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THERMOGRAVIMETRY AND SILK CONDITIONING IN LYONS. A LITTLE KNOWN STORY (1833 - 1974)

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SUMMARY

Silk is a very hygroscopic and very expensive fiber. Silk conditioning proposed by Talabot in 1833 has been adopted as a model procedure till nowadays. It is at the present time applied to many textile fibers. It consists of the determination of a "dry" weight of a fiber by dehydrating a sample to a constant weight. The balance which was in operation in Lyons and commercialized in many countries may be considered as the ancestor of thermobalances.

The history of silk became linked with the history of thermogravimetry in 1832, more than 150 years ago. It is this "Lyonnaise", technical and economic adventure that I am going to tell you about.

Silk is an extremely hygroscopic material which, in its driest state, in air and at room temperature, contains no less than 8 % of its weight in water and may contain up to 15 % without looking wet.

From a commercial point of view this property presents serious drawbacks as it can be used for fraudulent practices. We must point out that at the time when our story started, the price of a kilogramme of silk in Paris was 175 gold Francs, that is to say approximatively the price of a kilogramme of sterling silver. In order to actualize this price we have to multiply it by at least 30 which gives approximatively 6 000 F for a kilogramme. Selling a litre of water at the same price was so tempting that the "mouilleurs de soie"[1] or "piqueurs d'onces"[2] were in plenty and that it was necessary to put things right. It was in Turin (Italy) in 1750 that the first "Conditions des Soies"[3] was created. It was an establishment in which silk bales were brought to a so-called normal state by "artificial equilibrium" in appropriate, heat and moisture conditions. The "trade weight" of each 60 kg silk bale was then measured.

[1]"*silk wetters*"

[2]"*ounce pinchers*"

[3]"*silk conditioning house*"

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The Italian method consisted in opening each bale and in fragmenting its content. The raw silk was then suspended on iron hooks inside a large room well ventilated in summer and heated by four fireplaces in winter. When the silk had been so conditioned it was baled again and weighed.

Four private companies were created between 1780 and 1792 in LYONS (2), SAINT-ETIENNE and SAINT-CHAMOND. An area of 25 square metres was affected to the evaporation of each bale for 24 hours. At that time the silk market was in a state of such confusion that for instance a great number of merchants from Piemont and Italy refused to sell their silk on the LYONS market.

So, considering that silk conditioning was as essential as the control of weights and measures, Napoleon decided to withdraw this activity from the private industry and to entrust it to a public body.

By a decree passed in 1805 he conferred the monopoly of silk conditioning to the Chamber of Commerce of LYONS. The Chamber of Commerce reluctantly accepted this responsability, as it was convinced it would lose money since the scientific problems posed by silk conditioning had not yet been solved. Silk traders knew so well how important meteorological conditions were, so that buyers waited until they were favourable to conclude deals (northerly wind and rise of the barometer). As a consequence, as early as 1816 the Chamber of Commerce set the temperature of the drying rooms for each month of the year.

In 1831 many new ideas appeared :

1) FELISSANT proposed the combined use of the thermometer and of the SAUSSURE hygrometer.
2) ANDRIEU suggested that it was quite sufficient to use a proportional test, that is to say, to characterise one sample from each bale.
3) TALABOT who graduated from the Ecole Polytechnique deserves the merit of proposing a new method which is still in use nowadays.

At that time TALABOT was in charge of the ventilation and heating of the LYONS "Grand Théâtre". So the president of the Chamber of Commerce submitted his views to him on the reforms which were imperiously required by silk conditioning. By the end of the year TALABOT presented his conclusions (1).

a) Artificial equilibration in a conditioned room does not produce a better regularity of the moisture content that the natural equilibration which takes place inside a bale well wrapped in tarred paper.

b) The "conditioned weight" of a bale can be deduced, without noticeable error, from the conditioned weight of a sample submitted to "absolute dessication" (proportional test).

c) The dry weight is obtained by suspending the sample on the beam of a balance above an oven heated to a constant temperature of 105 - 108° C until a constant weight is obtained.

d) The conditioned weight or market weight is conventionally equal to the dry weight plus 9 % water. Later on silk traders demanded 11 % : conditioning was not compulsory and as the value of the moisture content was an observed average value buyers and sellers could in fact fix it by common accord.

The first device proposed is shown in figure 1 (2). It is definitely, according to the present nomenclature (3), an isothermal thermogravimetric apparatus working at atmospheric pressure. As the word thermogravimetry was coined only 50 years later, by the Japanese HONDA, this apparatus was simply called "TALABOT oven". At that time the most difficult problem was not the accurate weighing, up to a constant weight but the problem of isothermal heating. First TALABOT suggested using steam as shown in figure 2 (2). The water vapour circulated under controlled pressure inside a jacket shaped like an upside - down bell. D'ARGENT, a Member of the Institut de France, played a decisive part in the adoption of this method. In order to convince the members of a committee for standardization, he dipped a silk sample previously dehydrated up to constant weight in a TALABOT oven,into a bath of mutton suet heated to 170° C. No vapour bubbles appeared at the surface of the bath.

Whereas TALABOT's ideas about heat transfer and solid 1 $\rightleftarrows$ solid 2 + gas equilibrium were quite accurate, they were not on material transfers. Due to the lack of air-renewal around a sample weighing a few hundred grammes and to the slow diffusion of water vapour between the sample and the outside of the oven, achieving a constant weight required about 3 hours, which was much too long as the demand for analyses kept increasing.

In 1852 PERSOZ, Professor at the Conservatoire des Arts et Metiers of PARIS, came up with the idea of blowing a flow of air heated to 110° C directly onto the sample. The dessication time was then reduced to half-an-hour. Such an apparatus is shown in figure 3 (2). It was used from 1853 to 1973, that is to say for 120 years without requiring major changes apart from the methods used for heating the ovens. Originally, warm air pipes coming from a stove situated on the floor below fed a battery of 12 thermobalances (figure 4) (2). Some ovens were equipped with independent coal heaters (figure 5) (2), later with gas heaters (figure 6) (2) and finally with electric heaters. In order to eliminate the weighing error due to air convection, the valves on the circuit were closed each time the sample was weighed. So as to shorten the time required for these analyses, all the samples were previously preheated in a preparatory apparatus (figure 7) (2).

The TALABOT - PERSOZ - ROGEAT method met with immediate success. Twenty years after the first test, there were 124 ovens in France, 48 in Italy, 12 in Germany, 12 in England, 6 in Austria, indeed more than 200 in Europe alone. These figures show that France and LYONS in particular with 45 ovens, was the main centre for the silk industry in Europe.

Nowadays the conditioning process for natural or man-made fibers is still the same but the balance is a single-pan one. Silk is now conditioned in the producing countries, China producing 50 % of the total amount. Buyers and sellers usually trust one another and controls are very unusual. We must point out that the price of silk has dropped a lot since 1869 : 240 Francs or $ 40 a kilogramme instead of 6 000 Francs. Besides France's silk production is only 500 kg per year whereas it was 2 200 metric tons in 1953.

The "Bombyx muri" is at the origin of very old international relations. Silk fabrics were brought from China by caravans. In the 6th century, Byzantium organized the stealing of a few "grains" and of the secrets of breeding. Then from the 7th to the 16th century silkworm-breeding and the silk industry spread around the mediterranean sea together with Islamic culture. It reached Spain and then Italy. At that time Damasons was the greatest silk centre.

In 1466 LOUIS XI decided to create a silk factory in LYONS in order to limit the "grand vuydange d'or et d'argent du royaume"*. In 1685 when the Edict of Nantes was revoked, many Protestant silk makers had to flee to Switzerland, Britain, Prussia and Holland, which weakened the preeminence of the French silk industry.

Apart from thermogravimetry, the silk industry has always been associated with many other scientific and technical discoveries such as the JACQUARD weaving loom with punched cards and PASTEUR's work which made it possible to stop the 1853 pebrine epidemic.

The TALABOT balance was so useful, in scientific and technical fields as well as in trading exchanges that it should have a prominent place in the history of thermogravimetry and not just in the history of the textile industry.

* great drain of gold and silver due to silk buying

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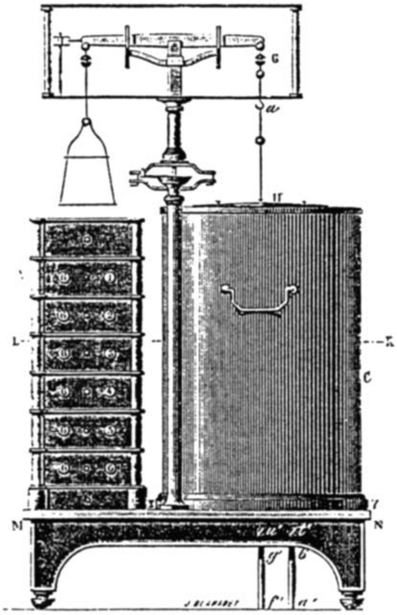
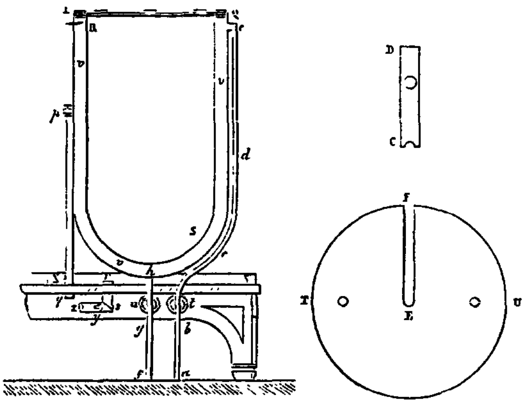


Figure 1 - TALABOT apparatus



2 a 2 b

Figure 2 a - Section of the inner bell

Figure 2 b - Lid

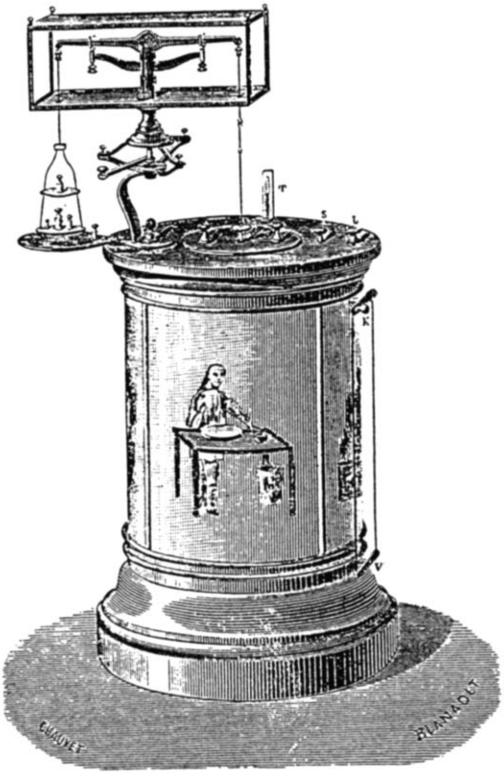


Figure 3 - TALABOT - PERSOZ - ROGEAT drier

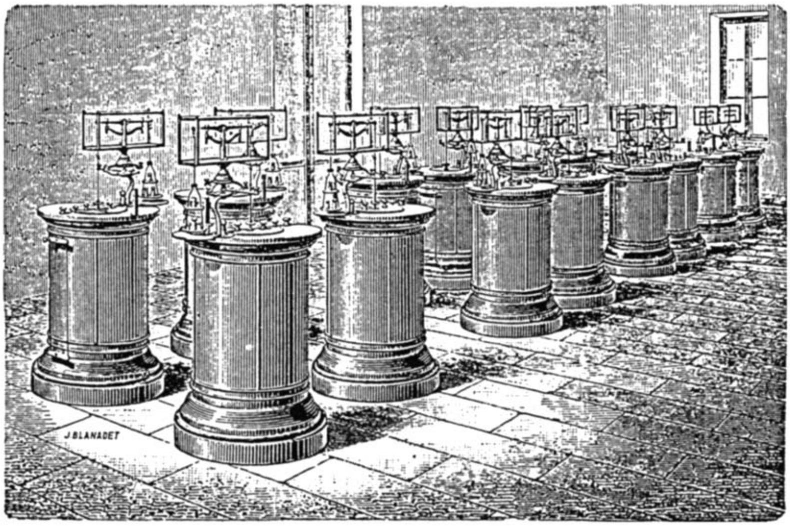


Figure 4 - General view of conditioning room

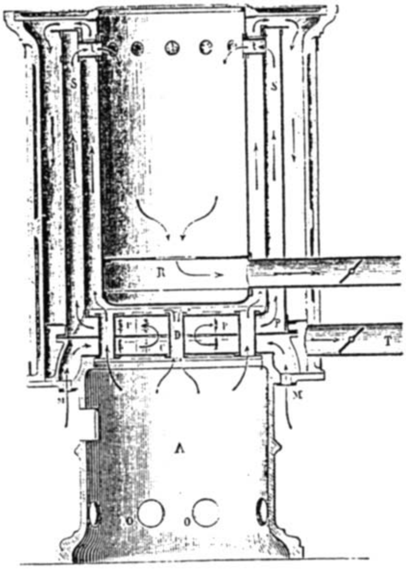


Figure 5 - Coal-fired apparatus

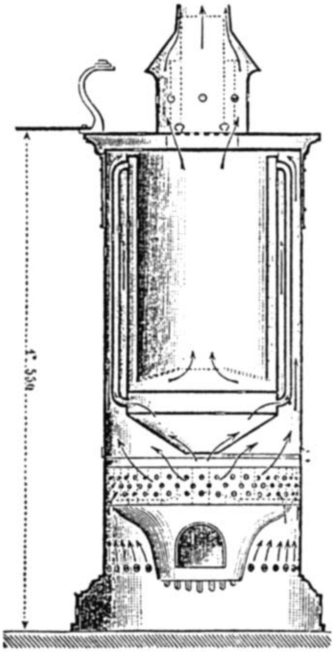


Figure 6 - Gas oven
(Basle Conditioning House)

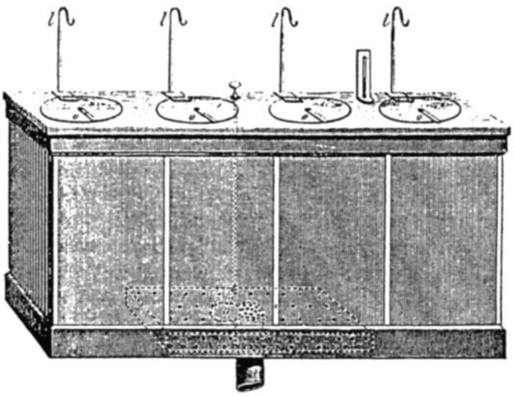


Figure 7 - Preparatory apparatus