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First Commercialization, Dead Rock, and Quick Decay after Temporary Prosperity of Cellulose Nitrate Rayon Industry as Predecessor of Chemical Fiber Industry*

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Synopsis: As a subsequent study a critical examination was carried out on a history of first commercialization of Chardonnet silk. Before establishment of the company, in 1889 Chardonnet displayed small spinning machine together with luster 'artificial silk' at Expo'89 at Paris. On 3rd. December, 1890 'Societe anonyme pour la fabrication de la Chardonnet' was registered by Besancon's proprieters including J. B. Weibel and his collaborators with capital of 6 million francs at Besançon, Dout, France. Chardonnet was not a member of the board, but a consultant engineer. The plant of the company was constructed during 29th January, 1891 and 1st May, 1892. The planned production capacity was 50kg/day. The plant started its operation on June, 1892. Records of expenditure, fiber production, and production cost during June, 1892 and 1896 were summarized. Several troubles encountered in large scale production were discussed. Among them the inflammability of 'silk' was the most serious and operation was suspended in Jan. 1894 ~April, 1894 and the factory scale experiments for improvement were performed. Chardonnet had worry about the flammability as early as 1886. He investigated in 1888~1890 numerous reagents for denitration. However, he adopted, at the time of starting of operation (1892), lackadaisical means, fearing the deterioration and cost-up of the fibers. Technology transfer of Chardonnet

Count Hilaire be Chardonnet
(1839~1924)

* This paper is dedicated to the memory of the late Mr. Kiyoshi Hosoi, Ex-director of Cellulose Nitrate Plant, Asahi Chem. Ind., Nobeoka, Japan, who guided the author into the cellulose nitrate industry when the author started his professional career.

process occurred first to Spreitenbach, Switzerland, where a private factory, owned by d'Asson in 1881, to whom Chardonnet licensed and gave technical guidance, was expanded to 'Societe' by Swiss capital (capital=200×10^3 francs.) in 1892. This 'second factory' started its operation in 1893, soon stoped due to the same troubles as those at Besançon. De Asson resigned and new management replaced him. Role of F. Lehner, if any, in improvement of the original Chardonnet's process was examined in detail. 'Lehner' artificial silk company (an English company) was formed in 1892 based on Lehner's two primitive patents, but it did not work well. Lehner, who had no practical (even bench level) experience, joined to Spreitenbach factory to assist in 1894 and learnt the secret of Chardonnet silk process. The Besancon factory reopened on June, 1894 and since then the operation became very successful. Production records in 1890~1909 at Besancon factory, Tubize, and Vereinigte Kunstseidefabrik (VKF) were summarized. The world production and its share of cellulose nitrate process decreased dramatically between 1909~1913 and the industry followed quick decay, due to poor cost competitiveness against cuprammonium and viscose processes. Profit and deviviend of Chardonnet silk companies during 1898~1921 were collected.

1 INTRODUCTION

In the previous paper[1] history of emergence of Chardonnet's artificial silk industry and the characteristic features of Chardonnet's invention and technology were inversigated in detail in connection with social circumstances before the industrialization and prehistory of artificial fiber. For this purpose, the eleven authoritative books on artificial silk, published hitherto and available[2~12], and the patent literature[13] were systematically analyzed.

In this paper, attempt will be made, following the same strategy as that in the previous paper and as a subsequent study, to investigate:

1 ; the establishment of first company of Chardonnet process,

2 ; production records immediately after the starting of factory operation and some serious troubles encountered,

3 ; denitration method as a remedy for improving the inflammability,

4 ; role of F. Lehner, if any, in improvement of the Chardonnet process,

5 ; achievement of the Chardonnet company after reopening,

6 ; technology transfer of Chardonnet process, and

7 ; Chardonnet silk since then.

2 FIRST COMMERCIALIZATION OF ARTIFICIAL SILK: ESTABLISHMENT OF THE SO-CALLED 'CHARDONNET'S COMPANY'

On May, 1889 Chardonnet displayed *une petite machine filant de la soie artificielle* and luster fibers at Group VI, classe 5I (Material des Arts chimiques, de la Pharmacia et de la Tannerie) in Exposition Universelle de Paris, en 1889, where Grand Prix was awarded to him. This news was reported in New York Times (dated 21th Nov., 1889) as Count Chardonnet's silk. Note that Chardonnet exhibited his artificial silks at Expo 89 before he established the company. Hard[14] (see Table 1) misunderstood that after the establishment of the company Chardonnet displayed the specimen manufactured by the company. Yamazaki[15,16] erroneously understood the date of establishment of the company as 1882 and that of Expo as 1899. They made scenarios of financial recovery of the company on the basis of the above-mentioned mistakes.

Table 1 illustrates the date of establishment of the *Société anonyme pour la fabrication de la soie Chardonnet* described in various books.[17~24] In the table coaxial double circle means the correct date. Surprisingly, the majority of the most authoritative books affords us very inaccurate and unreliable information. And even the specialist like Lehner, who had once worked with Chardonnet, described an incorrect date in the society journal.[24]

Another examples of erroneous description on the date of establishment are:

(1) *'His process was patented in 1885, but a year earlier (=1884) the Société Anonyme pour la Fabrication de la Soie de Chardonnet was founded.'* (R. W. Moncrieff[17]).

(2) *'Chardonnet made cellulose nitrate fibers on a commercial scale in France in 1885.'* (C. B. Chapman[25]).

Table 1 Date of establishments of (Société pour fabrication de la soie Chardonnet)

Date	Reference	Remarks
1884	R. W. Moncrieff (1975)[17]	
1884	V. Hottenroth (1928)[17]	
1884 or 1890	T. Lieser (1953)[19]	
1890	Y. Kami (1927)[20]	◎
1890, 3rd. Dec.	A. Demoment (1953)[21]	◎
1890, 3rd. Dec.	L. G. Fauquet (1960)[22]	◎
1891	F. Lehner (1906)[24]	
(1892) (Starting ofoperation)	D. C. Coleman (1969)[23]	

Table 2 Chardonnet's position in the company ('Besançon')

	Job position	Reference
(1)	ingenieur-conseil avec voix consultative dansce conseil	A. Demoment[21]
(2)	directeur technique	L. G. Fauquet[29]

(3) *'In 1884, Chardonnet made his first artificial fibres from nitrocellulose solution which was squirted through tiny holes, hardened in warm air and then treated chemically to convert it back to cellulose.'* (J. Gordon Cook[26]).

Note that Chardonnet made his first artificial fibers on laboratory scale probably in 1878[27,28] and on manufacturing scale in 1892.[27,28] Then, in any scale, 1884 is not the year when artificial silk was first made. And Chardonnet's first silk was not cellulose, but cellulose nitrate.

Table 2 illustrates the job position of Chardonnet at *'Societé'*. Chardonnet was not a member of board, but only an engineer-consultant. Then, *'Société'* was, in any means, never Chardonnet's company. Later (1888), he declared himself in British Patent No. 5,270 (1888) as proprieter.[30]

Name and occupation of members of the council were[21]: Maurice Bretillot (banker), Jean-Baptiste Weibel (manufacturer), le Marquis Henri Terrierde Lordy (proprieter) and Marie-Charles Broch d'Hotelas (proprieter).

The essential construction started on 29th January, 1891 and was completed on 1st May, 1892 with expenditure of 992,896 francs 06.[31,32] The spinning machines for artificial silk were built by M. E. Merts, of Basel.[33]

3 START OF OPERATION AND ENCOUNTERED TROUBLES AT BESANÇON AND SPREITENBACH

3.1 Planned capacity of the Besançon plant

Table 3 demonstrates production capacity or 'designed' amount of production of fibers at *'Societe'* at Besancon. Productioin capacity varies almost 20 times.

Estimation of production capacity at Besançon at the time of establishment:

The factory had the spinning machines with totally 25,000 bec (=hole).[32] Here, we can assume that

(1) several fibers (in this case, filaments) are grouped together, so that by their cohe-

Table 3 Production capacity and amount of out put of Chardonnet's factory at Besançon

Production capacity kg-fiber/day	Amount of production kg-fiber/day	Reference
1,000 (at the time of establishment)		L. G. Fauquet[32]
1,000		A. Demoment[34]
	50(1891)	F. Reinthaler[35]
	50(1891)	A. Hard[36]
	50(1891)	Y. Kami[37]
	50(~1894)	W. E. Wicht[38]
	50(1891)	V. Muthesius[39]

sion they form compound fibers (=yarn); A single yarn of 150 denier consists of 5~10 filaments,

(2) the weaving velocity of winding spool is 5 m/min[40], and

(3) the plant is operated 8 hr/day.

Then, the amount of fiber produced in a day is estimated to be (5 m/min) × (60 min/hr) × (8 hr/day) × (150 g/9,000 m) × (25,000/10 bec/fil) × (1/1,000 kg/g) = 100 kg/day.

It is evident from the above discussion that capacity of 1,000 kg/day (Table 3), evauated by Demoment[34] and Fauquet,[32] is too large and unrealistic for the said apparatus. If we take into consideration the accuracy of the assumptions employed and the yield of the product (here, we assumed 100% yield), 50 kg/day, which is the designed value at the time of plant construction without any previous actual experiments, can be accepted as reasonable magnitude for the installed machine.

3.2 Production records at early stage and the troubles encountered at Besancon

Artificial silk by nitrate process, also known as Chardonnet process, was first produced on commercial scale in June, 1892. Table 4 collects expenditure and production of 'Société' during 1892~1896. The table also includes the production cost. Fig. 1 shows the fiber production of 'Societe' during 1892~1896. Avram wrote erroneously that *'Rayon yarn was first produced in 1890 at Besançon...'*.[46] Hottenroth wrote *'in 1890 the capital had been reduced to* $1\frac{1}{2}$ *million francs and it was reconstructed with a further 6 million francs.'*[47]

Problems encountered in 1894 were:[48]

(1) L'inconstance des Collodions,

Table 4 Expenditure and production of Chardonnet's company during 1892~1896

Term	Expenditure (francs)	Production kg (fiber)	Production cost francs/kg (fiber)
1892, June~Nov.	746,280.33	275	217.95
1892, Dec~1893,31 July	380,647.57	1,537	15.05
1893,1 Aug.~31 Dec.	131,390.20	1,970	17.75
1894	deficit>800,000		
1894 May~Dec		27kg/day*b (3420)*a	20*b
1896		20,000	▲7*c
1913~1914			20*d

(Constructed from A. Demoment[41, 42])
*a; 240 days×kg/day×0.5=3,420kg/term, *b; W. E. Wicht,[43]
*c; L. G. Fauquet,[44] *d; Y. Kami,[45] ▲; deficit

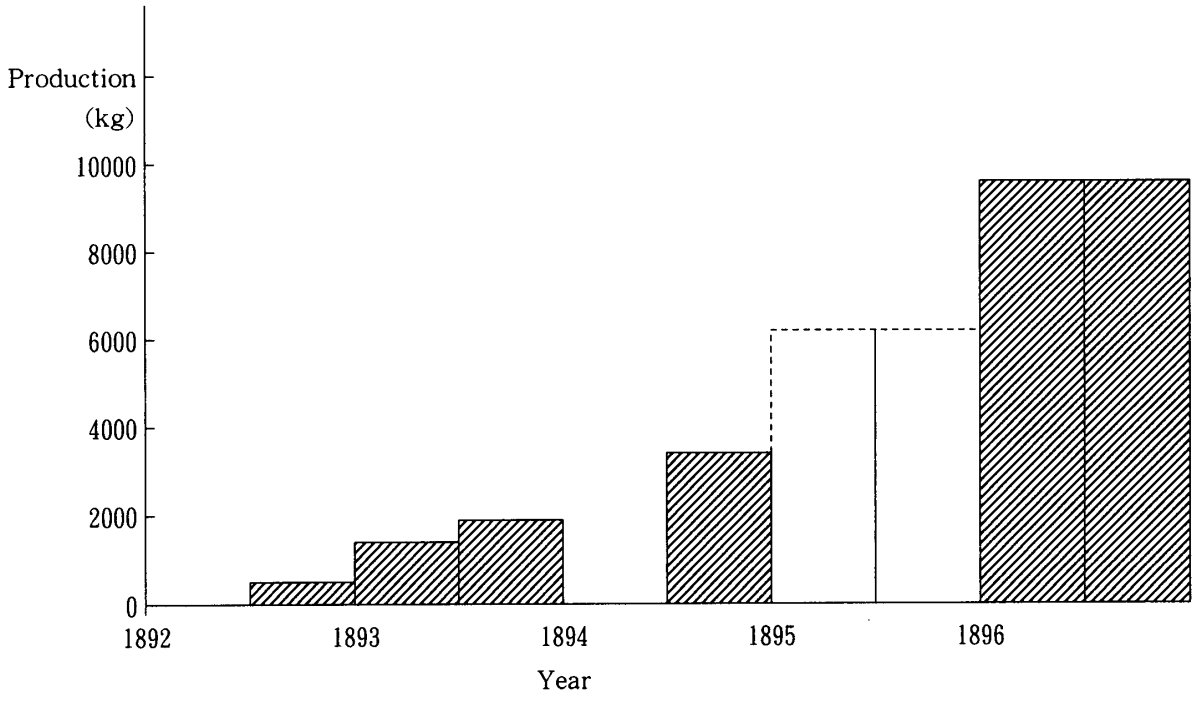


Figure 1 Fiber production of 'Company at Besançon' between 1892~1896
(Production record for 1895 is an estimated value)

(2) Le veinage a la teinture,

(3) Les irrégularitiés de la dénitrification,

(4) Les causes d'un mauvais dévaidage amenant,

(5) Un déchet considerable,

(6) L'inflammabilité, and

(7) L'education du personnel ou vrier.

Items(1)~(5)were concerned with problems met unavoidably with large scale produc-

tion and(6)was the most serious, which will be discussed in a next section. Item(7)is the problem of employer education.

The operating rate at the plant was less than 20% until 1893. In 1896 the production exceeded at last the initial capacity after the reformation of the process. The dangerous inflammability of *'Chrdonnet silk'* made its wide spread use as a textile material impossible[49], because so dangerous that the French government passed a law prohibiting its use in textiles.[50] Thorough denitration of the cellulose nitrate fibers was compelled in the early days of Chardonnet's work by the French government and later by the merchants (buyers), who refused to handle so inflammable a product, as well as assurance companies.[51,52] Much tension arose between Chardonnet and the directors and managers of the enterprise.[23] In the first half of 1894 whole operation of the factory was suspended, despite gradual yearly growth in out-put until that time (see Fig. 1). Later, Lehner commented to the 'Societe' at Besançon that *'Nach kurzer Zeit jedoch schon erwies sich diese Grϋndung als verfruht da erzeugte Produkt nicht marktfähig war.'*[2]

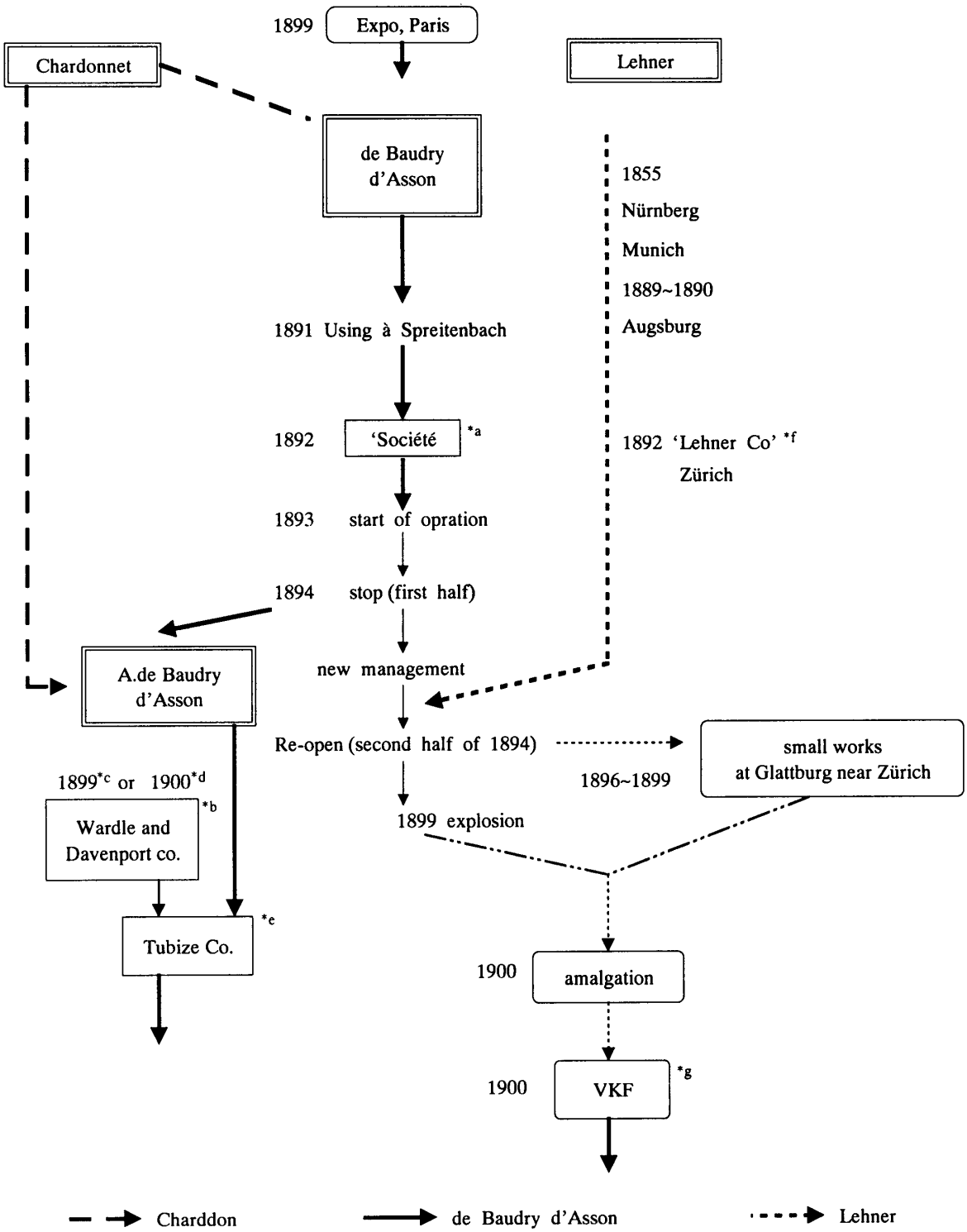
In 1894, *'Société'* run a deficit sêleve à 800,000 francs and after death of Weibel, Gabriel Jouvanceau was appointed as new president of conseil d'administration and Adolphe Trincano as new directeur.[44]

3.3 Chardonnet's process at Spreitenbach

Chardonnet's process was technically transferred to Spreitenbach, Canton d'Argovie, Switzerland.

Figure 2 shows formation and transformation of *'Spreitenbach factory'*. It is selfevident from the figure that *'Spreitenbach'* was built by Swiss capitals (with capital of 200,000 francs[55]) and first managed by Count Armand de Baudry d'Asson, who was an officer at Expo 1889 Paris and acquainted with Chardonnet's silk there. Chardonnet licensed to 'Spreitenbach factory' with promise of technical guidance. The small factory was built in 1891, one year earlier than establishment of *'Societe de la Soie Artificielle Spreitenbach'* (1892). The factory started the operation in 1893 (the record of the out-put was not available) and encountered the similar problems as in Besançon, resulted in temporally closure of the plant (1894). At this time de Boudry d'Asson resigned and new management took his position.

The Spreitenbach factory is often said 'A second company at Spreitenbach'[14] or 'Chardonnet's sub-factory',[55,56] but note that this company was independent of 'Besançon'. Hard wrote that *'A second company at Spreitenbach, also formed in 1884, was*



*a 'Societ de la Soie Artificielle Spreitenbach (30×10^5 francs)
*b Davenport & Co. Ltd., Chardonnet Silk Mill, Tubize
*c Coleman[54], p 7, *d Hard[55], p23~24
*e Societé anonyme fabrique de soie artificielle de Tubize
*f Lehnerr's Artificial silk Company
*g Verlinigte Kunstseidefabriken A.-G.

Figure 2 Formation and transformation of 'Spreitenbach factory'

financially unsuccessful for a considerable time.'[14] Coleman made similar mistake: *'a Chardonnet factory at Spreitenbach... had itself been originally started in 1893....*'[57] Note that d'Asson knew Chardonnet's invention at Expo '89 and 1883 or 1884 is far earlier than the time of establishment of 'Société 'at Besançon and is about 10 years earlier than the true year of the establishment of 'Spreitenbach plant'. Lehner himself reviewed that *'Sowie gleichzeitung (=1891 ?) durch Private eine weitere kleine Fabrik in Spreitenbach in der Schweiz.*[24]

4 EXPLOSION ACCIDENTS OF THE FACTORY AND STABILIZATION (IMPROVEMENT OF INFLAMMABILITY) OF CHARDONNET SILK BY DENITRATION

4.1 Explosion accidents at Chardonnet silk factories

Cellulose nitrate, if it is not stabilized, is liable to a slow spontaneous decomposition, which may accelerate into explosion.[1,58] There was a considerable danger of explosion during production. In particular, drying of cellulose nitrate is a dangerous process on account of its explosive nature. As early as 1865 an English chemist Abel found that long boiling of cellulose nitrate in water is effective for its stabilization.[59] Later, Robertson discovered that hydrolysis of cellulose-sulfuric acid ester is essential for the stabilization and the boiling in acid water is purposeful.[60]

Table 5 collects the explosion accidents occurred at Chardonnet's silk factories. It is interest to note that almost all Chardonnet silk manufactures seriously damaged by explosion accidents in 1893~1904.

Table 5 Explosion accidents occurred at factories of Chardonnet process

	Date	Factory	Sections	Reference
(1)	2nd Jan. 1893	Besançon	lab. & prep.& drying of pyroxylene (reconstructed two month after)	A. Demoment[61] (D. C. Coleman)[62]
(2)	1899	Spreitenbach	...d'inondie détrisit en grande partie la petite using	L. G. Fauquet[63]
(3)	1888	Paris	chem. lab.	A. Demoment[64]
(4)	1904	Tubize		L. G. Fauquet[65]
(5)	1904	Hungary	major parts of the plant	D. C. Coleman[62]

4.2 Improvement of inflammability by denitration

Swan (Later Sir Joseph), the first person, who carried out denitration of cellulose nitrate fibers, described in his patent [British Patent No. 5,978 (1883)][66] that *'I treat it with a*

solution of Hydro Sulphate of Ammonia or other equivalent deoxidizing agent, until it is no longer in a condition to burn explosively,' and in claim 14, *'subsequently treating the solid filament or filaments with a deoxidizing agent and then carbonizing the said filament or filaments substantially as hereinbefore described.'* This is all about the so-called 'Swan's method'. Then, it is clear that Swan did not attempt to denitrate cellulose nitrate fibers completely, but aimed to control the rate of combustion in a following carbonizing step. We should not overestimate 'Swan's method'.

Chardonnet too had a worry about the inflammability of cellulose nitrate fibers. Then, he said in British Patent No. 2,211 (1886)[67]: *'The threads prepared by spinning the said the filaments may be treated with a hygrometric or non-combustible preparation, and the fabric woven therefrom may be treated with an incombustible dressing, such as a mixture of gelatine, glycerine and sugar.* In 1888 Chardonnet explained the reason why metallic chloride and alkaloids are added to the spinning solution ((the first (1884)[68,69] and the second (1885)[70,71] patents), as: *'This process, when applied to artificial silk (spun collodion) renders it unnecessary to introduce into the mother solution metallic chlorides or alkaloids for lessening combustibility.'*[30,71] At early stage, he expected that the above treatment could suppress, to some degree, the inflammability of the textiles. These patents were applied at single spinneret-spinning machine stage. In 1888, he disclosed in British Patent No. 5,270 (1888)[30] that *'denitration occurs by dipping the fiber in nitric acid (with the specific gravity of 1.82) bath.'*

At the stage of bench plant operation (1889~1890), Chardonnet specified the more detailed recipe of denitration of artificial silk in British Patent No. 5,376 (1890)[72], France Patent No. 207,624 (1890)[73], and Deutsche Patent Nr. 56,655 (1890)[74], where he described as effective denitrating reagents: (1)nitric acid of 36° Be, (2)Sulphides, Polysulphides, (3)Sulpho-carbonates, and (4)Sulpho-hydrates of ammonia. He stated on (4)that *'it does not attack the fibres of pure cellulose, either after a long digestion in the cold, nor when digested for from 12 to 24 hours at* 60° *to 70°'*. (4)is a virtually identical idea, of which Swan thought. 1890 was just before the plant construction and Chardonnet had not yet considered that inflammability of the fiber was serious and fatal defect. He stated in British Patent No. 5,376 (1890)[72] and France Patent No. 207,624 (1890)[73] that *'It is preferable to stop at a certain point of nitration such as 2 to 4 per cent of nitrogen. The latter composition is preferable to pure cellulose on the ground of stability, elasticity and aptitude for dyeing.'* Now, it becomes evident from the above documents that Chardonnet had acted something for improvement of the product before starting the commercial production in 1892, but he

Table 6 Denitration reagents for Chardonnet's silk specified in patents by Chardonnet and Lehner

Reagents	Patent No.	
	Chardonnet	Lehner
1. Reducing agents such as sugar, acetic acid, alcohol, protochloride of iron, even water	BP 5,270(1888)[30]	
2. Nitric acid(density; 132)	BP 5,270(1888)[30]	
3. Dil.sulphuric acid		BP 11,831(1891)[80]
4. Mixture of gelarine, glycerine and sugar (coating)	BP 2,211(1886)[67]	
5. 80°C water(1hr)	DP 46,125(1888)[75]	DP 82,555(1894)[81]
6. Sulphides, Polysulphides	DP 56,655(1890)[74] BP 5,376(1890)[72]	
7. Sulfocarbonate(Alkalien, alkalischen Ende, Erden)	ibid	
8. Sulfohydrate of ammonia	ibid	
9. Crabonate of potash	BP 1,656(1890)[76]	
10. Kalzium monosulfur	FP 221,488(1892)[77]	
11. Kalzium sulfhydrate	ibid	
12. Sulfate of potash		BP 11,831(1891)[80]
13. A liquid constituting of sulfide of ammonia or other sulphur alkalis		BP 22,736(1892)[82] Complete specification (9th Sep. 1893) (≡DP 82,555(1894)[81]
14. 75% alcohol 30℃, 40~50℃	Zusatz patent(1887) FP 231,230[78]	
15. Calcium mono sulphide (8kg)+ammonium sulphate (4kg)+a hectolitre of water	BP 24,638(1893)[79]	

BP; British Patent, DP; Deutsche Patent, FP; France Patent,

adopted the lackadaisical means, fearing deterioration of the fiber performance and rise of cost due to insertion of the denitration process.

As mentioned before, artificial silk buyers, as well as assurance companies, have compelled the manufactures to perform the denitration thoroughly.[51]

Table 6 summarizes chemical reagents proposed by Chardonnet for denitration of cellulose nitrate fibers. In the table the reagents by Lehner are also included for comparison. At Besançon, calcium hyrosulphide (see Table 9) was obtained in the form of the waste from the works of Saint-Gobain à Saint-Fons, which manufactured caustic soda by Leblance process.[51]

5 LEHNER'S CONTRIBUTION, IF ANY, TO AN IMPROVEMENT OF THE CHARDONNET'S PROCESS

5.1 Career of Lehner: Lehner's Artificial Silk Company and his Glattburg plant

Career of Friedlich Lehner until 1896 is summarized briefly as:

1. Born in Nurnberg, Germany, on 8th June, 1855.[83]
2. Educated at Munich.[83]
3. Lived as apothecary at Augsburg at least, in 1889~1890 (see Table 9).
4. During working as apothecary, studied artificial silk and applied his first patent [Deutsche Patent Nr. 55,949 (1889)[85]] and second patent [Deutsche Patent Nr. 40,373 (1890)[89]] at Augsburg (see Table 8).
5. Traveled to London in 1891.[86]
6. Moved to Zürich (see Table 8) in 1892.
7. Built an English company in 1892[57,87] ['Lehner' Artificial Silk Company (Director, Oscar Berend, District Bank Chambers, Market Street, Bradford)[88]].
8. Worked at Spretenbach factory in (1893)~1894.
9. Applied the improved patents (denitration) in 1894 and a Swiss patent [Swiss Patent No. 82,555 (1894)][89]
10. Built small plant at Glattburg, near Zurich in 1896 (Table 7).

Table 7 collects various descriptions in the books on Lehner's factory. Samuel Cunliffe Lister (after Load Masham), an inventor of wool-coming machine and a succeeded wor-

Table 7 Lehner's Factory

Lehner's Factory	Time	Place	Reference
1. Works of an English company with output of 50kg/day ("Lehner" Artificial Silk Ltd.)	1892	Glattbrugg	A. Hard[90]
2. "Lehner" Artificial Silk Company	1892	——	Coleman[57]
3. A manufactory	after abandoned the use of all his patents (1894~)	Switzerland	J. Foltzer[91]
4. Kunstseiden Fabrik	after learning Chardonnet process (1894~)	Glattbrugg	Y. Kami[92]
5. Einen Kleine Versuchfabrik	(1896)	Glattbrugg bei Zurich	W. E. Wicht[38]
6. Die Fabrik	after joining to Spreitenbach	Glattbrugg	F. Lehner[24]

sted manufacture at Addingham near Bradford,[93] had an intension to utilize Swan's Process[66] for manufacture of textiles on large scale, but his attempt was not realized.[94] Lister wanted to find other possibility of profit rather than worsed. Lehner made a trip in 1891 to London,[86] probably in order to find a financial support. In 1892 Lehner' Articicial Silk Co., Ltd. was formed at Bradford (District Bank Chambers, Market Street, Bradford, Yorkshire[88]) by Lister. Lehner reminisced in 1906: *'Load Masham, alias Lister, der bekannte, inzwischen verstorbene Erfinder und Großindustrielle, hatte sich zu der Zeit, nach persönlicher Mitteilung mir gegenüber, mit dem Gedanken getragen, diese Verfahren im grossen Maßtrabe durchzüfuhren.'*[24] *Note that up to* 1892 *Lehner applied two inventions* (see, Table 8, No. 1 & 2), which were completed in tiny laboratory at Augsburg and whose practical applicability had not yet been examined in detail and in fact, these inventions proved very impractical and could not be materialized. Therefore, the company could not be considered to have produced artificial silk in 1892~1893. The company obtained a patent, with Lehner, on 'Improvements in Embroideries' (British Patent No. 2,595 (1896)).[95] This is an evidence supporting the existence of the company during 1892~1896. Muthesius wrote that *'Lehnersche, mit englischen Kapital durchgefuhrte Fabrikgrundung in Glattbrugg in der Schweiz,'*[96] Glattbrugg was chosen for a plant because of lower tax on alcohol than England, and the tiny plant was formed in 1894.[53] This might be a main reason why he moved to Zurich at the end of 1892 and not to Bradford. The plant did not work during 1894~1896, when they employed Lehner's original process. Lehner confessed that there were very many troubles for an English company to produce by his method fibers on large scale.[53] Foltzer pointed out that a manufactory became successful only after abandoned the use of all his patents.[91] It should be noticed that Lehner joined in 1893 to Chardonnet factory at Spreitenbach, where he received at first the practical training and experience of the massive production of artificial silk, learning the secret of the Chardonnet' process. And since then, Glattbrugg plant was built. Wicht wrote that *'In Deutschland und Schweiz arbeitete nach seinem Nitroverfahren, wie es genannt wurde, der 1896 in Glattbrugg bei Zurich eine kleine Versuchsfabrik errichted; die Hut-industrie in Aargau, später die Hersteller textiler Besatzartikel in Barmen und Elberfeld gehörten zu den ersten Abnehmern.'*[43] Courtaulds were mainly interested in a modification of the cellulose nitrate process, which had been used by Lehner in a plant in Switzerland.[97] After evaluation of Lehner process by C. F. Cross & E. J. Bevan, both inventors of viscose,[98] the company decided not to go further in this field.[97] It is interesting to note that new director of Chardonnet factory at Spreitenbach, Adolphe Trincano met in 1894 with Lehner in Switzerland: *Trincano accomplit le voyage d'etudes en*

Suisse, où le docteur Lehner essaye de mettre au point la fabrication de la soie Chardonnet, mais dans de meilleures conditions économiques qu a Besançon.[42]

5.2 **Lehner's inventions: What is Lehner's process?**

Table 8 collects the list of all the Lehner's 16 patents, licensed on artificial silk of cellu-

Table 8 List of patents on artificial silk applied by F. Lehner

No. Category	Sch. P*a	DP*b	FP*c	BP*d	USP*e
1. Spinning solution	——	55,949*(1889)	221,901(1892)	11,831*(1891)	559,392
2. Apparatus & denitrarion	3,740	58,508*(1890)	224,460(1892)	22,736**(1892)	562,626
3. Alminum tube	——	——	——	24,003**(1893)	
4. Denitration	4,984	82,555**(1894)	243,612(1894)	10,868(1896)	562,732
5. Embroidaries	——	——	——	2,595***·**(1896)	

*at Augsburg **at Zürick,
***with Coassignee, the "Lehner" Artificial Silk Company Ltd.
*a; Schweis patent, *b; Deutsche patent, *c; France patent, *d; British patent, *e; US patent

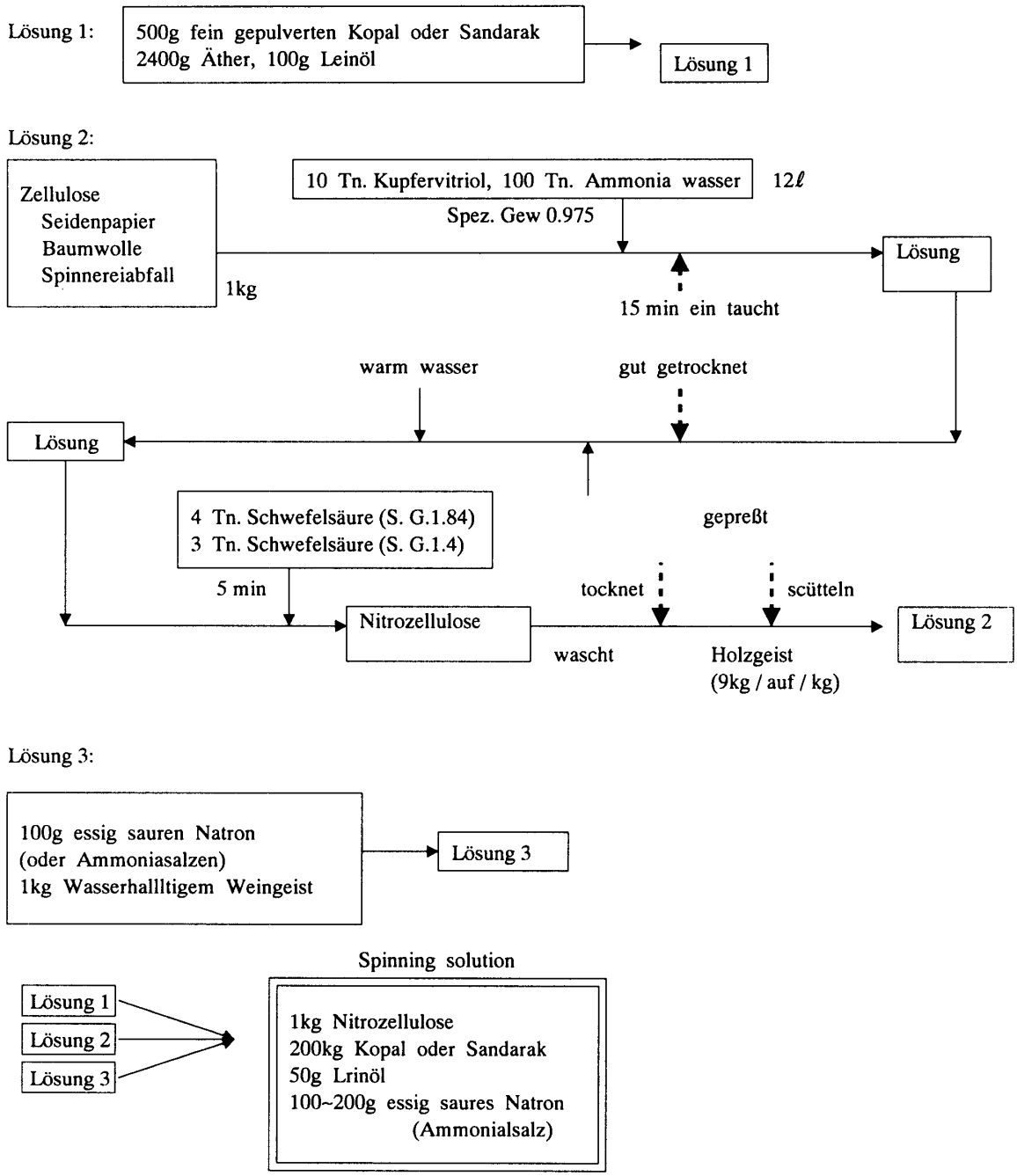
lose nitrate process. The patents with the same contents of specifications are located on the same line of the table. Lehner made inventions, classified into totally 5 categories.

Table 9 Locations where Lehner carried out the development of artificial silk

Date	Place	Patent No. or ref.
1891, 11th July	Augsburg	BP No. 11,831(1891) Provincial Specification
1892, 11th April	Augsburg	BP No. 11,831(1891) Complete Specification
1892, 10th December	Neptunstraß 30 Zürich	BP No. 22,736(1892) Provincial Specification
1893, 9th September	Neptunstraß 30 Zürich	BP No. 22,736(1893) Complete Specification
1893 ,12th December	Neptunstraß 30 Zürich	BP No. 24,003(1893) Provincial Specification
1894, 13th September	Neptunstraß 30 Zürich	BP No. 24,003(1893) Complete Specification
1894, 15th November	Neptunstraß 30 Zürich	DP Nr. 82,555
1896, 2nd November	Neptunstraß 30 Zürich	BP No. 2,595(1896) Complete Specification
1906, 2nd November	Neptunstraß 30 Zürich	Z. Angew. Chem **37**,1581(1906)

BP.; British Patent, DP; Deutsche Patent

Note that the patents on the same line of Table 8 are not always absolutely identical each other. Lehner had made research & development of cellulose nitrate process for 7 years during 1889~1896. Seven years is significantly short, if we compare it with 40 years (1884~1924)[99] in Chardonnet's case. Lehner put an end to the research when his small plant had got off the ground and never applied, since then, any patent on artificial silk by any method.



F. Lehner : No. 1 [DP Nr. 55,949 (1889)]

Figure 3 Preparative method of Spinning solution for artificial silk (Lehner)

Table 9 compiles the locations (address) where Lehner carried the development of artificial silk. From the table it is evident that the first patent (Category 1) was applied from Augsburg, where he stayed up to the time between April~December, 1892. Other patents were completed during December 1892 and 1896 in Zurich, where he was ascertained to live in 1906.

Fig. 3 demonstrates the Lehner's preparative method of spinning solution claimed in Deutsche Patent Nr. 55,949 (1889) (No. 1 of Table 8)[84], which is the first invention, constituting the method together with No. 2 of Table 8. The method is unreasonably and impractically too complicated and in addition, scientifically nonsense. Note that Chardonnet set various traps in his first patent in order to protect his invention from possible mimicry.

Fig. 4 shows the metamorphosis of Lehner's process revealed from this patent specifications. In the figure, six major elements are chosen for this purpose. First line for each element corresponds to his first invention made before joining to Spreitenbach

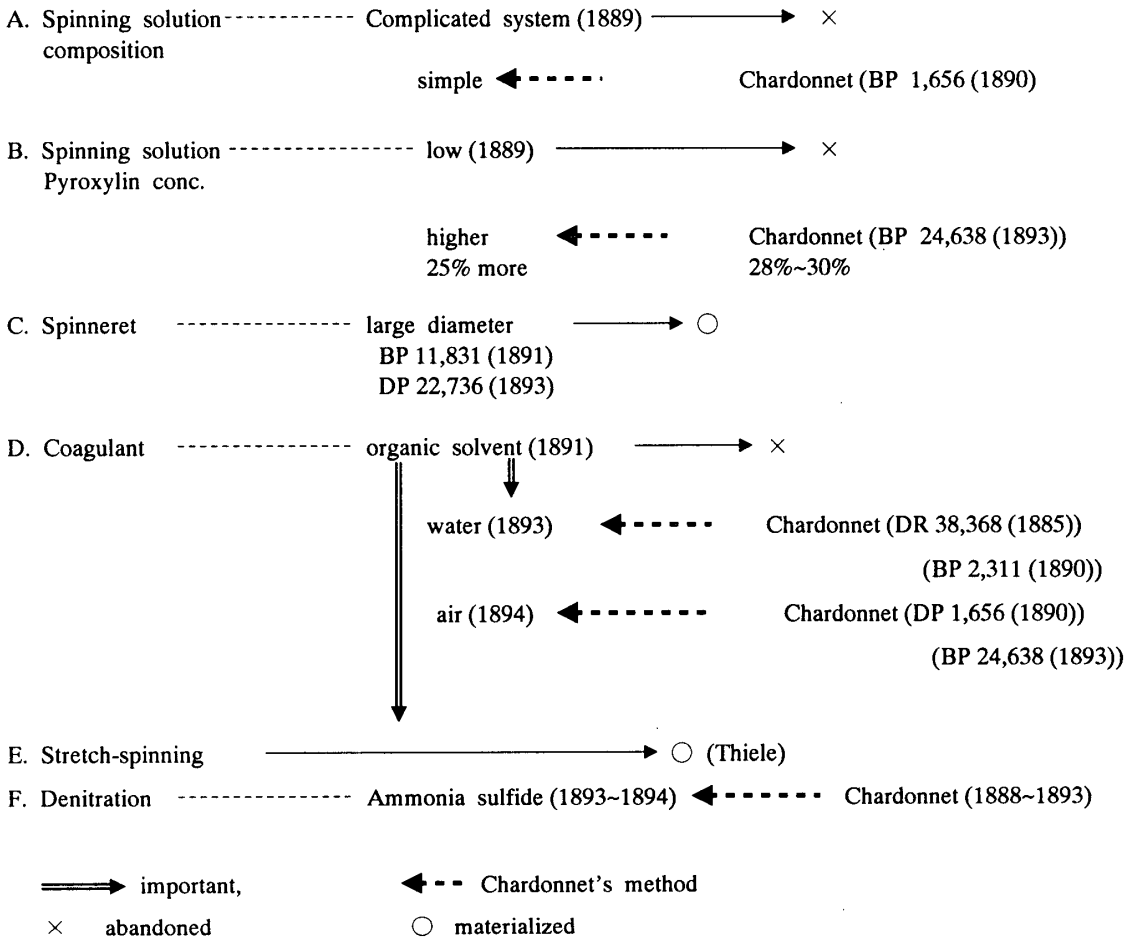


Figure 4 Metamorphosis of Lehner's process

factory. In this figure, x means that the invention proved useless and abandoned, and O means that the invention proved useful and materialized. ⟹ means that specifications in the first and second patents were modified into technically disconnected ones. In other words, the so-called improved inventions had no technical continuity with the primary ones, suggesting that the former is not the fruit of further development of the latter. Fig. 4 also shows the heavy influence of Chardonnet's concept on the Lehner's improved (or strictly, 'mimic') patents (◀···). Note that all major 'improvements' were made on the line of Chardonnet's technology.

Examples of the patent specifications employed for construction of the figure are illustrated below:

A: Composition of spinning solution

(1) Provisional specification of British Patent No. 22,736 (1892)[82]; *'a fine stream or filament composed of nitrocellulose dissolved in a ethylic alcohol, wood spirit, acetic acid with addition if desired of silk resin, salts or organic compound.'*

B: Polymer concentration

(1) Complete specification (9th September, 1893) of British Patent No. 22,736 (1892)[82]; *'Nitrocellulose is dissolved ...to form a solution containing... about 5% of solid material. Such solution will produce a thread.'* Note that 5% is less than half of those used by Chardonnet. Lehner learnt the importance of high polymer concentration. He wrote in the above patent specification that *'when however in order to obtain stronger thread the nitrocellulose in solution is raised to 10%.'*

C: Diameter of spinneret die

(1) British Patent No. 11,831 (1891)[80]; *'It may be allowed to flow out of an opening for instance a small but not too narrow pipe with an opening of about 1/2 millimeter, under a pressure of a few centimeters.'* (2) Deutsche Patent Nr. 82,555 (1894)[86]; 'Diese werden dadurch erhalten, dass man die flüssige Masse ausweiten Glasröhren von 1/4~1/2 mm Durchmesser des Ausfluß öffnung durch die eigene Schwere...'.

D: Coagulants

(1) British Patent No. 11,831 (1891)[80]; *'It may be allowed to flow out...into turpentine oil, juniper oil, benzene, benzole, petroleum or other liquid hydrocarbon or bisulphate of carbon,*

but not into water. (2) Provisional specification (10th Dec., 1892) of British Patent No. 22,736 (1892)[82]; *'A thread...may be produced by carrying through a solidifying fluid such as terpentine oil, water or petroleum....* 'And the complete specification of the same patent,' ... *is caused to flow from small orifices into a liquid such as water, terpentine oil, petroleum or other hydrocarbon,....'* (3) Complete specification (11th Sept., 1893) of British Patent No. 22,736[82]; *'...is caused to flow from small orifices into a liquid such as water, terpentine oil, petroleum or other hydrocarbon, ...'* (4) British Patent No. 24,003 (1893)[100]; *'which solidifies when entering air, or liquid such as petroleum, or, water, ...'* (5) Deutsche Patent Nr. 82.555 (1894)[81]; *'in eine Flüssigkeit order auch direct in die Luft austreten lasst.'*

E. Stretch-spinning

(1) Complete specification of British Patent No. 11,831 (1891)[80]; *'The filament so forming in the liquid may be drawn finer therein and...'* (2) Provisional specification of British Patent No. 22,736 (1892)[82]; *'2. The formation of the thread is different, the same being drawn fine while in solidifying fluid.' And '3. There are no mechanical drawing devices used for this purpose, to draw the thread in the fluid.'*

Now, it is obvious that even Lehner's original (primary) process was carefully specified in such manner that his process is to be outside of the Chardonnet's process, which were licensed earlier. Lehner's original process did not work well as expected from the examination of the patents (see, for example, Fig. 3). Finally, Lehner abandoned everything except die dimension, adopting the concept of Chardonnet's inventions.

Avram described that *'The only important difference was that Lehner coagulated the cellulose nitrate thread in a water bath instead of depending simply on the evaporation of the solvents, alocohol and other in air.'*[101] Lehner used oil as coagulant in his first patent, where he noticed that water is not included. Since then, he adopted water as effective solvent, learning Chardonnet's process. He also recommended in other patents dry-spinning in the air. The usage of water is not Lehner's invention and also he employed air. Therefore, Avram's description is against the historical facts.

Edmund Thiele, a famous inventor of strech-spinning method,[102] mentioned in his patent[103] (British Patent No. 8,083 (1902)) that *'Lehner, who effects the formation of the filament in such manner that a comparatively thick filament issuing from a not very fine opening such as 1/4 or 1/8 th m. m. is reduced to a fine condition by drawing it out to a greater or less extent.'* Muthesius commented that *'Die Verringerung des Drucks bedeute einen sehr*

wesenteichen Fortschritt: Lehner konnte von 60 auf 8 Atmosphären berung heruntergehen, für den industriellen Betrieb ein unschäftbarener Vorteil.'[104] This is Vereiningte Granzstoff Fabriken (VGF)'s assessment to Lehner's process. A 5~10% solution exhibits lower viscosity and can be flowed out through pipe under low pressure. Then, only primitive and rough apparatus is quite adequate for fiber production: Lehner's process was able to adopt the original process employed in the manufacture of filaments (carbon conductors) for incandescent electric lamps. In contrast, Chardonnet used highly concentrated solutions and narrow opening dies. Both required high pressure operations of expensive and precise apparatus. Paradoxically speaking, large pore die was an inevitable consequence of primitive level of machinery technology.

To which side gave participation of Lehner to Spreitenbach benefit?

(1) Opinion A; Lehner learned much from Spreitenbach

(a) Foltzer wrote: *'he did not succeeded in producing a saleable thread until he abandoned the use of all his patent substances, such as..., and employed only the pure nitrocellulose of Chardonnet.'*[91]

(b) Hottenroth wrote: *'He had acquired knowledge of the Chardonnet process at Spreitenbach.'*[47]

(c) Coleman wrote: *'F. Lehner, after working at a Chardonnet factory at Spreitenbach, made certain improvements in process hepatented in 1880 and 1890.'*[57]

(2) Opinion B; Lehner contributed to Spreitenbach

(a) Hard mentioned: *'He greatly improved and simplified Chardonnet process.'*[90]

(b) Fauquet wrote: *'...le Docteur Lehner apporta aussi une contribution notable aux perfectionnements de la filature de la nitro-cellulose.'*[105]

(c) Muthesius noted: *'Augsburger Chemiker Friedlich Lehner, der in den neunziger Jahren wichtige Verbesserung des Spinnprozesses entwickelte, für die Leitung dieses unternehmens.'*[104]

From this study it becomes evident that Opinion A is undoubtedly adequate.

5.3 Lehner's method for denitration of cellulose nitrate fiber

F. Lehner was asked to join Chardonnet factory at Spreitenbach in 1894. Lehner was chosen because his address (30 Neptunstraß, Zürich) was near to Spreitenbach and in addition, he was very few known chemist with some speciality in artificial silk, even if it was limited at laboratory level. Since Chardonnet was very busy to work for Besançon factory he might have approved Lehner's assistance.

Then, what was the Lehner's denitration technology?

(1) In his first invention (Deutsche Patent Nr. 55, 949 (1889))[84], he did not mention about denitration.

(2) In his second invention (Deutsche Patent Nr. 58, 508 (1890))[106] Lehner described: *'Die weitere Behandlung des gebildeten fadens bezwecht die Denitrierung des Pyroxylins und Entfernung des anhängenden Terpentinöls oder Petroleum. Zu diesem Behufe wird der Faden etwa 1 Stunde lang mit wasser auf etwa 80° C erwarmt.'* Note that long time boiling had been discovered by Abel in 1860s and Abel's classical researches resulted in the adoption of long boiling. This kind of treatment may contribute to improvement of stabilization of cellulose nitrate, but inflammability can not be improved utterly.

(3) In British Patent No. 11, 831 (1891)[80], Lehner wrote: *'The threads made are very inflammable. To correct this if desired they may be steeped in (a) dilute sulphuric acid, then will be washed and steeped in (b) a dilute alkaline solution or finally washed therein. Or they may be steeped in (c) a solution of sulphate of potash in water of about 1.26 specific gravity. This removes the nitrogroups without hurting the thread.'* Claim 16) specifies *'The methods of denitrifying the threads herein described.'* (a) and (b) are simple method for only preventing spontaneous combustion and (c) is denitration method. He inserted 'if desired' into the specifications, suggesting the degree of recognition of seriousness of inflammability of fibers at that time.

(4) Provisional Specification (10th of December, 1892) of British Patent No. 22,736 (1892) contains no description of denitration, but Complete Specification (9th of September, 1893) describes: *'a denitrating liquid consisting of sulphide of ammonia or other sulphur alkalis'*[82]

(5) The final recipe of denitration was given in Deutsche Patent Nr. 82,555 (15th. November, 1894): *'Konzentriertes Ammoniumsulfhydrat, in bekannten weise hergesellt, wird mit Wasser bis zu etwa 10% verdünnt und daren einbeliebiges neutrals Magnesiumsalz in ungefahr äquivalentem Verhältnis aufgelöst. In diese Flüssigkeit werden die Fäden bei etwa 40° C solange einge taucht,*[81] ... and *'Patentansprüche: 3. Die Desoxydation dernach Auspruch 1 und 2 hergestellen Fäden mittles Alkalisulfhydrates und eines Magnesiumsalzes, welchem eventuell noch ein Ammoniumsalzes beizufügen ist.'*[81] Note that the above Lehner's patent is practically the same as the claim 3 of Chardonnet's patent [Deutsche Patent Nr. 81,599 (1893)][107].

Lehner stated in Deutsche Patent Nr. 82,555 (1894), which was applied after the inflammability of the fiber products became social problem, that alkali sulfhydrate plus magnesium salt are effective for desoxydation and an example was 10% aq. solution of ammo-

nium sulfhydrate and to the solution the equal weight of neutral magnesium salt is added. This method is a modification of Swan's invention.[66]

Summarizing, as far as denitration process is concerned, it is evident that Lehner had not played significant role (or even a central behind-the-scenes role). All reagents specified in his patents (see Table 6), had already been become public as denitrating reagents. He did not recognize well until 1892 the fatal nature of inflammability of cellulose nitrate.

6 COMMERCALIZATION OF DENITRATED PRODUCTS

6.1 Re-opening of the plant operation

During temporary suspension of plant operation (Jan. ~April, 1894) factory-scale experiments were performed thoroughly to overcome the above-mentioned difficulties. The factory reopened in May, 1894 the production of Chardonnet silk, which was now regenerated cellulose (pure cellulose) fiber.[108] The new thread was very quickly appreciated on account of its brilliance, which greatly surpasses that of natural silk.[51] During May~December, 1894 Busnçon produced '27 kg/day of silk',[108] 108 which was approximately half of the plant capacity.

The Spretenbach works also resumed manufacture successfully under new management.[33] A serous explosion accident in 1899 (See Table 5), which was induced by fire, destroyed major parts of the small plant.[63] However, its reconstruction was financially impossible so that the plant was suspended and amalgamated in 1900 with Lehner's Glattbrugg plant and soon sold to a new company, Vereinigte Kunstseide Fabriken A.-G. (VKF), formed in 1900 by German capitals at Frankfurt. Lehner took a position of director of VKF, which built two another factories at Bobingen, near Augsburg, Bavaria (1901; 1,000 kg. day) and at Kelsterbach-am-Main (1903; 1, 500 kg/day). In 1900s, VKF had totally four plants for production of artificial silk. VKF acquired from Chardonnet sole selling rights in Germany and Switzerland.[109]

6.2 Some mechanical properties of artificial silk

Table 10 illustrates the effect of denitration on some mechanical properties such as tensile strength and tensile elongation of Chardonnet silk. All data in the table, which were cited from two different original sources, coincided perfectly. We can not explain this agreement. By denitration, Chardonnet silk lost both tensile strength and elongation, in particular when wetted. Natural silk was unquestionably superior, in all respects, to artificial silk.

Table 10 Mechanical properties of Chardonnet silk in 1900~1905

	Tensile strength (g)	Tensile elongation (%)
Chardonnet silk	150	23
Ditto, after denitration and drying	110	8
Ditto, after denitration, but undried	25	0
Natural silk	300	18

(Table was constructed from J. Foltzer[110] (data from Journal of the Industrial Society of Mulhouse for 1900) and Y. Kami[111] (data by R. Bernard (1905).)

Table 11 Fineness of yarns (denier) and some mechanical properties of natural and artificial silks

	Natural silk	Chardonnet silk		Lehner silk*b
		(Spreitenbach)	(Wolston)*a	
Denier (d)	2.3	80	100	120
Tenacity (g/d)	2.50	0.93	1.26	1.42
Elongation (%)	21.6	8.0	7.9	7.5

*a; New Artificial Silk Co., Wolston, UK
*b; VKF
(Table was constructed using data in Y. Kami.[112])

Table 11 shows the total denier (denier is weight (in gram) of filament or filaments of 9000 m in length)) and some mechanical properties of artificial silk by cellulose nitrate process (Chardonnet silk and Lehner silk).

7 TECHNOLOGY TRANFER OF CHARDONNET SILK

7.1 Period 1890~1905

Under Chardonnet's auspices, several plants of artificial silk by cellulose nitrate process were set up in France, Switzerland, England, Belgium, Italy and Hungary.

Following companies adopted Chardonnet process during 1890~1905.

(1) Société anonyme pour la fabrication de la soie de Chardonnet (established 1890; start of operation 1892) France.

(2) Société de la soie artificielle, Spreitenbach (est. 1891; start of operation 1893), Switzerland → amalgamation (1899) → Vereinigte Kunstseide Fabrik (VKF). (est. 1900), Frankfurt, Germany.

(3) New Artificial Silk Spinning Co., Ltd. (est. 1896; start of operation 1898), Wolston, near Rugby and Coventry, UK → New Artificial Silk Co., Ltd. (est. 1899) → liquidation (1900).[87,53,113]

(4) Davenport & Co. (est. 1899 or 1900) (founder; Silk company, Leek, UK) Leek,

UK[114,115] → Société anonyme fabrique de Tubize

(5) Vereinigte Kunstseidefabriken A.-G. (VKF) (est. Feb., 1900, capitals 250×10^4 DM) → (1925 or 1926) → subsidiary co. of VGF (Vereinigte Glanzstoff Fabriken).[116-119]

(6) Société anoyme fabrique de Soie Artificielle de Tubize (est. 1900; capitals 80×10^4 francs: A. de Baudry d'Asson, Administrator, 1900～1925, and president of Council, 1925～Dec. 1929).[53,114,120-121]

(7) Kirklese Ltd. (est. 1893～4) → viscose process → survived until after world war two as viscose rayon manufacturer (Chardonnet resided at Manchester Road, Burry, Lancashire for several years).[114,122,123]

(8) Société pour la fabrication en Italie de la soie artificielle par le procede de Chardonnet (est. 1904) Pavia Italy → liquidation (1905)[124～126]

(9) Société anonyme hongroise pour la fabrication de la soie de Chardonnet (est. 1905), Hungary[127,128] (explosion of plant in 1904) (See Table 5).

Among nine companies, only three ((1), (5), and (6)) could earned profit and others disappeared except(7).

7.2 Period 1905～1920

During 1905～1920 the names of following companies were known in addition to (1), (5), (6), (7), and (9) in 7.1 as cellulose nitrate rayon producers. In 1906, there were already 22 artificial silk works: 7 in Germany, 6 in France, 4 in Switzerland, 3 in Italy, and 2 in England.

France:

(1) Compagnie de la soie de Beaulieu, Beaulieu (est. 1904; capitals 200×10^4 francs, similar to Besancon)[129]

(2) La Soie Artificielle Francaise (Reunes) (600×10^4 francs) → liquidation[130]

(3) Société de la artificielle Vallete de Lyons (est. 1904)[131]

(4) Société pour la fabrication de la cellulose de Lyons (350×10^4 francs)[131]

(5) Compagnie francaise de la soie Parisienne (200×10^4 francs; devident 14% in 1907) → cuprammonium process[132]

Germany;

(1) Kunstfäden Gesellschaft G. m. b. H., Julich, Germany → cuprammonium process[133,134]

Italy;

(1) Sobieta artificielle di Pavia, Pavia Italy (est. 1905, 240×10^4 lira; 10×10^4 kg/year) → viscose process.[135]

(2) Societa artificielle di Padova, Padova, Italy → sold to other company[136]

Belgium;

(1) Fabrique de Soie Artificielle de Tubize (Chardonnet process −40% (1927) (250×10^4 francs; combined out put 20,000 *lb*/day), Tubize, Belgium.[137~140]

(2) Fabrique de soie Artificielle d'Obourg ($1{,}000\times10^4$ francs), Obourg, Belgium.[141]

(3) S. A. des Soieries de Maraasart (750×10^4 francs)[141]

Poland;

(1) Tomaszowska Fabryka Sztuczneyo Jedwabin Sr. Ake. (est. 1910 by 'Tubize' Co.,).[120,142,143]

Hungary;

(1) Magyarorai Muselyemgyar, Magyarovar, Hungary (est. 1911 by 'Tubize' Co,).[120,144]

USA;

(1) Tubize Artificial Silk Co. of America, Hopewell, Va., USA (est. 1920; 500×10^4 $, 350×10^4 *lb*/year)[145,146]

(2) General Artificial Silk Co., Landsdown, Pa., USA → Genasco Silk Works... American Viscose

8 OUTPUT AND PRICE OF CHARDONNET SILK

8.1 Production of Chardonnet silk

Table 12 summarizes volume of output of artificial silk in three major manufacturers, Besançon, Tubize and VKF during 1890 and 1928. The records are collected from a variety of sources. In the table, there is not strict distinction between production capacity and output record. For example, in 1891, output was yet zero (Table 4) and number for 1891 is the plant capacity. The production increased at Besançon since 1892, attaining in 1907~1909 approximately constant (~2,000 kg/day), which is 20 times of the initial full capacity (see, Table 3). The capacity of 1,000 kg/day was considered an economic unit in European artificial silk industry at that time.[151] The Chardonnet's Besançon plant matured momentary in 1907~1909, although the world production increased continuously until 1909~1910. According to Avram,[152] there were handicaps to be contended with for some local authorities do not favor manufacturing operations where the plant capacity exceeds 1,500 kg to 2,000 kg per day, with the result that manufacture is distributed among a great many small factories widely scattered, often with a scarcity of proper labor.

Table 13 compiles the world production and share of artificial silk by the cellulose nitr-

Table 12 Production of Chardonnet silk since 1890

	Production kg/day (kg/year)		
Year (AD)	Besancon	Tubize	VKF
1890			
1891	50*a~*c		
1892	100~150*c, *d		
1893			150*d
1894	100*b, *c		
1896	(200×103)*e		
1900		200*g	(2,000)*h
1901		300*g	1,500*i
1904	1,500*b		
1907	1,800*a, *b~2,000*a, *b		
1908	(700×103)*f	(500×103)*f	(425×103)*f
1909	2,000*b, *c		1,500*j
1913		4,000*j	
1925	(800×103)*b, *l		
1928			5,000*k

*a; Y. Kami[37], *b; Y. Kami[45, 56], *c; W. E. Wicht[38], *d; A. Demonent[61], *e; L. G. Fauquet[44], *f; Y. Kami[145] *g; L. G. Fauquet[46], *h; Y. Kami[147], *i; L. G. Fauquet[148], *j; C. Köningsberger[149], *k; R. Reinthaler[150], *l: viscose rayon

ate method between 1890~1928. The production of artificial silk by this method got off the ground in 1896 and thereafter output increased monotonously up to 1909. The manufacturers enjoyed prosperity for short period. The share of Chardonnet silk among whole artificial silks was, of course, 100% until 1896. However, conversion of Chardonnet

Table 13 World production of artificial silk by cellulose nitrate method

ear (AD)	Out put (10^3 pounds)	Share of the cellulose nitrate method (%)
1890	30*a	100*a
1896	1,250*a	100*a, *b
1903	4,818*a	73*a, *b
1906	6,996*a	53*a, *b
1909	7,920*a	48*a, *b
1913	1,008*a	4.0*a, 27*b
1924	1,786*a	1.4*a, 18*b
1925	——	18*c
1928	——	3*b, 9*c

*a; 30 *Years History of Asahi Bemberg Plant*, p. 7, Table 2, 1962.[153]
*b; S. Ohhara, *'Chemical Fiber Industry'*, p. 48, Table 3, Tokyo Univ. Press, 1961.[154]
*c; M. H. Avram[155]

process to other competitive processes occurred catastrophically and consequently, output of Chardonnet silk dramatically diminished until 1920s, when the share (%) downed to single figure. This was absolute decisive decline and no recovery was observed again since then. In 1890~1909, all the data of ref. 153 and 154 coincide with each other. But, from 1911 onwards, there are great discrepancies in estimation of the share. Note that it is widely recognized the difficulty of finding the reliable statistical data of artificial silk at its infant period.[156]

8.2 Price of Chardonnet silk

Table 14 collects selling price of Chardonnet silk at Besançon and Tubize in the period

Table 14 Price of Chardonnet Silk

Year(AD)	Price(francs/kg)		
	Besancon		Tubize
1894	25.0~27.0*a, *b		
1895	27.00*c	30*d(10s11d/lb)*d	
1896	30.00*b	26.5*d(9s71/2d/lb*d	
1897	26.5,*b	21.75*d(7s11d/lb)*d	
1898	21.75,*b	25*d(9s1d/lb)*d	
1900	37.0*c		(12s/lb)*e
1903	40.0,*a, *b		
1905	35.0*c		
1910	18.0*c		
1911	20.0,*b		
1912	20.0,*b		
1913~14	25~27,*b		
1915	[14.5]*c		
1916	[12.5]*c		

*a; W. E. Wicht[38], *b; Y. Kami[45], *c; Y. Kami[157], *d; J. Foltzer [51], *e; A. Hard[114],
[ ]; Average price of artificial silks in France

Table 15 Comparison of prices of artificial silk to those of natural silk in Germany

Year(AD)	Price DM/kg		
	Artificial silk	Natural silk	Ratio
1903~1904	32	(40~50)*a	0.64~0.80
1905~1912	13~16	40~50	0.26~0.40
1920	175~275 (180d) (90d)*b	1350	0.13~0.20 (90d) (180d)

(Table was construted using the data in Kami.[159])
DM; Deutsche Mark, *a; assumed value, *b; total denier of rayon

1894~1914. When denitrated silk was to be put on market in 1894 the selling price was 25~27 francs/kg-fiber. The price of Chardonnet silk underwent to a great fluctuation over 1894~1914, showing insignificant trends. Jumping of the price in 1903 was said due to a decrease in its production.[45] Determination of the factors governing the price of Chardonnet silk seems very complicated and is open for further study. Because of its superior quality, the price of Tubize was always on average 1 franc/kg higher than other companies.[158]

Table 15 shows comparison of prices of artificial silk with those of natural silk in Germany between 1903 and 1920. The period inversigated in Table 15 can be qualitatively classified into three terms: I. Growth term (1903~1904), II. Golden term (1905~1912), and III. Decline term (~1920). It seems likely that the price ratio of Chardonnet silk to natural silk decreased from 0.64~0.80 (in I), to 0.26~0.40 (in II) and to 0.13~0.20 (in III), according to , probably, lowering of scarcity value of artificial silk by massive production.

9 PROFIT AND DEVIDEND OF CHARDONNET SILK COMPANIES

Table 16 compiles the date of first profit and first dividend in Besançon factory, described in the books. Hottenroth wrote that *'in the following year (1895), the first dividends were distributed.'*[160] Hard stated that *'Besançon was earning by 1895 large profit.'*[36] Moncrieff said *'by 1895 it (the Societe) was paying dividends.'*[161] The above descriptions are far from the truth, if we take into account the following historical facts: (1) In the first half of 1894, operation of the factory was suspended and (2) in 1894, the total deficit exceeded more than 800,000 francs[163] and (3) in 1896, the factory had suffered losses of 7 francs/kg-fiber (Table 4) (i.e., the total deficit of 140,000 francs) and reduction of production cost was a capital problem.[164]

Table 17 collects the profit and dividend of Chardonnet companies; Chardonnet (Besançon), Tubize, and VKF between 1898 and 1921. Besancon earned the first profit

Table 16 Date of first profit and first devidend earned and distributed by 'Besancon'

Year (AD)		
First profit	First dividend	Reference
——	1895	Hottenroth[160], Monicrieff[161]
1895	——	Hard[36]
1898	1898	Kami[55]
1898	——	Coleman[23, 162]

Table 17 Profit and deviviend of three major manufacturing companies of Chardonnet silk

Year (AD)	Chardonnet		Tubize		VKF	
	Profit ($\times 10^{-4}$f)	Deviend (%)	Profit ($\times 10^{-4}$f)	Deviend (%)	Profit ($\times 10^{-4}$f)	Deviend (%)
1898	20.2*a	6.25*a				
1899	76.8*a	6.25*a				
1900	30.1*a	6.25*a				
1901	61.8*a, *b	8.75*a	20*e			
1902	75.7*a, *b	15.0*a				
1903	24.1*a, *b	12.5*a				
1904	500*a, *b	150*a	148*f			
1905	321*a	60*a	150*e		237*h	35*h, *i
1906	240*a	30*a			88.4*h	20*h
1907	105*a	30*a	192*g	45*g	67.8*h	15*h
1908	115*c	60*c	229	50	52.6*h	10*h
1909		0*d	332*g	50*g	63.7*h	8*h, *i
1910		0*d			△140*h	0*h
1911			250*e			
1914						0*h
1919			418*g			6*h
1920			710*g	6.0*g	27.0*h	9*h
1921	43.1*e	40*e	520*g	6.0*g	296*h	15*h

*a; Y. Kami[165], *b; A. Demoment[156], *c; Y. Kami[145], *d; Y. Kami[131], *e; L. G. Fouquet[120], *f; Demoment[167], *g; Y. Kami[168], *h; Y. Kami[169], *i; Fouquet[170], △; deficit

and paid the first dividend of 6.25% (on its stock) in 1898. The Besançon company maintained the dividend over 1898~1908, which increased from 6.25% in 1898 to 150% in 1904 and then, decreased with some fluctuation. The company could not pay dividend from 1909 until 1914 when the Chardonnet silk factory was converted to gun cotton factory.[171] Note that the total deficit (larger than 800,000 francs) in 1894 was comparable in magnitude to the summation of profits in 1898 and 1899.

On the other hand, Tubize company, who followed Chardonnet process, yielded profit from the next year of its establishment (1901)[120,172] and the profit continued to increase until 1920.[168] Note that profit of 'Tubize' company is due not only to Chardonnet silk, but also to viscose rayon.[140] The dividend of the company attained maximum in 1909. 'Tubize' made larger profit as compared with two other companies.

Two plants in VKF were converted to viscose process in 1911 and others followed in 1913.[121,173] VKF made deficit in 1910 and since then, no dividend was paid until 1919.[169]

10 TECHNOLOGICAL ADVANCE OF CHARDONNET PROCESS AFTER COMMERCALLIZATION

10.1 Efforts to reduce the production cost

These efforts were made since starting of operation. For examples,

(a) Recovery of mixture of sulphuric and nitric acids in a centrifugal machine and reuse of the separated acid mixture with addition of new acid (see, for examples, Britisch Patent No. 5,376 (1896)[72] and US Patent No. 455,245 (1891))[174].

(b) Separation and recovery of ether~alcohol (see, Britisch Patent No. 2,211 (1891))[67]. For this, many instrumental inventions were made and dry-spinning method was re-introduced.

10.2 New technological knowledge acquired by Chardonnet

(1) Cotton and wood pulp are the most suitable.

(2) Resource cellulose should be completely dried. For this purpose, hot water (90~100°C) was circulated in copper tube.

(3) Degree of esterification, defined by the nitrogen content (N%), is primarily determined by the concentration of nitric acid in the acid mixture.

(4) The solubility of cellulose nitrate in ether~alcohol mixture is governed by N%.

(5) For preparation of spinning solution, cellulose nitrate with water content of 10~20% is recommended to use. Half-dried cellulose nitrate is washed without heating.

(6) When cellulose nitrate is completely dried the possibility of explosion develops. Partial-dried cellulose nitrate easily dissolves into ether~alcohol mixture as the completely dried samples does. In addition, the solution prepared thus can be extruded in air with considerable velocity.

(7) As solvent ether (4 volume) and alcohol (6 volume) mixture is suitable (to that mixture 20 wt% (against solvent) of protochloride of reducible metallic (Fe, Cr, Mg, Sn) plus approximately 0.25% of organic base (quinine, aniline, rosanine) are added).

(8) Alcohol soluble dye is added to the solvent in advance.

(9) The density of ether is larger and can be removed by powerful aspirator.

(10) In order to suppress the possibility of inflammability of cellulose nitrate fibers, denitration is carried out. As deesterification reagent alkaline hyrosulphide is the most suitable (in particular, magnesium salt has the following advantages: low cost, highly

reactivity and the relatively high tenacity of the treated fiber)

(11) Mechanical properties and luster of the fiber depend on the kind of dentrated reagents used and the reaction conditions.

11 SIMILAR PROCESSES OF ARTIFICIAL SILK, BASED ON CELLULOSE NITRATE, TO CHARDONNET'S PROCESS

Table 18 Solvents employed in place of ether~lcohol mixture

	Solvent(s)	Inventor(s)	Reference
(1)	Dilute alcoholic solution of various salts (i.e.,chlorcalcium)	E. Bronnert, Th. Schlumberger	DP 93,009(1895) BP 6,858(1896) USP 573,132
(2)	Alcoholic solution of Merhalchliride	J. M. de Suverzac	FP 402,950
(3)	Acetone	Fr. Lehner	DP 82,555(1894)
		P. Cazeneuve	FP 346,693 FP 350,723
		P. Germain	FP 360,395
		Ch. Bouillot	FP 373,947
		H. E. Vitternet	DP 171,629(1905)
(4)	Mixture of acetone, amylalcohol and ethlacetate	G. Gorrand	FP 354,424
(5)	Mixture of acetone, acetic acid and metylalcohol	J. Duquesony	DP 135,316(1900)
(6)	Mixture of acetone, acetic acid and amylalcohol	J. Duquesony	DP 135,316(1900)
(7)	Acetic of Fethreiche, chlor, brom, alcdehydle, and ether derivatives	E. Huward	FP 383,555
(8)	Aceton and acetic acid	J. A. Briller	FP 368,190
(9)	Sulphuric acid	Fr. Lehner	BP 82,555(1894)
(10)	Acetic acid	M. P. E. Gérad	DP 40,373(1886)
(11)	Glacial acetic acid	Du Vivier	DP 52,977(1889)
(12)	Mixture if 4 parts of alcohol and 1 part of glacial acetic acid	H. D. Jurgard	FP 344,845
(13)	Wood spirit	Fr. Lehner	DP 55,949(1889)
(14)	Mixture of wood spirit or ether(3 parts) with ethylsulphuric acid(1 part)	Fr. Lehner	DP 58,508(1890)
(15)	A meisensäure, methyl und-äthylester	A. Wohl	FP 425,900
(16)	Essigsäuremethylester	A. Wohl	FP 425,900

Announcement of Chardonnet's inventions stimulated the followed inventions similar to Chardonnet's such as those of M. P. E. Gerard (Deutsche Patent Nr. 40,373 (1886)[175]), J. H. du Vivier (Deutsche Patent Nr. 52,977 (1889)[176]) and F. Lehner (Deutsche Patent Nr. 55,949 (1989)[84]). These patents specify addition of third component including polymeric materials (resins and gums), but the fibers obtained by these methods lucked in luster and had inferior mechanical properties. The above short points could not be overcome and the development was suspended at laboratory scale, except Lehner.

Table 18 collects solvents proposed in the followed patents in place of ether~alcohol mixture as spinning solvents. Note that no solvent in Table 18 could not be commerciallized.

12 CHARDONNET AND DESTINY OF CHARDONNET SILK

The original factory of Chardonnet process at Besancon continued to operate until 1914 when it was converted to the manufacture of gun cotton by the French Government.[171] Since during 1909~1914 the Societe at Besancon earned no profit and could not pay dividend (see Table 17), management of the company seems to have lost, by 1914, enthusiasm of further improvement of economical crisis. After the World War I (1918~) the Chardonnet silk factory was sold to European associates of the Du Pont interests,[117] and new company (Soie Artificielle de Besançon) (capitals, 2,000,000 francs) used the old Chardonnet factory at Besancon by remodeling it to convert to viscose rayon process (3,300 pounds per day in 1925)[177]. Comptoir des Textile Artificiels served the old Chardonnet company by making it change its process to viscose.[178] Note that data of Besancon in 1921 in Table 14 correspond to those of new company.

In 1934, the production of Chardonnet silk in USA ended by labor's strike at Tubize company of America, Hopewell, Varginia, which was stabled in 1920 as a subsidiary of 'Tubize' and after alliance and rapture, in 1946 was amalgamated by Cellanese.[179]

In 1949, the last remaining Chardonnet silk factory in the world, situated in Brazil, was burned down and any commercial production of the Chardonnet silk ceased.[113,180]

In 1914, Chardonnet was awarded Perkin Medal by the Society of Dyers & Colourists (UK) at Bradford, who recognized his life work well.[36,181~184] Chardonnet was the first, who understood the great difference between pure science research and related technology development. He explained the reason why his research needed 30 years as[181,183,185] : *'The time employed over this work would appear to be exaggerated if one did not remember that the establishment of so new and so complex an industry necessitates a whole series of studies, dis-*

coveries, and inventions...Note the difference existing between researches in pure science and those relating to applied science, especially when it is a question of constructing a work complete in every part. In the realm of pure science each discovery in itself extends the field of human knowledge; on the other hand when applied science is in question an isolated discovery is valueless. Every problem which arose must be completely solved. The smallest badly laid stone will bring down the edifice. Sometimes it is only after months or years of industrial practice that the best solution of a problem is found.'

We are marveled to know that Chardonnet was a strong-willed hard worker and even after artificial silk by his process became decisively unpopular, loosing its economic impact, he did not suspend working through path and died in endless battle 12th March, 1924. C. F. Cross mourned in a very impressive obituary for Comte Hilaire de Chardonnet.[182]

13 CONCLUDING REMARKS

(1) A history of commencement, development and decline of Chardonnet silk industry was systematically summarized. For this the most comprehensive data base was built, according to the strategy employed in the preceding paper, from widely scattered fragments.

(2) Chardonnet was no more than an inventor at Besancon to the end and his authority and responsibility in the enterprise, formed by the local proprietors, were limited, reflecting his position as consultant engineer, which was not a position of decision making. The role of engineers played in chemical fiber industry in late 19th~20th century is open for further study.

(3) Numerous troubles met in the plant at its infant stage are those, ordinary often observed when new industry is commercialized even at present time. In particular, the safety of the process and products was the priority, which should be secured first. Chardonnet silk might be the first case where the safety of industrial commodity, made by mass production, became a serious public problem in the consumer revolution.

(4) F. Lehner played only insignificant role in the reformation of 'Spreitenbach' plant and 'Lehner' process was indicated, from the detailed examination of patent literature, a mimic of 'Chardonnet process'.

(5) Chardonnet's denitration method was compared with Swan's and Lehner's. Swan's invention is very simple and concise (rather an idea). In contrast, Chardonnet studied the most comprehensively numerous denitrating reagents with proper assessments. Influence of Swan's idea on Chardonnet is not evident, because we cannot judge whether

denitrating reagents such as ammonium sulphate was public at that time or not. Lehner's patents were a mimic to Chardonnet's.

(6) The financial success in 1898~1908 of the Besançon plant after its reformation stimulated intensely new development of other types of artificial silk, which defeated 'Chardonnet silk'. Then, the success ironically brought about its too early and untimely decline.

(7) High cost of the production, particularly due to high tax rate against alcohol, of Chardonnet silk was a fatal fault. But, Chardonnet silk, which was not, of course, competitive to natural silk, had the best quality (lubricant, colour brightness, and fineness) among artificial silks. Chardonnet continued research even at his age of 84, with belief that cellulose nitrate process could be more improved. Note that the destiny of the industry is very complicated functions of the existence of competitive commodities, social needs, fashions, ways of life, production technology, energy consumption, environmental damage etc., (all of these factors are very tome-dependent). For example, we know that cuprammonium rayon, which consumes expensive copper and ammonia in the production process, was said in 1910s to be economically uncompetitive to 'cheap' viscose rayon. Owing to numerous technological innovations applied to cuprammonium process and energetic development of new market, cupammonium rayon industry is successfully surviving at the present time.[186~190] Therefore, we mustn't lable Chardonnet silk the most uneconomical one.

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