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TITLE: RESEARCH ON AND PERFECTION OF ON-LINE SENSORS AND CONTROLLING FOR CONTINUOUS TEXTILE FINISHING

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Research on and Perfection of On-line Sensors and Controlling Processes for Continuous Textile Finishing

Publishable Synthesis Report

Introduction

Quality and quick response are the keys of the European textile finishing industry in "competition with low wage countries. Today, in summary about 1O % of the total costs of production are related to repeated treatments because of deviation in quality.

To be able to manufacture a well-defined product the 'adjustment of the process will depend to a far extent on the nature of the raw material which vary widely in textile finishing. For that reason, the flexibility of the finishing processes used is becoming increasingly important because the average size of batches to be processed is decreasing.

In order to realize a product with well defined properties, controlling of the various process parameters is essential. Due to the processes, the main parameters determining the end-use properties of most textiles are the consumption of chemicals and the relaxation during drying, heat-setting and swelling. Although these parameters are very important for the quality there are still no arrangements available measuring the consumption of chemicals during bleaching or the relaxation behaviour of textile materials on a continuous production line in textile finishing.

The ultimate aim of this work is to optimize the processes bleaching and heat-setting respectively mercerizing by imploying sensor systems able for a more effective control of the hydrogen peroxide concentration in the bleaching liquor and to follow-up the internal stresses of textile goods changing during heat-setting respectively mercerizing "as a function of dwell-time.

Results

1. H_2O_2-sensor-system

Voltammetry - i.e. the measurement at sensoring electrodes of a current flow in dependence of electrode potential applied - has been considered for developing a sensor system for H_2O_2. The underlying electrochemical changes for hydrogen peroxide to be monitored at the electrodes are as follows:

Oxidation: $H_2O_2 \longrightarrow O_2 + 2\,H^+ + 2\,e^-$ (neutral and acid media)
Reduction: $H_2O_2 + H_2O + 2\,e^- \longrightarrow H_2O + 2$ &/-

The equations for reduction and oxidation of hydrogen peroxide given above give rise to a limiting diffusion controlled current plateau in voltammetric analysis which is proprotional to the concentration of H_2O_2.

To obtain a reproducible bleaching result, the concentration of H_2O_2 in the bleaching bath has to have "a constant level of ±10 % at a concentration of 60 ml/1 of H_2O_2 (35 % solution) Within this concentration range the system has to be controlled.

Because of the complexity of the bleaching solution composition and of voltammetric techniques two research institutes decided to follow different strategies for sensor evaluation. The strategies are given in Fig. 1.1. .

Both strategies had to take into account different electrode materials and configurations and/or different solution flow situations. For the implementation stage and for testing in praxi a joint strategy of both research institutes with. the partners of the technical side (i.e. machine constructor and textile finisher) have been programmed.

In the first stage of the investigations following the strategy given in Fig. 1.1 a relatively large number of possible electrode materials for the construction of the sensor were tested. These include Pt, Pd, Glassy Carbon, graphites, steels, Sn, Zn, Rh, Ag, Au, Cr, Ni, Ti, Ir, Zr, Rh.

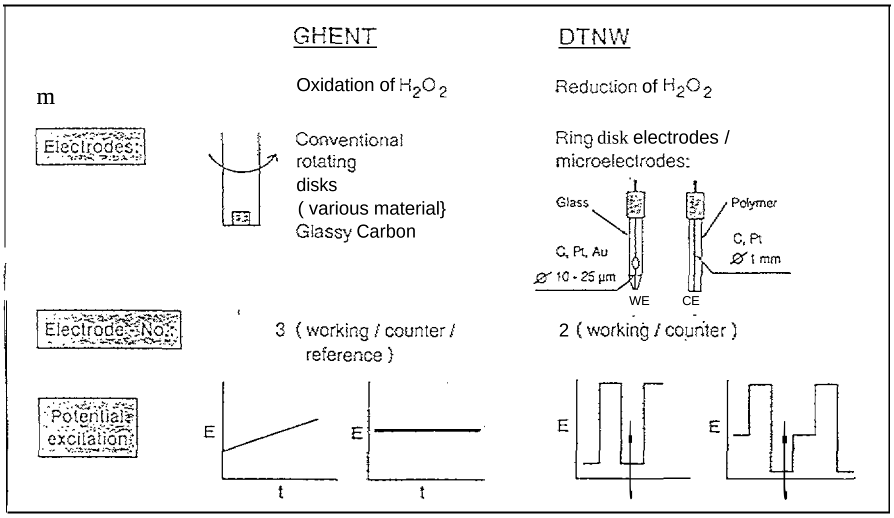


Fig. 1.1: Strategies for H_2O_2 -Sensor Evaluation.

Using macroelectrodes and **linear** sweep-voltammetry **suitable potential** ranges **on the different** electrode **materials were selected. Very promising results** *were* **obtained by the use of a rotating configuration** of a disk electrode made from Glassy Carbon (GC).

The results on the GC-electrode **are based** on **the current voltage curves as obtained by** linear-scan-voltammetry (Fig. **1.2). The current-plateau at about 0.45 V** was used **for calibration. The calibration curve obtained is** linear **up to** 1 **M** H_2O_2, **while the experimental errors remain limited to** not **more than 4 %.**

The influence **of the bleaching bath additives on the response with** GC-electrode **is negligible. As a result, most major conclusions drawn from the experiments done in the absence of the additives are:**

- the linearitity of the calibration line in presence of high concentrations of hydrogen peroxide without being disturbed by the presence of additional constituents of the bleaching liquor
- the long term stability und reliability of the GC-electrode.

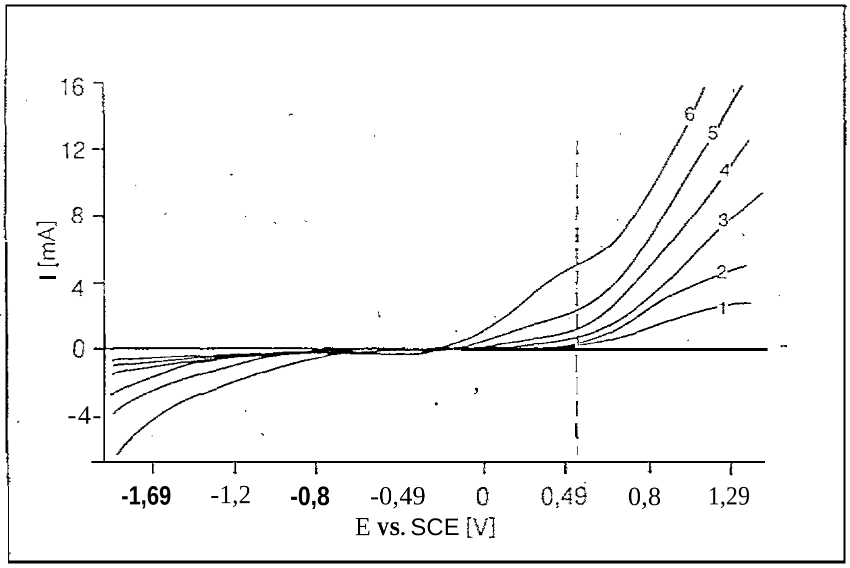


Fig 1.2: **Current-potential curves of H_2O_2 in alkaline medium at glassy carbon rotating disk electrode of 3 mm diameter; H_2O_2 concentration for curves 1 to 6: 23, 46, 91, 180, 350 mmole per liter; the dotted line indicates the preferred measuring potential.**

Micro-electrodes (active diameter less than 50 µm) (s. Fig. 1.1) were investigated. Using Pt and stainless steel micro-electrodes of 20 to 25 µm diameter limiting currents for the detection of H_2O_2 in solutions containing water glass at pH 13 were obtained. Using only a two electrode measuring system - counter electrode and measuring working electrode - simplifies the electronic equipment needed and avoids the risk of poisoning the reference electrode used in potentiostatic work with macro-electrodes. In addition potential stepping provides internal cleaning cycles for the electrode surface.

It turned out that a triple potential excitation for a stainless-steel-electrode seems to be favorable. A potential cycle of 4 s at -1.5 V, 4 s at -2.1 V and 30 s at +0.5 V was found to work best. A calibration curve for H_2O_2-determination up to 25 g/l pure H_2O_2 is demonstrated in Fig. 1.3. The curvature at concentrations >15 g/1 could be encountered for by electronic compensation. The long term stability for the stainless-steel-micro-electrode (25 pm) so far exceeds 20 days

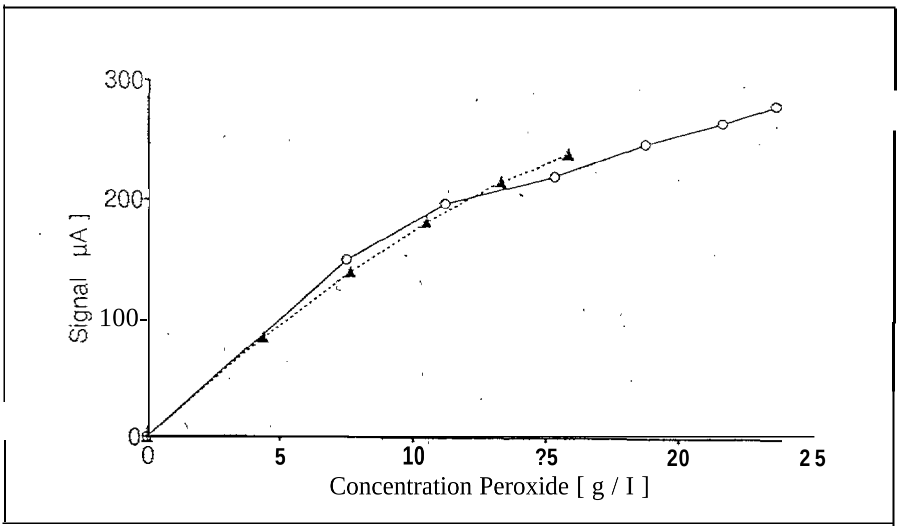


Fig. 1.3: Reproducibility (short term, 1 day) of calibration curve(s) for peroxide determination in hot-bleaching bath using a stainless-steel micro-electrode.

A pilot station was constructed for simulation experiments which resembles a by-pass situation for the actual roller-vat machine. The pilot-station consists of a liquor vessel, a suction-pipe line a circulating pump and a back leading liquor vessel. The cell carrying the two electrochemical sensor systems (G C-macro-electrode - and Pt-microelectrode) was built into the suction pipe line. A proper electrical isolation had to be built-in in order to prevent the influence from stray potentials upon the measuring electrode signal.

Using this apparatus electrode responses were tested under technical conditions varying H_2O_2-concentration, temperature and pH-value. Experiments have been done both in fresh solutions and in bleaching liquors where 5-10 km of cotton fabric have been treated.

Experiments showed that the formerly rotating GC-macro-electrode does not need any rotation - the streaming liquor creating equivalently a stable diffusion gradient of H_2O_2 towards the electrode. Results for H_2O_2-monitoring using this electrode configuration are shown in Fig. 1.4. These results resemble almost perfectly the results obtained in earlier stages of investigations. Pt-micro-electrode on the other hand showed aging phenomena. ,

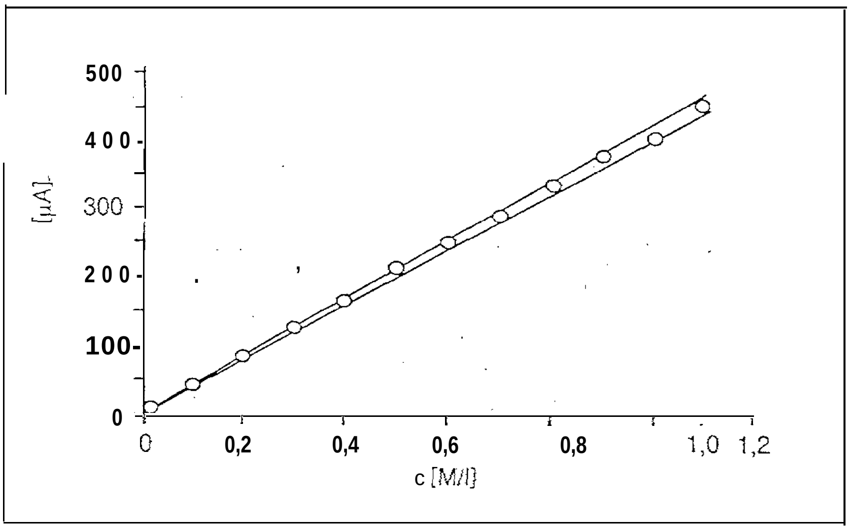


Fig. 1.4: Calibration curve of H_2O_2 at stationary GC-elctrode positioned in the flow stream of the by-pass system; measuring potential 0.42 V.

For a better survey of the results obtained up to that stage most characteristics of the GC-macro-electrode and of the micro-electrodes so far as the service ability of a H_2O_2-sensor is concerned are summarized in table 1.

Table 1: Characteristic's of the prototypes of H_2O_2-sensors.

Characteristics	Prototype Macro-Electrode Glassy Carbon (RU GHENT)		Prototype Micro-Electrode of Platinum (DTNW)	
Output proportional to hydrogen peroxide concentration	excellent	i-++	excellent	+++
Long life time	depends on kind of preservation	++	independent on preservation	+++
Long term stability	excellent	+++	insufficient	
Mechanical specialities	none, no rotation of sensor necessary	+++	none	+++
Output signal	mA-level minimal amplification	+++	µA-level high amplification	++
Response time after variation in concentration	few seconds	+++	few seconds	+++
pH dependence of output	perfect compen-sation necessary	+	compensation necessary	++
Temperature dependence of output	compensation necessary	++	compensation necessary	++
Potential Cycling for cleaning steps	none	+++	potential cycling necessary	+
Costs of sensor	low	+ + +	low	++ •l-

Even under industrial conditions the GC-macro-electrode system showed prominent characteristics concerning the precision and accuracy of H_20_2-concentration measurement, life time, stability, response time and towards adverse influence of bleaching debris. This configuration was chosen for further development of a sensor prototype because of best long term stability is given by the glassy carbon electrode without rotation in a streaming liquor. This system does not need any rotation and has a current in the range of 250 to 500 µA. This is an order of magnitude sufficient for a relatively easy amplification necessary for the control system.

It was decided for the first prototype sensor system to use the Glassy Carbon Macro-Electrode.

For presentation purposes a model of the sensor equipment has been constructed. This model comprises an electrode housing compartment for the electrode configurations required for use of GC-macro-electrodes (working electrode, counter electrode, reference electrode, and pH-reading electrodes and temperature sensor). A strong circulating pump and a metering equipment for addition of H_2O_2 is provided. All will be controlled by electronics comprising pH-compensation, temperature-compensation and generation of a control signal for the metering device (output 4-20 mA).

A patent has been taken out for the Glassy-Carbon-Sensor. The complete equipment has been shown at the ITMA exhibition during October 1995 in Milan. A schematic drawing of this equipment of the H_2O_2-sensor system is given in Fig. 1.5.

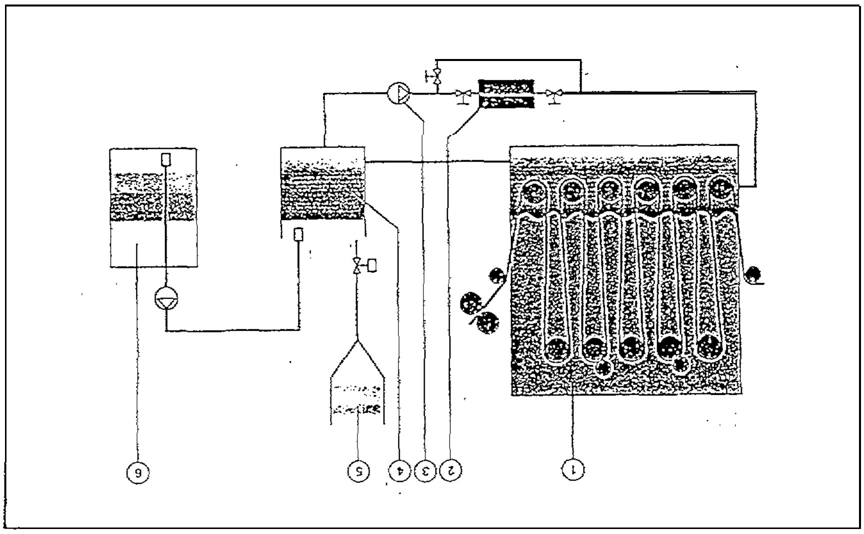


Fig 1.5: Final assembly for hydrogen peroxide sensor system;
1 roller- vat, 2 Probes for H_2O_2 (electrodes), pH-value and temperature, 3 circulating pump, 4 mixing vessel, 5 entrance of H_2O_2 through vent (open/closed position), 6 optional continuous control by metering pump.

Beside the use as a sensor system to control H_2O_2 in a bleaching liquor for the textile bleaching process" it is also intended to make it usable for other industrial fields in which H_2O_2 is employed; like paper-, cellulose-manufacture, environmental technology, cleaning, cosmetics and others. "

2. Relaxation Measurements in Continous Processing

2.1 Heat-Setting

'The relaxation-tensions during heat-setting are determined by the temperature dependent shrinkage force. To analyse these relaxation-tensions the shrinkage force of textile materials were determined as a function of dwell time. The results received on PES-fabric indicate that the shrinkage-force increases with time. Above a certain dwell-time shrinkage-force as a function of time reaches a value at which the differential change in the slope is zero.

The relaxation tension as a function of time depends in fact on one specific property of the material which is called the effective "temperature (T_{eff}). This is a premelting point strongly related to the heat-setting temperature and the dwell time of heat-setting. The relationship between T_{eff} and the tension of "fabric is demonstrated in Fig. 2.1.1.

The tension of relaxation in transverse direction of the fabris as a function of dwelling time is demonstrated for a fabric of technical use in Fig. 2.1.2. The shrinkage force of this fabric indicates that at the beginning the shrinkage-force increases quite rapid by and then levels out into a slow linear increase. The same behaviour has been detected analysing other fabrics.

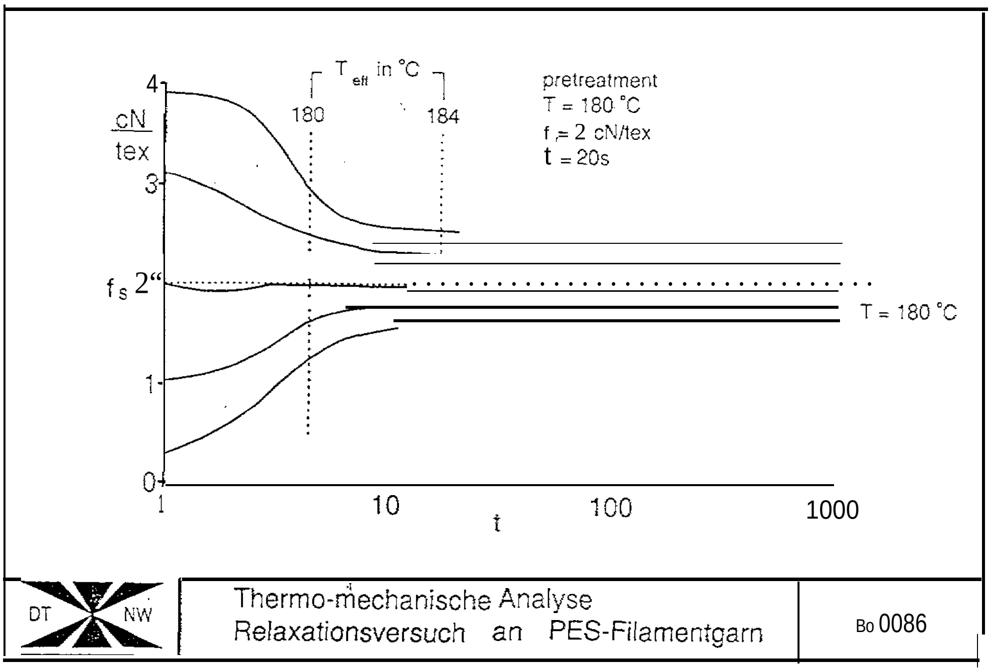
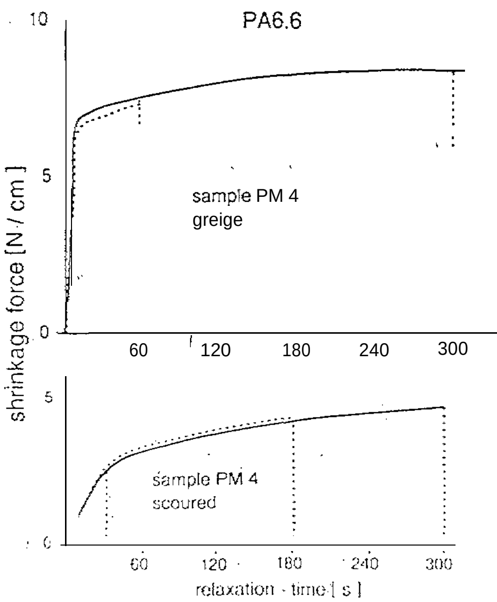


Fig. 2.1.1: Relation between effective temperature (T_{eff}) and effective tension, demonstrated on PET-material.



Sample	Fabric width (cm) rated value	Fabric width (cm) actual value	Fabric weight (g/m²) rated value	Fabric weight (g/m²) actual value
PM 4 greige heat setting at T 215°C				
t 0s	210	210	120	108
t 60s	210	213	120	115
t 300s	210	214	120	114
PM 4 scoure heat setting at T 215 °C				
t 0s	210	208	120	111
t 30s	210	204	120	116
t 180s	210	203	120	118
t 300s	210	205	120	130

Fig. 2.1.2: Relaxation-tensions during heat-setting and dimensional stability.

Because of the relaxation behaviour the heat-setting time necessary to attain a fabric with certain properties like thermal stability, (T_{eff}) dyeability, dimensional stability, and specific weight of the fabric is closely connected to the tension as brought about during the heat-setting process.

The prolongation of heat-setting time leads to width values above the rated one. This indicates that the dimension of a fabric 'finally received after heat-setting is directly controlled by the tension developing during heat-setting.

One of the basis of the previous discussed shrinkage force measurements and their analysis it became obvious that shrinkage forces as low as 0,1 N/cm occur during heat-setting of medium weighted fabrics. Additional requirements a tension measurment-system for a stenter frame has to meet are thermal stability upt to 250 'C and long term stability at the other boundary conditions. For the developed measurement-system to be implemented into the stenter frame three types of sensors were tested:

a) capacitiv microsensor
b) piezo load sensor
c) DMS

The capacitiv microsensor is a silicium cell and its design and dimension allows an installation into the chain guiding elements of the stenter frame. The disadvantage of this sensor-type was the insufficient mechanical stability and signal disturbances at high frequency vibration. The tests of the piezo load sensor result in an excellent mechanical stability. The disadvantage of this type of sensor is its inefficient accuracy with load signals < 10 N/cm. In addition a DMS sensor was tested but so far as temperature and mechanical stability is concerned does this sensor type need further development, which was beyond the scope of this work.

Because of the excellent reliability of the piezo load sensor this sensor type was tested in a broad range of temperature up to 250 "C. The sensor-type was capsulated in a gas-proofed and anticorrosive housing.

The piezo sensor system consisting of 8 sensors was mounted into the stenter frame in such way that the load-cells are only protected by a 1 mm thick metal piece. this metal piece is continuously overrun by the bearing-rollers. The bearing rollers are mounted in a distance of 6 cm in the chain leading elements and overrung the load sensor continuously.

A sensor electronic-system was developed to transfer the impuls-like load amplitude into a static signal system. The repeated peak occurence depend on the speed of the' velocity of chain 5 m/min correspond to 1.38 Hz and 150 m/min correspond to 41.6 Hz. A main task in the development of the load sensor system was the improvement of the electronic for special amplifiers needed.

Each piezo force-sensor is accompained by an amplification-system with low pass filter and a reset electronic. The low pass filter supresses ail fast changing value fluctuations brought about by. mechanical vibrations of the stenter frame. The reset electronic is necessary to avoid dissipation of charges by the isolation. To accomplish this a reset-system was developed. After each measuring impuls registered by the micro-processor the amplifier system receives a reset-impuls. In this phase of measuring the piezo-load sensor is in a short circuit condition for 10 p.s. in this state the eventually existing rest of charge is eliminated.

The measured signals are digitized in a 8 channel multiplexer with AD transformer. The rate of conversion amounts to 8x2 kHz. The measured impuls shown in Fig. 2.1.3 are scanned with a rate of 2 kHz. Using this procedure each impuls delivers 12 values. The CPU calculates within each measuring phase the highest value of amplitude. This value is stored. After the lowest value of ampiitude is registered, a limited value the reset impuls in triggered. in a value register the average of-a certain number of values is calculated. These values are transferred to the PC.

With the developed load sensor measurement system built-in into a stenter frame industrial-tests were started. The parameters iike heat-setting temperature, dwell-time and width of fabric were varied. The tests results received indicate that the change in dwell-time (change in speed of the running material) is very distinct. The equilibrium in shrinkage force - relaxation of tension - is shifted towards the end of, the heat-setting zone with increasing speed of fabric {s. Fig. 2.1.4).

In additional test-series the influence of change in fabric width at the feeding end, the dwell-time and the humidity of the fabric was tested.

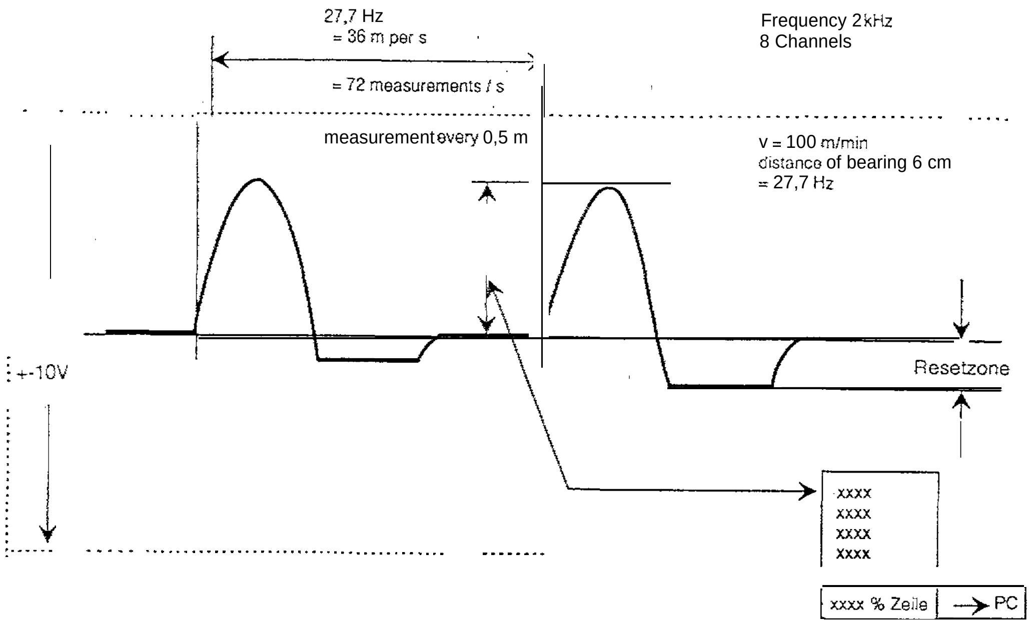


Fig.2.1.3: Schematic graph of the reset-system.

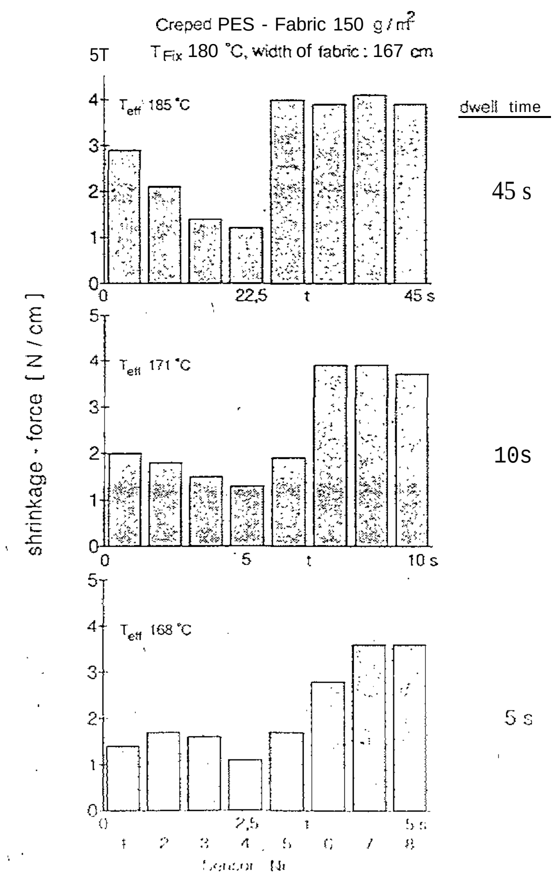


Fig. 2.1.4: Tension-Profile during Heat-Setting.

The tension developed in the fabric during heat-setting is highly influenced by the change in width at the feeding end. The registered tensions document a complex course. A fabric having an original width of 160 cm is stretched to 184 cm develops immediately a decrease in tension. Entering the heating zone" of the stenter frame this decrease in tension is overlapped by the temperature caused relaxation. Both phenomena lead to the complex course in the slope of the relaxation tension of fabric.

Dynamical measurements of tensions deliver a complex signal corresponding to the different properties of the varies fabrics. the results obtained on industrial scale indicate that possibly the friction forces between the yarn-systems of the fabric influence, in addition to the shrinkage forces caused by the change in fibre structure during heating the complex tension as registered by the sensor system.

The tensions as developed during heat-setting are considered as the finger-print of each individual fabric and its properties so far as dyability, dimensions stability, elasticity etc., are concerned are ruled by this tension.

At this time this tension can be measured by the developed tension control-system during heat-setting. For standard qualities the data of the relaxation tension are stored and in regard to high quality such a control-system will patronize the target of total quality approach,

2.2 Mercerizing

The alkali-treatment of cotton and cotton blend fabric in the presence of high tensions modifies the crystalline network of the cotton fibres. Because there is no sensor system controlling the fabric tension during processing in most cases the dimensions are rated and a few procent of residual shrinkage are taking into account. Because the tensions which are brought about during mercerizing are not known. For this reason measurements first had to be done on laboratory scale to gain knowledge of the order of magnitude in the tensions developed during processing.

The design of the mercerizing machine „Dimensa" is subject of the development of a tension control-system to compensate for the shrinkage-forces caused by the swelling of cotton material and memorized in the fabric. To characterize the shrinkage forces first laboratory tests were executed. Further investigations were first done on a pilot installation to win knowledge about the order of magnitude in tension developing during mercerizing. The results as received by the test done indicate that the transverse loads are about 450 N/m to 750 N/m..

To register the relaxation tension in the weft direction on the moving fabric as a function of dwell-time in the stabilization-zone of the mercerizing machine „Dimensa" tensiometers in an appropriate distance were first built-in into the chain leading elements of the stenter frame of the mercerizing machine. Several load sensor types were tested under the environment conditions of mercerizing. Load peaks are registered every time the chain leading element passes the senosr. The tension developed in the fabric during mercerizing is demonstrated in Fig. 2.2.1. The results of long term test with the different load sensors indicated that because of the outstanding environmental conditions the different small sensor types (ISM, DMS) are not applicable in the stenter frame of mercerizing.

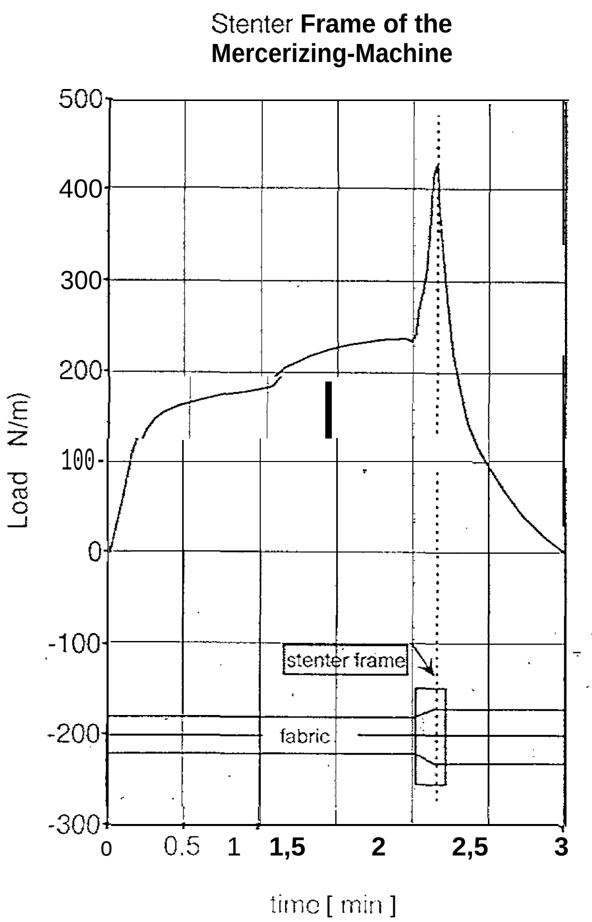


Fig. 2.2.1: Tension during Mercerizing.

Because of the malfunction of the small sensors in production the measurement system was changed in so far as the tension of fabric is registered indirectly by „Kraftmeßbolzen". This is a sensor of very robust construction. This type of sensor is mounted into the adjustable spindle drives of. the stenter frame. This modified sensor system consists of six load sensors. With this sensor assembly it is possible to follow up the change in tension of the running fabric along the stabilization-zone of the mercerizing machine. Tests were carried out to investigate the functionality of the tenison-control-system. The results received on 5 fabrics are demonstrated in Fig. 2.2.2.

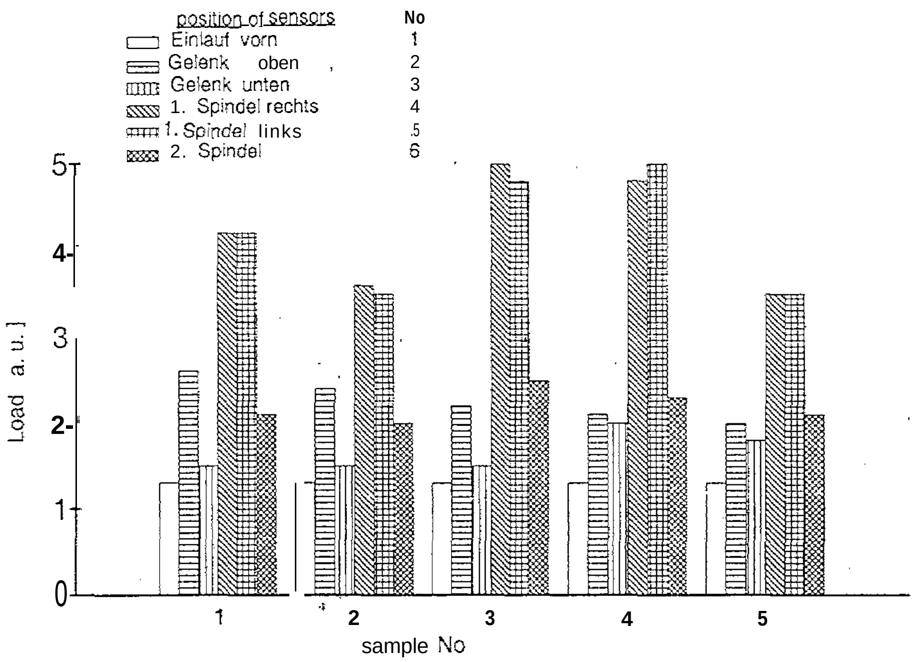


Fig. 2.2.2: Tension during Mercerizing of different Cotton-Fabrics.

From this results it is noticed that the maximum in tension (1. Spindel) and the tension at the delivery end (2. Spindel) differes to a great extent from fabric to fabric. Because of the evaluation of these data it was recognized that there is a, relationship between the value of the maximum tension (1. Spindel) and the residual shrinkage of fabric in preceding processing steps.

Conclusions

In cooperation of partners representing the textile finishing industry and textile machinery industry assisted by textile institutes sensor systems 'were developed to control:

- H_2O_2 concentration in the bleaching process,
- relaxation behaviour of textiles during heat-setting and'
- relaxation behaviour during stabilization of mercerized cellulosic textiles.

For the H_2O_2 sensor-system the voltammetric technique was chosen. The evaluation of the oxidation signal and working with a special prepared glassy-carbon electrode turned out the most successful method measurig the high concentration of H_2O_2 in a bleaching bath.

Using this system, a compensation of pi-i-value and temperature is needed. The automatic control system being implemented into the bleaching process on production line delivers reproducible and reliable results.

A patent has been taken out for the sensor by the UNIVERSITY OF GHENT. For its commercialisation a close cooperation exists between the University OF GHENT, where the sensor was developed, KÜSTERS GmbH, Krefeld, responsible for its implementation in practice and INTEC GmbH, Stuttgart.

The registration of accurate relaxation tensions in dimensional controlled continuous processes requires the adaption of sensor-systems stable in relation to outstanding environmental conditions. In a stenter frame the most outstanding conditions are the high temperature (250° C). The 'sensor-system developed using piezo load sensors gives indication that the system is sensitiv enough to register the small changes in tension as a function of time at a given temperature. The results are of innovative and commercial interest. The aspect is seen in the quite advanced form of registering tension of the individual fabric being still under process conditions. A patent has been taken out for the sensor system.

The registration of accurate relaxation tensions in the dimensional controlled stabilization-step of mercerizing machine „Dimensa" requires a sensor system with an outstanding stability to high concentration sodium hydroxide solution at elevated temperatures. Suitable sensors meeting this requirements are not available at the time. Therefore, the change in tension during processing was measured by a robust indirect measuring system a so called „Meßbolzen-System“.

From the analysis of the loads measured at the different positions of the stenter frame it can be concluded that the load measured at the end of the extension field gives information about an average tension of the fabric in process. This tension is also in a very good agreement with the textile properties like dyeability and dimensional stability.