CHIMICA & TRASFERIMENTO TECNOLOGICO



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UNIVERSITY AND LARGE INDUSTRY FOR SUCCESSFUL TECHNOLOGY TRANSFER

PART 1: GIULIO NATTA AND SYNTHETIC RUBBER

A recent study by Bank of Italy has highlighted the critical state of technology transfer (TT) in Italy, and stated that the priority is to strengthen the public component of basic research to support private innovation. The cooperation between University and a large industry is a successfull model for TT. Here is the cooperation between Giulio Natta and Pirelli for the production of synthetic rubber. Natta got also in contact with Montecatini and laid the foundations for the research that led to the Nobel Prize.

Technology transfer in Italy

Technology transfer is the process by which scientific knowledge, technologies and innovations developed in institutions such as universities and research centres are transferred to industry and society for commercialisation and economic exploitation.

A recent study by Bank of Italy [1] has highlighted the critical state of technology transfer in Italy. The poor spending for education and research and development (R&D) is indicated by data in Tab. 1.

In spite of this situation, the number of high-quality publications [2] in STEM subjects has increased significantly (by 60% between 2009 and 2023), and Italy's share of the global total has remained virtually stable at around 3%. Universities and research centres are therefore a great potential source of innovation.

However, there is a huge difference between Italy and other countries when it comes to technology

Spending on	Italy	Comparison
Tertiary education	1	1.3 EU
R&D	1.31 (1.33 in 2014)	3.11 Germany, 2,19 France, 1,49 Spain and 2,22 EU.

Tab. 1 - Spending for education and R&D (% of GDP) in 2023

transfer. Italy has a low level of patenting activity: patents applications filed by Italy are half compared to France and one fifth compared to Germany, altough the 22% increase from 2015 to 2024 is in line with the overall growth in patent applications to the European Patent Office. Patents filed by Italy are concentrated in mature sectors such as logistics, transportation, and civil engineering. About chemical engineering, the percentage of EPO patent applications from applicants residing in Italy is in line with the rest of the world (about 3%) compared to about 2%). Universities have modest patenting activity. The first five Universities in Italy from 2000 to 2020 filed less applications than the first University in France. Technology transfer offices in Italy have approximately 20% fewer staff than the European average. There are no incentives for university people to engage in technology transfer. For example, patents have no impact on a researcher's career.

The Bank of Italy study states that it is a priority to strengthen the public component of basic research as a lever to support private innovation in sectors with the highest growth potential.

The Bank of Italy study seems like a good opportunity to reflect on the situation of technology transfer.



A model for technology transfer: cooperation between university and large industry

It is well known that there are various models of technology transfer that see the university as the source of innovative ideas [3]. In this article, the model of the cooperation between a university and a large industry is proposed.

There is nothing better than referring to the most illustrious examples in the history of the Italian chemical industry, which refer to Giulio Natta and tell the story of the production of fundamental substances such as (i) synthetic rubber, (ii) methanol, (iii) isotactic polypropylene. Here is the first story, about synthetic rubber. Few references will be made to the research on methanol. Isotactic polypropyene will be the subject of a forthcoming article.

To report on the production of synthetic rubber in the last century, with Giulio Natta playing a leading role, is not about writing history of chemistry. Natta wrote in his autobiography [4] that the synthetic rubber adventure of the 1930s and 1940s was the cultural and professional basis for his research into stereospecific polymerisation. Moreover, there is the role that a large industry could play to achieve a succesfull technology transfer. Furthermore, it is discussed how university can establish the scientific foundations for industrial technologies.

Documents [5] and brilliant analyses [6] and reviews [7] on the chemical aspects are available. This article aims to highlight the model for technology transfer, in the frame of the industrial organization.

The synthetic rubber Pirelli and the synthetic rubber

In 1937, at the internation motor show (Salone Internazionale dell'Automobile) in Milano, Aerflex Tyres made with synthetic rubber were presented by Pirelli. In 1939, at the Invention exhibition (Mostra delle Invenzioni) in Milano, Pirelli presented Raiflex tyres, with also rayon fabric in place of cotton. These first examples in Italy of tyres made with synthetic rubber are shown in Fig. 1. In Fig. 1b, you can also see a bale of synthetic rubber. The objective of Pirelli was to manufacture syn-

thetic rubber on an industrial scale, with elasticity

and resistance properties identical if not superior



Fig. 1 - (a) Aerfex tyres. Stand Pirelli al Salone Internazionale dell'Auto di Milano, 1937 (foto Ancillotti, courtesy Fondazione Pirelli); (b) Raiflex tyres [8]



to those of natural rubber. Alberto Pirelli stated that "the state of the art is that synthetic rubber is of inferior quality to natural rubber and is much more expensive in Italy. But synthetic rubber production had already been developed in Russia and Germany. If the industry was to be established, Pirelli could not remain a stranger" [9].

The cooperation of Giulio Natta with Pirelli. The model

The cooperation of Giulio Natta with Pirelli and thus its contribution to the production of synthetic rubber began in 1937, when he still was at Torino Polytechnic, after periods spent at the universities in Pavia and in Roma. The model is summarized in Fig. 2. Pirelli and IRI established in 1937 the Institute for the study of synthetic rubber (hereinafter:

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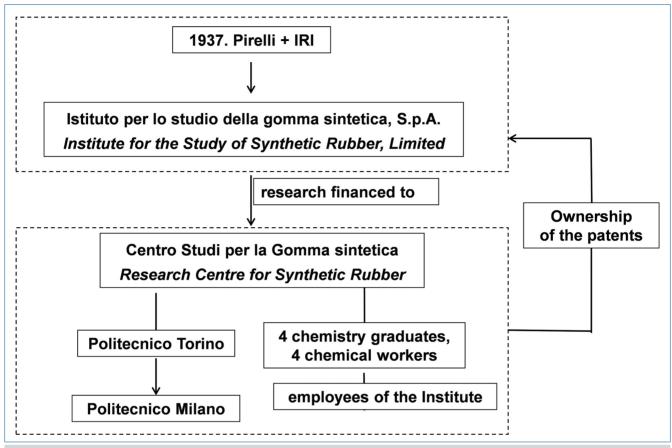


Fig. 2 - The research for the industrial production of rubber. The model

Institute), that financed the research for synthetic rubber to the Research Centre for Synthetic Rubber, directed by Natta and located first in Torino and then moved to Milano Polytechnic, where Natta took the chair of industrial chemistry in place of Mario Giacomo Levi, expelled as a result of the racial laws of the fascist regime (1938). The Research Center's workforce was employed by the Institute, which also owned the patents, but was at the disposal of Natta, who received from the Institute a sum equivalent to approximately €4,000 per month (on top of the salary of a university professor), in addition to expense reimbursements. This model was then applied in the 1950s to research into stereoregular polymers, which led to the Nobel Prize, when Natta could direct the work of the "Montecatini graduates". The Institute established, in the Pirelli facilities in Milano Bicocca, labs for organic and analytical chemistry, technological development, compounding and physical-mechanical testing. From 1938, pilot plants and semi-industrial plants were installed.

In 1939, the Institute founded the Synthetic Rubber Industry Limited Company (Società anonima industria gomma sintetica, Saigs), whose president was Alberto Pirelli, for building industrial plants in Ferrara and in Terni.

The synthetic rubber from dienes

The first attempts to produce synthetic rubber were based on isoprene. In 1909 Fritz Hoffmann patented the preparation of synthetic rubber from isoprene (and won the Emil Fisher medal of the German Rubber Society) and Continental in 1910 prepared tyres from synthetic isoprene rubber. However, synthesising isoprene from *p*-cresol via adipic acid proved a complicated process. Once it was understood that the properties of natural rubber could be obtained by polymerizing a diene, efforts focused on butadiene.

But where could butadiene be obtained? Natta reported [10] that the fermentation of carbohydrates to butyl alcohol had low yield, as did the catalytic



dehydrogenation of butylene, which produced a mixture of products that were difficult to separate. In nature, there are few other compounds with a 4-carbon chain, suitable for industrial development. The choice was thus for compounds with 2 carbon atoms: ethanol and acetylene. In the synthetic route to butadiene, both of these building blocks pass through acetaldehyde, a substance that was already the subject of Natta's research. The project from ethanol was based on the organization above reported and the whole activity was developed in Italy. The synthesis from acetylene was developed in cooperation with I.G. Farben, in Germany. The priority was given to synthesis from ethanol, because the fascist regime wanted to develop autarchic materials and to rival and prevail over its nazi ally [5].

Synthetic rubber from ethanol

Ethanol could be obtained from the fermentation of carbohydrates, beet sugar or glucose from the hydrolysis of cellulose, moving from a process investigated by Natta [11]. It has been recently reported that "starting from cellulose instead of sugar could make ethanol's climate math much easier" [12].

Natta was convinced of the superiority of synthetic processes: 'you can get what you want, whereas natural products are what they are' [10]. However, already in 1938 he proposed a sort of proto-manifesto of green chemistry: "I do not believe that synthetic processes using coal should be preferred to those that exploit agricultural products... in reality, even farmers can be considered chemical workers, as they oversee the most important organic synthesis known to man, chlorophyll synthesis, in which energy is provided by the sun and the raw materials are water and carbon dioxide" [13].

The use of ethanol as a raw material led to the rubber factory being established in the industrial area of Ferrara, where there were sugar factories and methane gas deposits. The use of ethanol had been already proposed by Ostromyslenski and Lebedev in Russia and the synthesis of butadiene is known as the Lebedev process. Alexander Maximoff, who had worked with Ostromyslenski, became the director of Pirelli's chemical research laboratory.

The reaction consists of successive steps. A decade ago, a new mechanism, alternative to the one accepted for seventy years [6] and shown in Fig. 3a, was demonstrated [6].

Natta recalled [10] the complexity and delicacy of this catalytic reaction and the impressive amount of research (ten years) carried out on a laboratory and industrial scale. The catalyst must have dehydrogenating, dehydrating, and condensing properties. Natta published in 1947 [14] an hystorical paper, the first with the description of the catalysts [7], unknown in the Lebedev process. The catalyst was based on MgO-SiO₂, optionally doped with Cr. With quantitative yields (not achieved in the 1930s and 1940s), two molecules of ethanol should produce one molecule of butadiene, one of hydrogen and two of water. This process and even the low catalyst efficiency led to proto-examples of a bio-refinery. For example, due to excessive dehydration, ethylene was formed, that was indeed used in the plant for the synthesis of styrene. The poor quality of the russian rubber was due to the low chemical purity of butadiene. Natta obtained high purity monomer through a patented extractive distillation technology, where a solvent was added during the distillation of the C₄ mixture, allowing butadiene to be extracted from the bottom and the other components to escape from the

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(a) CH_3CH_2OH \rightarrow CH_3CHO + H_2 (b) 3C + CaO \rightarrow CaC_2 + CO
CH_3CHOHCH_2CHO \rightarrow CH_3CH=CHCHO + H_2O
CH_3CH=CHCH_2OH \rightarrow CH_2=CHCH=CH_2 + H_2O
CH_3CHOHCH_2OH \rightarrow CH_2=CHCH=CH_2 + H_2O
CH_3CHOHCH_3CHO \rightarrow CH_3CHOHCH_3CHO + H_2
CH_3CHOHCH_3CHO \rightarrow HOCH_2CH(OH)CH_3 \rightarrow CH_2=CHCH=CH_2
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Fig. 3 - Mechanisms for the synthesis of butadiene (a) from ethanol (b) from coal

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top [15]. Styrene as comonomer and the emulsion copolymerization led to synthetic rubber with good quality for tyre production. In October 1941, the pilot plant was put into operation in Ferrara, followed by the industrial plant in April 1942, with an annual production of 13 ktonnes. The price of synthetic rubber was twice that of natural rubber: it was the war that motivated its production.

Synthetic rubber from coal

Germany had enough coal and energy to develop the synthesis of butadiene from coal. The mechanism is summarized in Fig. 3b. Acetaldehyde is the common building block with the Lebedev process. From the aldol, butylene glycol was obtained and finally, through dehydration, butadiene, that was polymerized with Natrium to the Buna rubber. In 1937, Pirelli initiated relations with I.G. Farben and a cooperation was established, obviously involving Natta, who visited the German labs. The pilot plant was in operation in Bicocca in 1939, construction of the plant began in Terni in 1940, using german procedures and machinery, near the only Italian plant that produced carbide and the energy source of the thermal springs of Larderello. The plant was almost ready in 1942.

The fate of industrial plants and companies

The evolution of the war led, after the armistice of 8 September, to the withdrawal by the Germans of the equipment from the Terni plant, which never went into operation, and to the bombing by the Allies of the Ferrara plant, which was closed in 1944. However, Alberto Pirelli expressed his pride for the technological achievements [9]: "as participants in its creation, we cannot help but remember with pride the success of the Ferrara plant, as well as the rationality of the unfinished plant in Terni".

From 1944, Natta was board member of Saigs. In 1946, Pirelli and IRI left the world of synthetic rubber transferring the Ferrara and Terni plants to Polymer Industrie Chimiche, a company belonging to the Montecatini Group, which transferred the Ferrara plant to another company (Italia Settentrionale) whose Natta was a board member. Natta in 1951 he was tasked with incorporating the Ferrara plant into another company (Gomma Sintetica) in view of the merger with Montecatini. The Institute, taken

over by Saigs after Pirelli's withdrawal, was transferred to Montecatini as well.

Elastomers made from coal and natural sources had then been replaced by those made from petroleum. Plants had to be converted to the new technologies. The transition of elastomer synthesis from the large rubber industry to the large chemical industry was thus achieved.

Methanol

In the late 1920's Natta worked on the catalytic synthesis of methanol from the water gas. It was highlighted [16] the complexity of the equipments: reactor operating continuously at 300 atm, with CO produced *in situ* using a coal gasifier and electrolytic H₂. It was stated that the Natta's paper of 1930 [17], based on about 500 experimental results, is one of the first published in the world, presenting a scientific approach to the preparation of mixed oxide catalysts. The patented technologies enabled Società Metanolo e Derivati, using coal from Sulcis, to begin industrial production of methanol at its plant in Oschiri, Sardinia, which was transferred in 1931 to Merano, to a Montecatini factory.

In a nutshell

The examples of the cooperation between university groups leaded by Giulio Natta and large industries reveal succesfull models for technology transfer accompanied by innovative and in-depth scientific research. In 1962 (before obtaining the Nobel prize), the achievements of synthetic rubber projects were defined by G. Bosco, Minister of Education, at Accademia dei Lincei, "one of the most beautiful pages of applied research in Italy" [18]. Natta got in contact with Montecatini and laid the foundations for the research that led to the Nobel Prize.

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Università e grande industria per un trasferimento tecnologico di successo

Un recente studio della Banca d'Italia ha evidenziato lo stato critico del trasferimento tecnologico (TT) in Italia e ha affermato che la priorità è rafforzare la componente pubblica della ricerca di base per sostenere l'innovazione privata. La cooperazione tra l'università e una grande industria è un modello di successo per il TT. Qui si riporta la collaborazione tra Giulio Natta e Pirelli per la produzione di gomma sintetica. Natta entrò anche in contatto con Montecatini e gettò le basi per la ricerca che portò al Premio Nobel.



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