temperature. This overheating caused some tears at the covering of the transformer (see fig.11a, b). This misfunction is reported to the suppliers, the German companies SIGRI and RUHSTRAT. They try to explain this effect, which is responsible for such a damage.

5.3.4 Lack of Spare Parts

It is absolutely necessary in any case to have enough spare parts when using the carbonization furnace. Especially the W/Re-thermocouple and the heating elements are not available in Brazil.
There are also some electronic parts for controlling the speed of trios. The parts which cannot be bought in Brazil are listed in table 1.

The CTA group has now some experience in producing heating elements with different design but the same electrical resistivity like those from SIGRI.
One of these heating elements will be tested at the research labs of SIGRI (see fig.12).

5.4 Cleaning Conditions for the Carbon-Fibre-Plant

There is still no sufficient solution to guarantee clean room conditions for production of carbon fibres. The big production room (see fig.13) has no possibility for inlet of clean air. In summer, when all windows are opened, there is contamination of the fibres by dust.
The carbon fibre group will solve this problem by an air-inlet with dust-filtration, perhaps with air-conditioning when there is enough money for to do it.

A short solution will be a dry cleaning every day with additional wet-cleaning each week. The windows should be closed and the inlet of fresh air will come from the inside of the neighbour rooms.

5.5 Handling of the Waste Gas of Stabilization and Carbonization Furnace

The use of the multi-tow from SIGRI for carbonization has shown some lack in the exhauster system. The exhaust of the carbonization furnace should be changed to exclude tarry byproducts can drop back on the surface of the furnace (see fig.14) and cause contamination.

Furthermore the big amount of waste gas can come back into the production room by the air-conditioning system.
The carbon fibre group will simulate the distribution of the waste gas by coloured smoke. In any way it will be necessary to change the position of the waste gas outlet. Perhaps the only solution will be to burn the waste gas especially when using the stabilization furnace simultaneous to the carbonization furnace. The amount of poisonous waste-gas in this case will be too high.

6. Surface Treatment of Carbon Fibres and Testing of Carbon Fibres in Model Composites

The equipmen 'or anodic oxidation is now connected to electrical power. It is now possible to oxidize the carbon fibre directly after carbonizat.on. When usind multi-tow instead of special tow the rollers in the oxidation cell have to be changed (see fig.15). In this case rills on the surface of the rollers are not practicable.
The composite group uses the dry-winding technique (see fig.16) to produce prepregs for model composites. They try to construct a new winding system with a larger bobbin and the possibility to use the wet-winding technique.

7. Proposals for Future Investigations

7.1 Polymerization experiments

The radical polymerization of homopolymeric fibre and fibres only with itoconic acid is necessary for comparison with those compositions which are just synthisized. Samples of the synthisized composition are now in ICT Karlsruhe for comparison of the results from DSC at CTA.

7.2 Spinning Experiments

The used FISIBA polymer should be spun with higher stretching values to study the influence on the mechanical properties of the resulting carbon fibres.
Samples of the spun fibres are now in ICT Karlsruhe to get some further information by thermoanalytical investigations Furthermore the synthesized polymer material (compare 7.1) should be used for spinning experiments to get different precursor material for stabilization and carbonization.

7.3 Determination of Temperature/Time Profile for Stabilization Treatment

The necessary temperatures and residence times for the fibre should be determined by DSC and TMA experiments. They will be different for each fibre type and can be influenced by the spinning conditions.

7.4 Determination of Temperature/Time Profile for Carbonization Process

A lot of experiments are done during my stay in Sao José-
It is now necessary to look for the mechanical properties of these produced carbon fibre multi tow in correlation to the used carbonization temperature. These experiments should be completed by carbonization temperatures between 400^{o} and $1000^{o}C$.

7.5 Elemental Analysis (C, H, N, O) of the Intermediate Products (Stabilized PAN) and the End-Product

The stabilized PAN-fibres and additional carbon fibres sould be investigated by an elemental analyzer to information about the stabilization mechanism and degree of carbonization.

7.6 Optimization of the Surface Treatment of Carbon Fibres

The ne anodic oxidation cell should be used to find out best oxidation conditions. The oxidized fibres should be tested in model composites produced by dry- and wet-winding technique to get information about the sufficience of the oxidation process.

8. <u>Finding of the Mission and Recommendations to the Government</u>

The possibilities for research experiments at CTA are remarkable. With the new stabilization furnace from SANTA CLARA they will be able to produce commendable results which can contribute to clear the complicated chemical reactions during carbon fibre production.

In any way the success will be influenced by the responsible manager of the project who should have a very extensive knowledge about scientific problems to coordinate all necessary steps for a good research work.

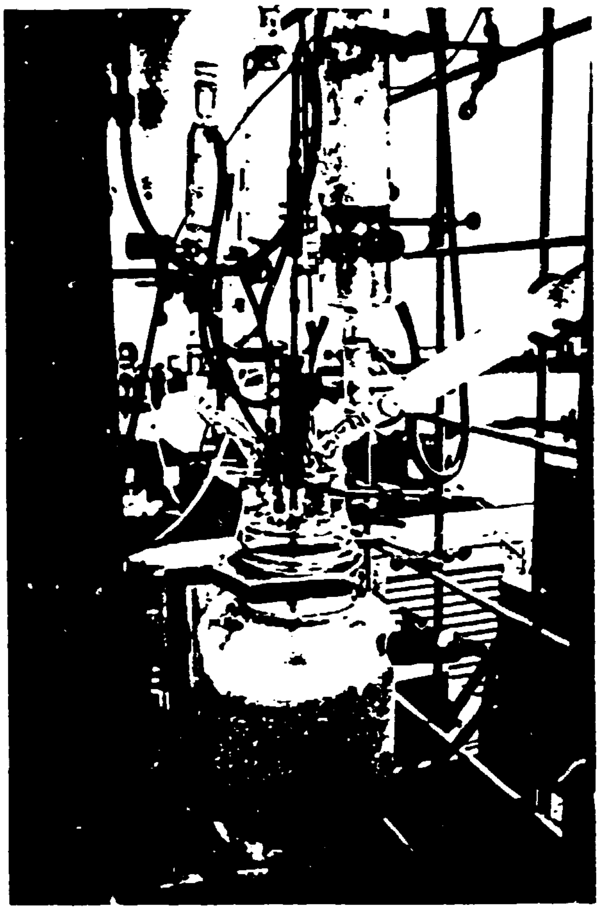

Fig. 1: Polymerization reactor to produce sufficient amounts of polymer material

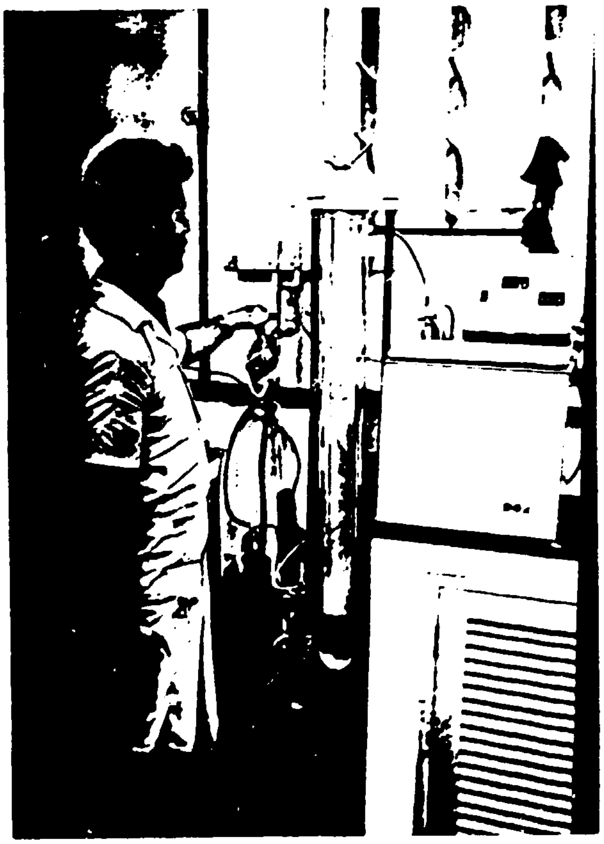

Fig. 2: Fluidizing bed arrangement for drying the polymer powder

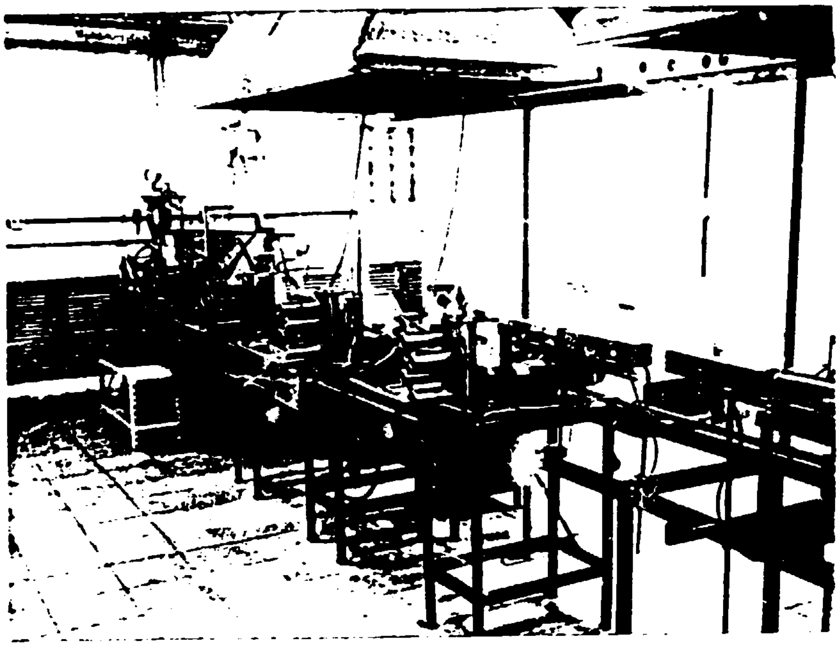

Fig.3: Wet spinning assembly

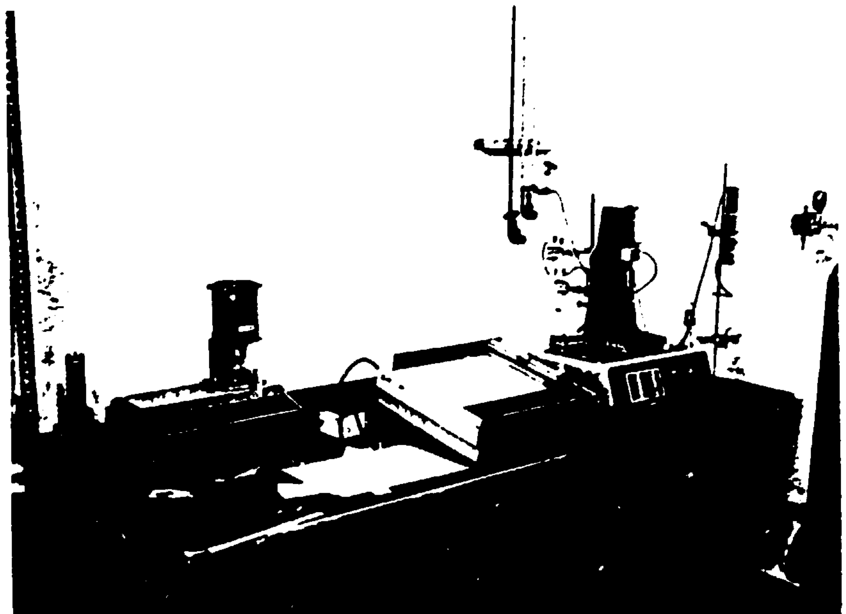

Fig.4a: Thermoanalyzer from DUPONT (DSC/DTA, TMA)

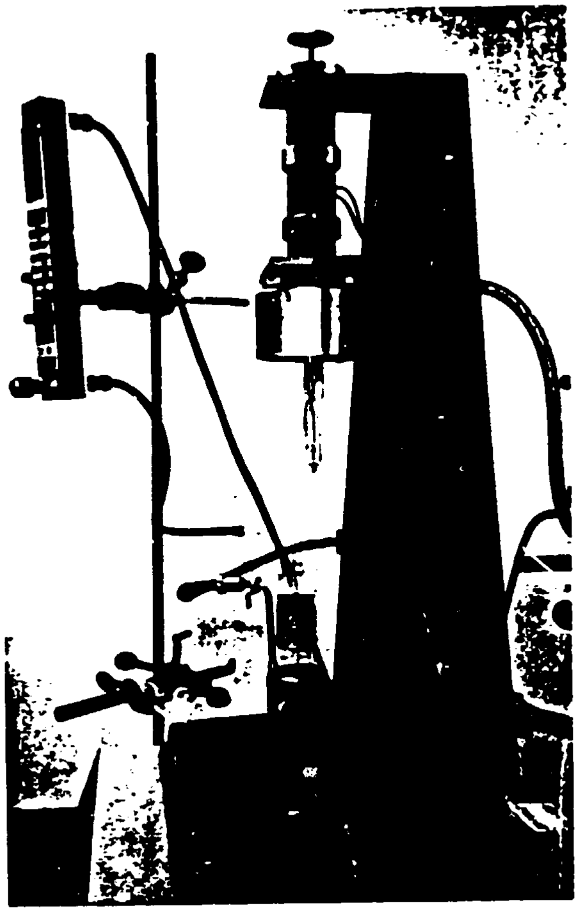

Fig.4b: Thermomechanical analyzer (TMA)

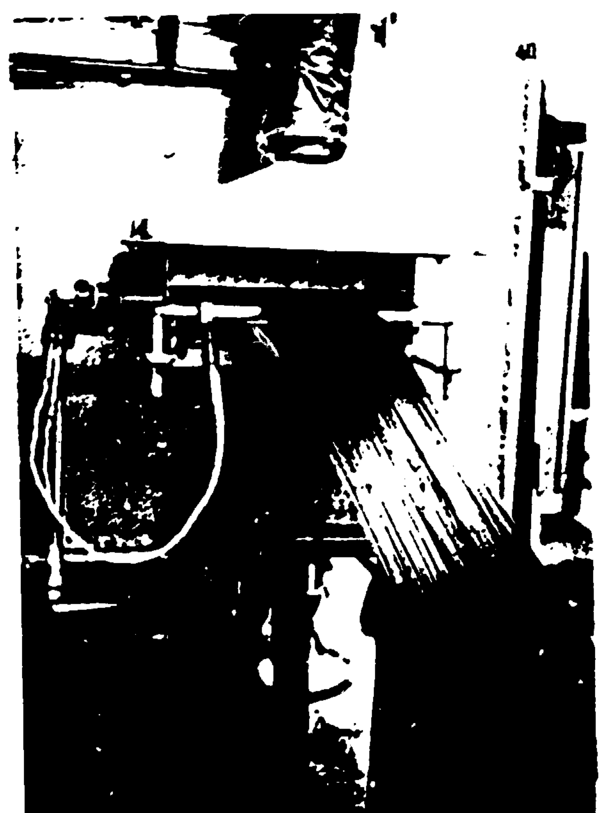

Fig.5: Outlet of carbonization furnace

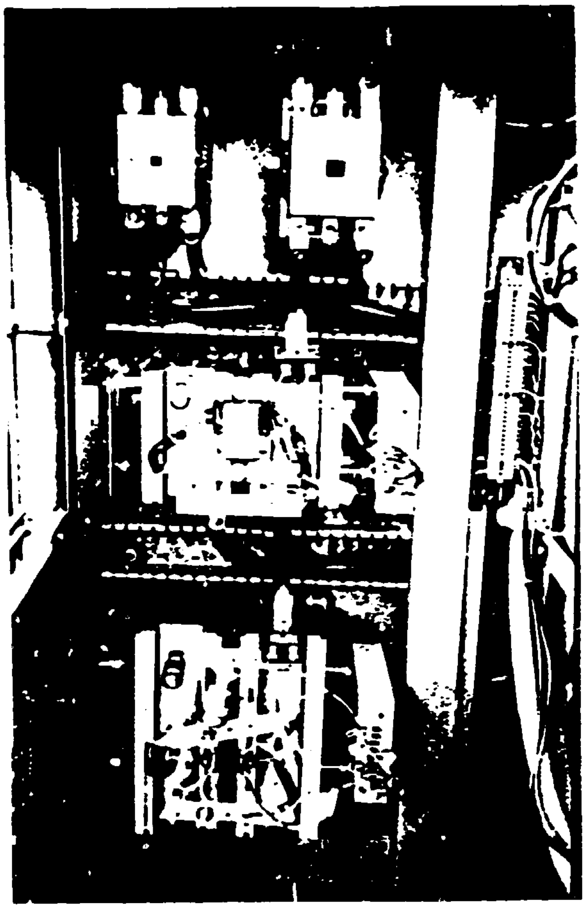

Fig.6: Electronic control for carbonization temperature

Fig.7: Multifilament-tow from SIGRI

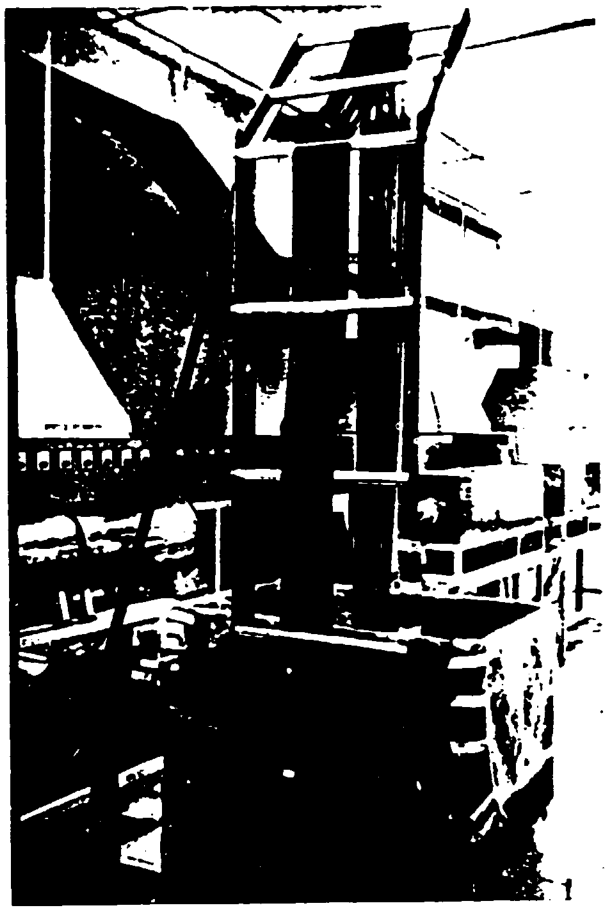

Fig.8 : Guide system for handling of multifilament-tow from SIGRI

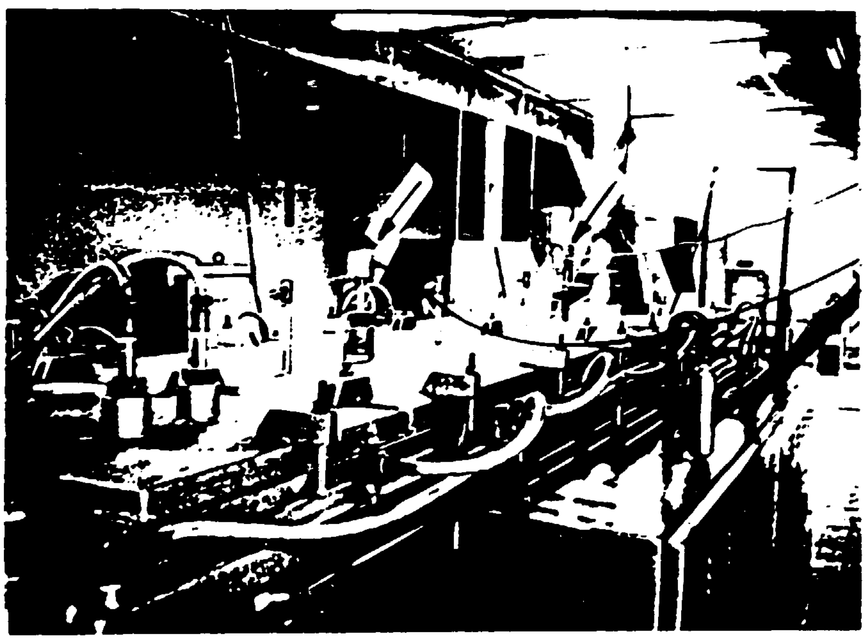

Fig.9: Position of the thermocouples at the carbonization furnace

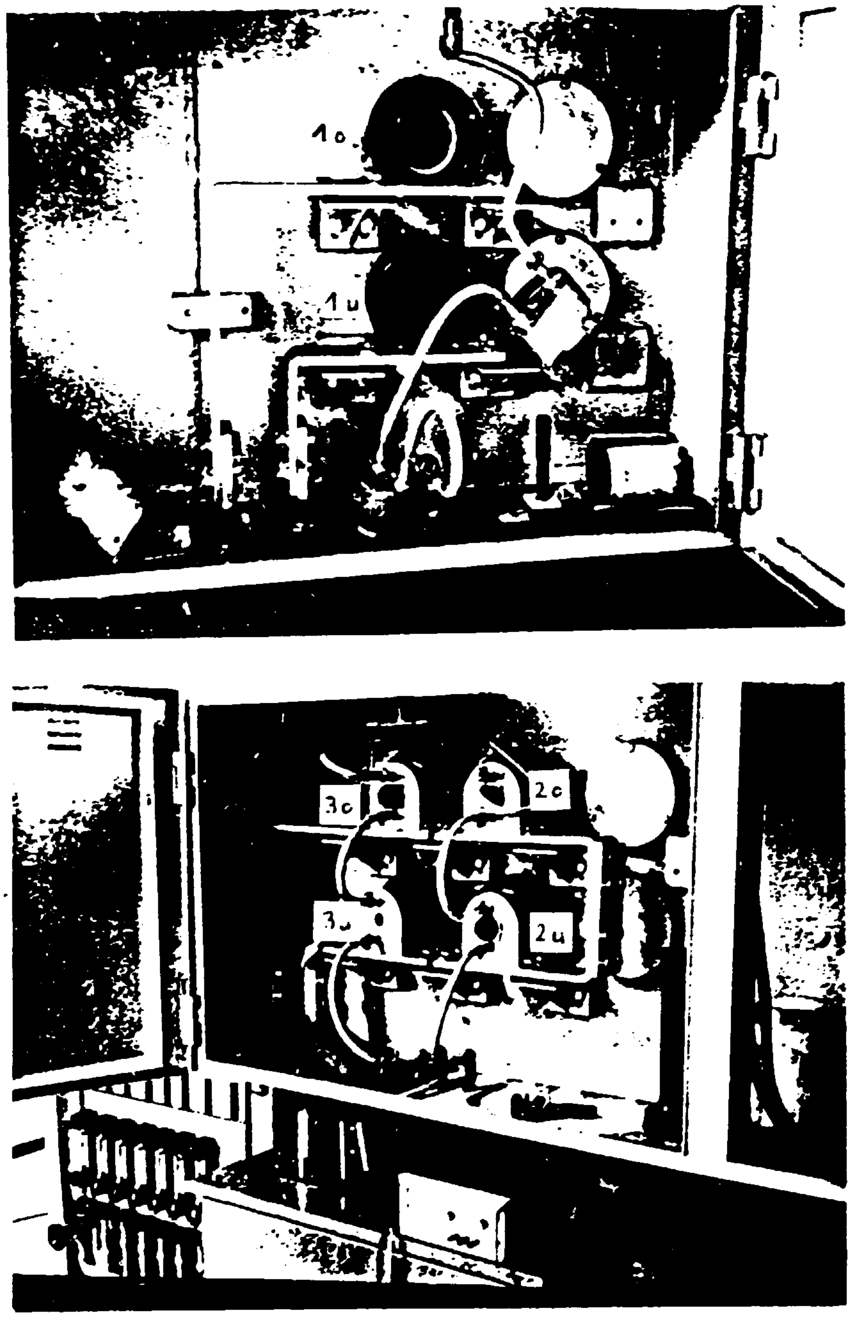

Fig.10a: Position of the heating elements inside of the furnace

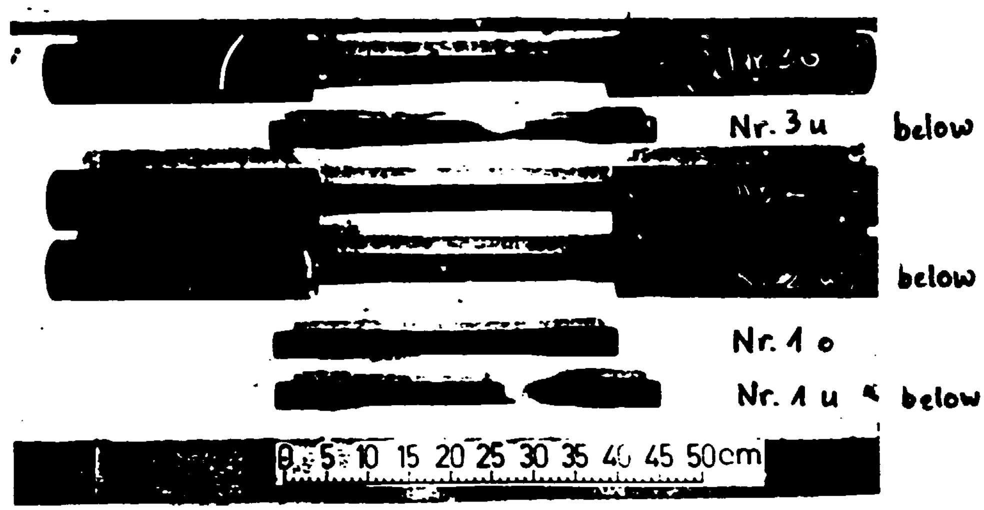

Fig.10b: Damages, especially at the heating elements in position below the heating zone.

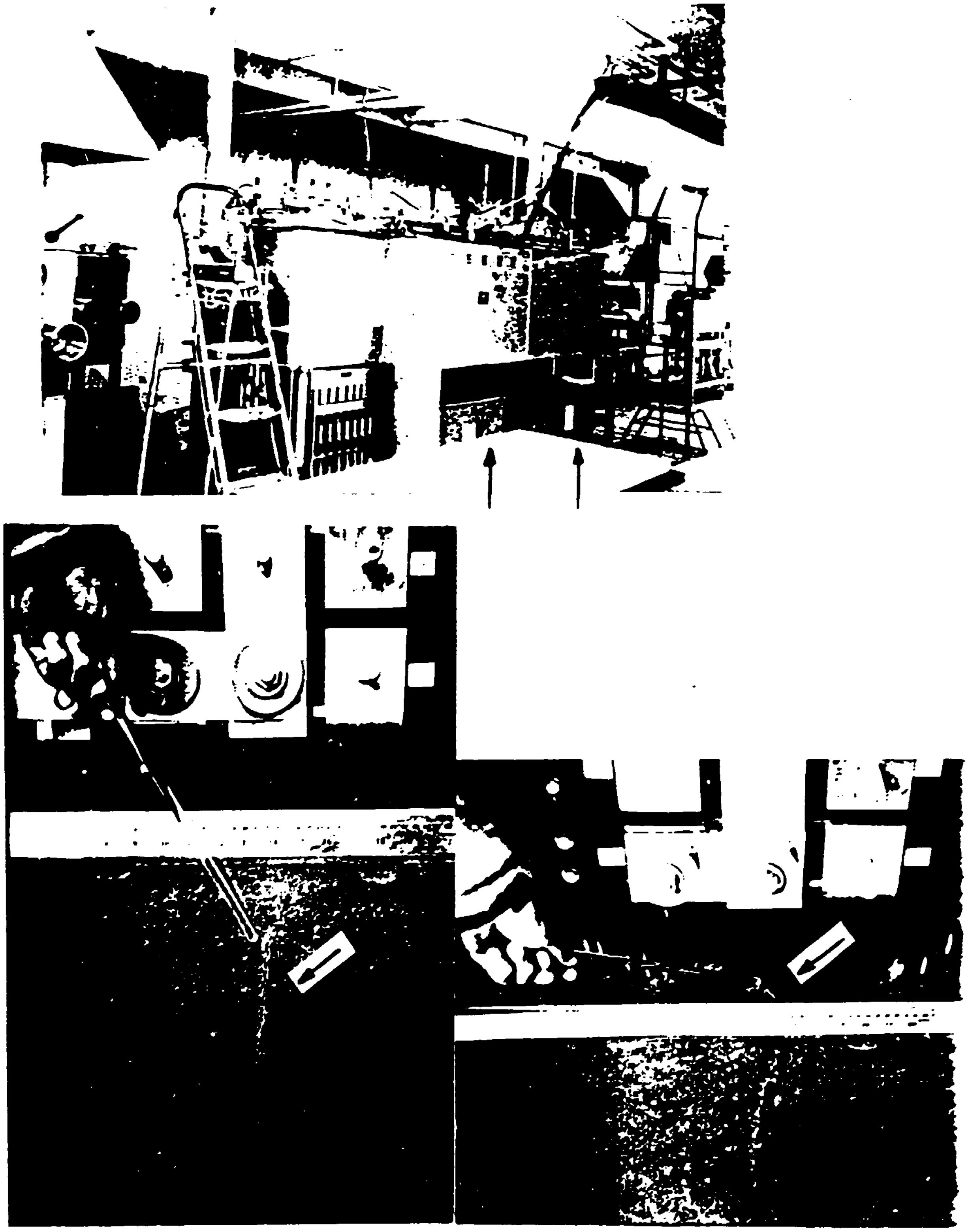

Fig. 11 a) Position of the transformer below the carbonization furnace (at the right: heating zone 1; at the left: heating zone 2)

b) Tears at the covering of the transformer 2 after overheating

Amount	Specification
2	RC 4157 DC
16	RC 4156 DC
2	SN 75466 N
4	GE CNY 17
10	FET TIS 75

Table 1: Necessary spare parts for speed control of trics

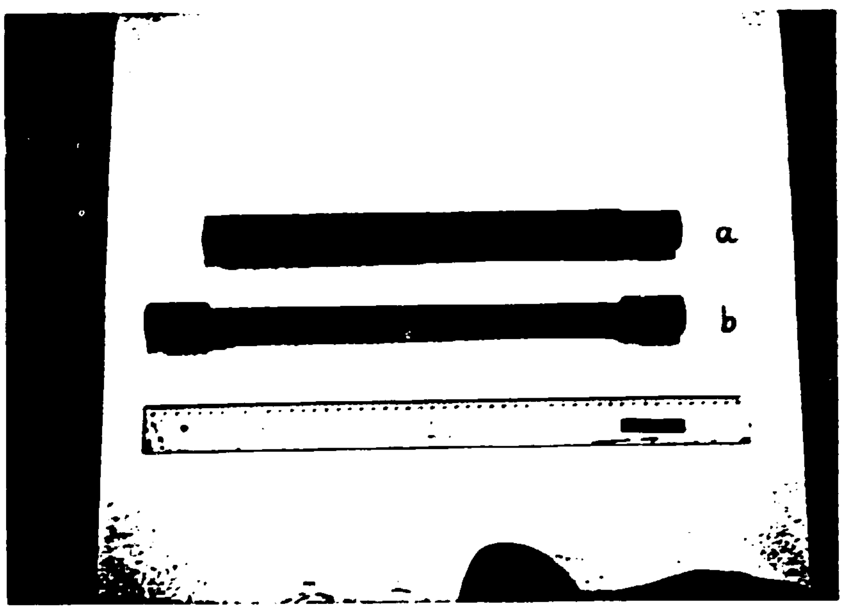

Fig.12: a) Heating element produced by SIGRI
b) Heating element produced by CTA

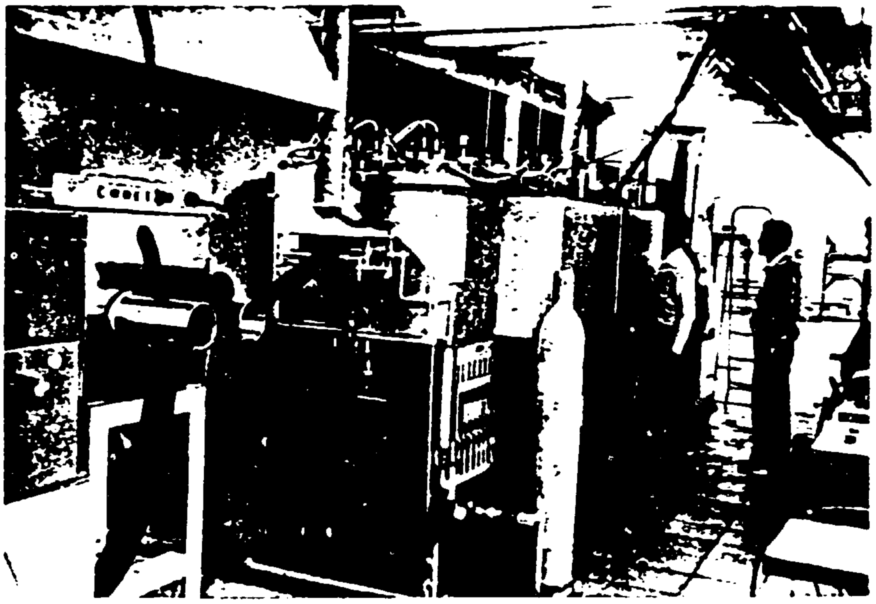

Fig.13: Production room for carbon fibres

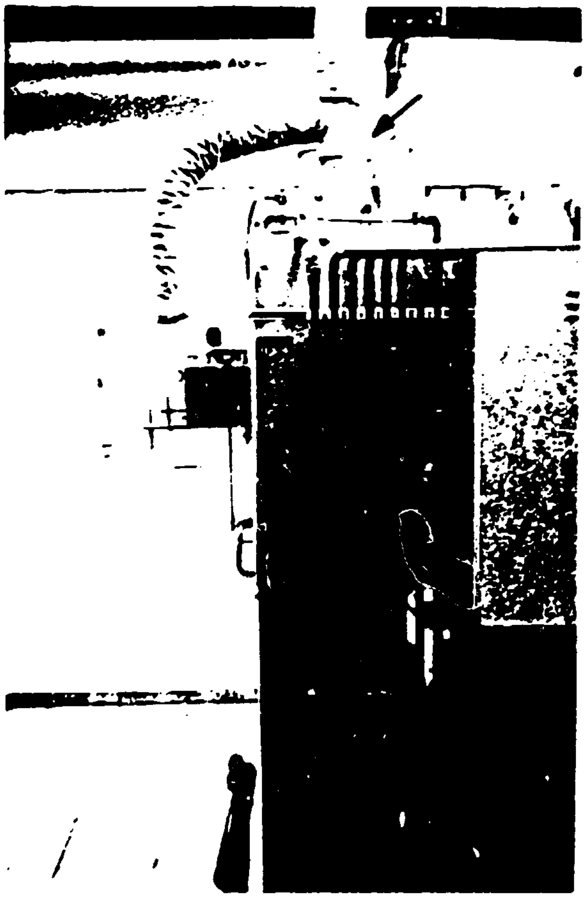

Fig.14: Tarry byproducts can drop on the fibre surface

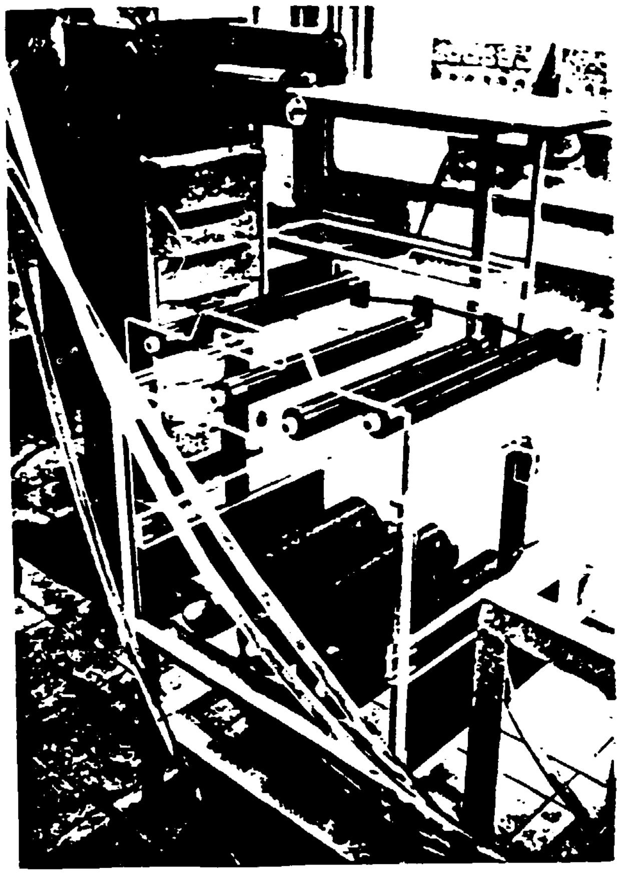

Fig.15: Cell for anodic oxidation of special tow

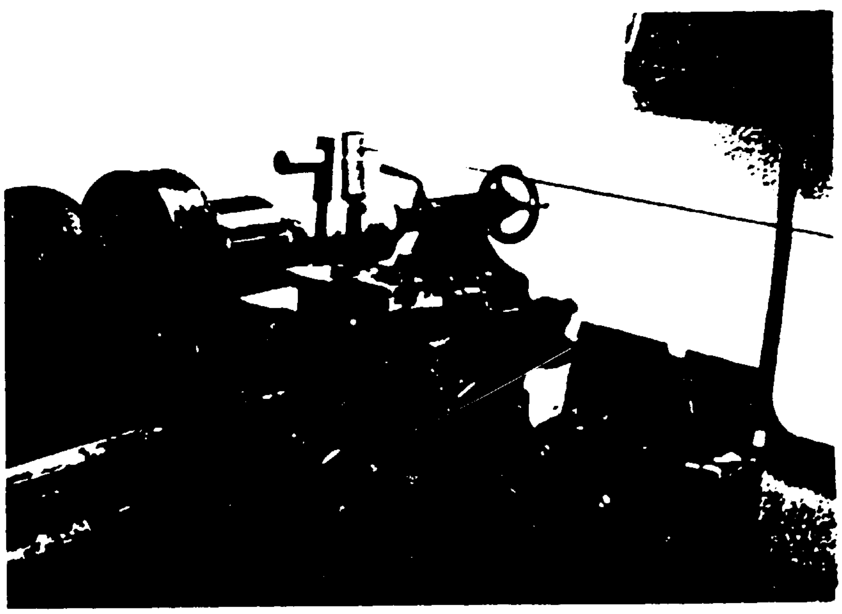

Fig.16: Dry-winding equipment for producing prepregs for model composites