1. History of CA and Evolution of the Markets

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Summary
An overlook is given of the 100 years of technical, industrial and chemical development of cellulose acetate. CA has been used as raw material in the fields of laquer, plastics, textile, Filter Tow, film, membrane and others. In the field of applications for plastics and textiles CA was quite successful for many years, but was then slowly substituted by other polymers. Total cellulose acetate demand is growing, especially for Filter Tow in cigarettes filters and film for polarisers in LCD-displays.

Keywords cellulose acetate history

The first mention of cellulose acetate is from Schützenberger in 1865[1], who synthesized it by heating cellulose in a sealed glass tube with acetic anhydride. Already in 1879 Franchimont[2] found, that with sulfuric acid as catalyst CA can be produced at room temperature, but failed to recognize the potential of this discovery.

The first patents were applied for in 1894 of cellulose triacetate by CROSS and BEVAN[3] targeting on the replacement of collodion and nitrocellulose with the hardly inflammable CA. Immense efforts in industrial research have been made and early patents appeared for the application of the CTA as photographic film (Eichengrün[4, 5] Becker[6] 1902), artificial silk (Wagner[7], Eichengrün[8] 1904) and hornlike plastic material (Lederer[9]1905).

But the commercial success of all this research work remained poor for two major reasons:

- The properties of CTA seemed to be close to collodium and nitrocellulose, but in fact the solubility and elastic properties, of CTA were very different from the other products.
- For the processing CTA new methods had to be developed.
- The cost of the raw materials for cellulose triacetate was exorbitantly high, as cellulose triacetate had to be produced with specially cleaned cotton linters and with 5 - 6 times more acetic acid and anhydride. As artificial acetic acid was not yet available, the price of those substances was a big cost factor.

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The commercial breakthrough came with the discovery of cellulose diacetate by Miles 1904[10] (mixture of di- and triacetate) and Eichengrün 1905[11], as CDA is soluble in acetone and other readily available solvents like methyl acetate and ethyl acetate and its mechanical properties are close to collodion.

The first important application was in the field of coatings for airplanes. At that time, the wings of the planes were made with heavy rubber tissue. A cellulose diacetate coating on linen tissue gave a light, water, oil and petrol resistant material. Upon drying, the acetate laquer automatically brought the linen under tension and made a very flat surface [12].

Thus, cellulose diacetate became the quite a successful product "Cellit" from F. Bayer & Co, where industrial production began already in 1905. Starting in 1912 the Dreyfus brothers in Basel produced laquer and films, which they called "Cellonit". After the outbreak of World War I, the Dreyfus brothers were invited to found CA plants in France, Italy, England (1914) and in the United States (1917) to satisfy the growing demand of the strategic aircraft industry[13].

Textile Cellulose Diacetate

Since the plane applications dropped strongly after World War I, new applications for cellulose diacetate based on the existing industrial capacities were needed. In England, the Dreyfuss brothers successfully developed a spinning process for the new British Celanese Co in Spondon[14] for a silk like yarn textile called "Celanese".

They managed to separate the acetone air mixture from the winding up of the thread and recovered the solvent, this represented half of the manufacturing cost. The commercial success of the acetate silk was very poor in the first years as the dying of the fibers was very difficult.

Rapid growth [15] of CA textiles occurred only after Clavel found a way to apply dyestuffs in acetate spinning, and after many dyes were quickly developed.

In 1924, the Dreyfus brothers switched entirely to the US where acetone and acetic anhydride were cheaply available. Shortly afterwards, some new companies started with the manufacturing of acetate fibers. In 1927, the following companies produced cellulosediacetate yarn [16]:

British Celanese Ltd. in Spondon, American Celanese Corp. in Cumberland, Canadien Celanese in Drummondville-Quebeck, Celanese Française in Lyon, La Soie Artificielle de Tubize in Tubize (Belgium), Société Française de Tubize in Venissieux (France), Tubize Artificial Silk Co.

of America in Delaware, Lustron Co in Boston (America), Société Rhodiaseta in Roussillon (France), Courtaulds Ltd. in Coventry (England), La Soie de Chatillon in Mailand, Lonza-Werke in Basel, Aceta GmbH I.G. Farbenindustie in Lichtenberg and in Worringen, Deutsche Rhodiaseta in Freiburg (Germany). Many patents appeared in the first half of the last century which describe the strong technical evolution of the acetate spinning technology (see fig.1).

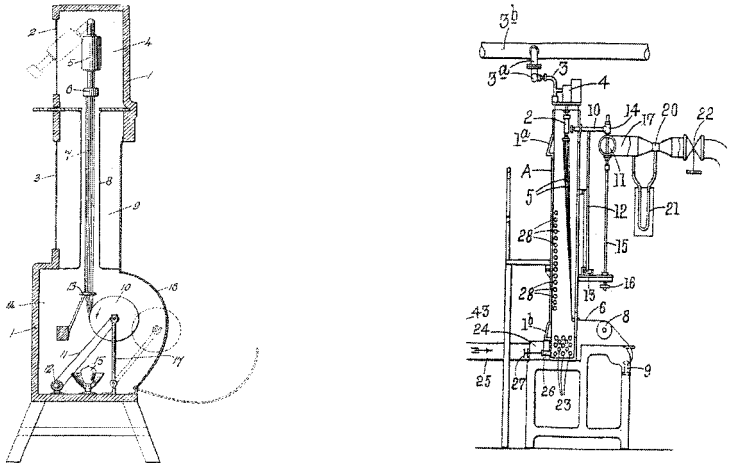

fig. 1 : Rapid developments in the technology of cellulose acetate spinning were patented and applied in the 1920's. Left: Spinning machine from G.F.J. Bouffe [17], (5) filter, (6) nozzle, (7) threads. Right: Spinning machine from J.F. Buggs and W. Yorks [18], spinning cabinet and wind up are already separated (5), filaments, (6) thread, (10) air outlet, (28) heating pipes.

By the late thirties, the cellulose acetate silk industry had made itself a permanent place in the family of textile fibres, side by side with cotton, wool, natural silk and viscose and other regenerated cellulose rayons. After World War II, acetate plants were also constructed in Japan (Daicel, Mitsubishi) and Korea (Sunkyong).

When other man-made fibers such as nylon and polyester appeared on the textile market, acetate demand slowed down. Despite its agreeable textile characteristics, the usage of acetate continue to decline; this is mainly due to with the higher fiber strength demanded by high speed textile machines. Textile acetate will keep its niche in the areas of silk like (see fig.2) women's apparel.

Filter Tow

Since its first usage in cigarette filters in 1952[19], CA Filter Tow has seen a tremendous and almost linear growth which in 2003 stands at about 600 000 metric tons (see fig. 3). Today nearly 95% of the world's cigarettes are sold with a CA filter. This success is directly related to the specific retention behaviour of CA, which gives the cigarette an agreeable "taste signature", a high speed technology for rod making, and a large variety of possible filter characteristics[20].

Plastic Applications of Cellulose acetate

Cellulose tri- and diacetate in combination with plasticisers as well as mixed esters are used to produce transparent thermoplastics with excellent clarity and good mechanical properties. They are nonyellowing, resistant to embrittlement and provide good electrical insulation. EICHENGRÜN invented in 1908 the first injection moulding machine, which was capable to press 8 grams of plastified heated CA into a cool mould [21]. By injection moulding or extrusion, plasticised CA or mixed esters are transformed into many products like tool handles, toothbrush handles (Cellulose acetate propionate, CAP), combs, barrettes and toys. Historically many automotive parts like steering wheels (CAP), signal glasses, etc. have been made from CA. Since the 1980's, CA has been replaced by other polymers in many of these applications [22]. An important market is the frames for spectacles.

Cellulose acetate Film

CA film was previously proposed for photografic film in 1901[23]. Despite the lower inflammability of CTA, it took a long time to replace the less expensive but easily inflammable Celluloid. Only after the tenacity, the adhearence for the photografic layer and the dimensional stability of the CTA had been improved, did CA become the preferred material for photographic film as well as for professional motion picture films [24]. CA is preferred even against PES film due to its superior handling characteristics such as rupture and splicing. Other important usages of the acetate films were the construction of security glass for automobiles and electrical insulator films i.e. in condensators[25]. Today there is a growing demand for CA film is today in LCD flat screens.

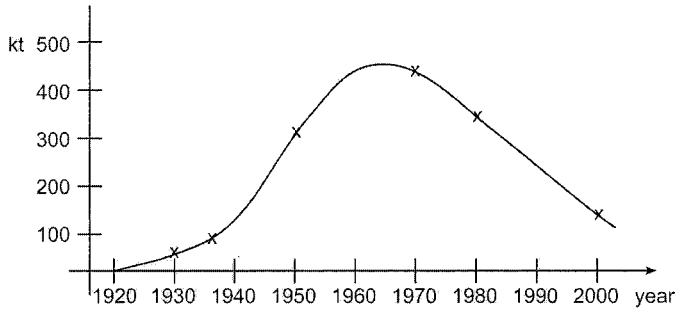

fig. 2.: Development of the worldwide Textile CA Market [26][27]

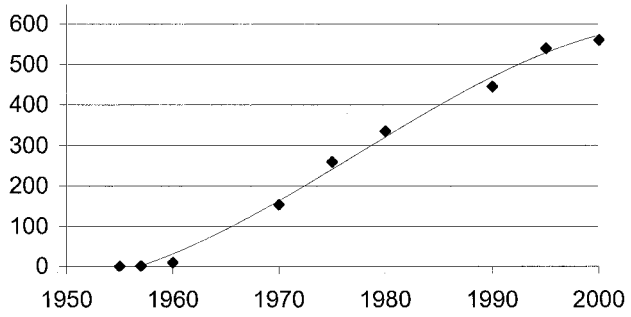

fig. 3.: Development of the worldwide CA Filter Tow Market [27][28]

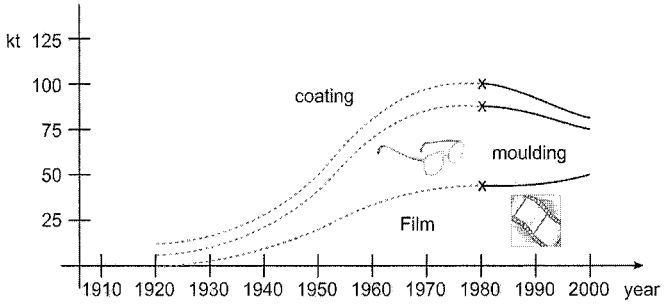

fig. 4.: Development of the worldwide volumes of CA for film, moulding and coating [22]

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