The History of the Science and Technology of Electrospinning from 1600 to 1995

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ABSTRACT

This paper outlines the story of the inventions and discoveries that directly relate to the genesis and development of electrostatic production and drawing of fibres: electrospinning. Current interest in the process is due to the ease with which nano-scale fibers can be produced in the laboratory.

In 1600, the first record of the electrostatic attraction of a liquid was observed by William Gilbert. Christian Friedrich Schönbein produced highly nitrated cellulose in 1846. In 1887 Charles Vernon Boys described the process in a paper on nano-fiber manufacture. John Francis Cooley filed the first electrospinning patent in 1900. In 1914 John Zeleny published work on the behaviour of fluid droplets at the end of metal capillaries. His effort began the attempt to mathematically model the behavior of fluids under electrostatic forces. Between 1931 and 1944 Anton Formhals took out at least 22 patents on electrospinning. In 1938, N.D. Rozenblum and I.V. Petryanov-Sokolov generated electrospun fibers, which they developed into filter materials. Between 1964 and 1969 Sir Geoffrey Ingram Taylor produced the beginnings of a theoretical underpinning of electrospinning by mathematically modelling the shape of the (Taylor) cone formed by the fluid droplet under the effect of an electric field. In the early 1990s several research groups (notably that of Reneker who popularised the name electrospinning) demonstrated electrospun nano-fibers. Since 1995, the number of publications about electrospinning has been increasing exponentially every year.

INTRODUCTION

Electrospinning is a dry spinning process that uses electrostatic force to draw fibers from a liquid polymer solution or melt. The process of fiber formation from the liquid is entirely physical, either by loss of solvent or freezing of a melt. The process has recently achieved widespread popularity in the laboratory as a method for the manufacture of continuous nano-scale fibers. There is also a well-established industry using electrospinning to manufacture highly efficient filters.

The history of any particular technology is always difficult to tease out from the general progress of science and civilization. To reduce this paper to manageable dimensions we have limited the story to the inventions and discoveries that directly relate to the genesis and development of electrospinning. The story of the inventions, for example current electricity generation and insulation, without which electrospinning would not have been possible are regretfully neglected. We have briefly covered the early days of electrostatic work, the development of spinnable polymer solutions, and the establishment of a market for artificial fibers. The theoretical background that is now drawn on to explain the process is also covered. During the middle years of the twentieth century there was considerable activity in patenting aspects of the process, which again we have only covered in outline. At the time of writing, the Soviet contribution to the patent history was not available to us, except in summary [1]. In selecting from the wealth of material available to us, milestones in the development of electrospinning were selected by their significance and, to a lesser extent, number of citations. Except where there is a clear contribution from research, we have of necessity not covered the parallel development of the electrospinning industry. It is unfortunate that the considerable body of both research and development work undertaken in the industrial sector, the success of which is measured by the production of industrial quantities of electrospun material, is to a large extent hidden from acknowledgement by its commercial sensitivity[1].

The year 1995 was chosen as a convenient time to finish the story as beyond then, the volume of publications becomes too large to précis in a single publication.

It is commonly supposed that the story of electrospinning starts with the considerable contributions of Anton Formhals in the 1930s. However, the direct history of the industrial process begins thirty years before then with J.F. Cooley, and the description of the process by C.V. Boys ten years previous to that. The science behind the technology of electrospinning predates Newton's laws of motion. The wider story of the process begins with the earliest days of objective scientific investigation, at a time when the more incautious investigator could be burnt at the stake if it was felt that he challenged the current religious orthodoxy.

THE SEVENTEENTH CENTURY

The first record of the electrostatic attraction of a liquid was observed in the time of Queen Elizabeth 1 of England and Ireland by William Gilbert (or Gilberd, or perhaps Gylberd). Gilbert was the personal physician to the queen for the last two years of his life and president of the Royal College of Physicians. He was an early proponent of scientific investigation, opposing the unsupported interpretation of the works of the classical philosophers. He disproved that garlic affected the working of the magnetic compass and that rubbing a magnet with a diamond would reverse its polarity, and demonstrated that magnetic and electrostatic attractions were different phenomena. Observing that amber exerts an attractive force that is not transmitted by movements in the air Gilbert said:

"indeed it plainly does draw the body itself in the case of a spherical drop of water standing on a dry surface; for a piece of amber applied to it at a suitable distance pulls the nearest parts out of their position and draws it up into a cone; otherwise, if it were drawn by means of the air rushing along, the whole drop would have moved"[2]

This is the first record of the deformation of a drop of liquid into what would eventually become known as the Taylor cone. He went on to relate force and distance:

"As far as the effluvia are sent out, so far it allures; but as the body approaches, its motion is accelerated, stronger forces drawing it"

Gilbert died of the Black Death in 1603, his court position obliging him to live in the unsanitary conditions of the city of London. He outlived his royal patron by eight months.

In 1665 Robert Hooke used his compound microscope to examine a number of plant, animal and manufactured origin specimens [3], coining the use of the word "*cell*" for the functional basic unit of life. He suggested that it might be possible to duplicate silk artificially using an unspecified *"artificial glutinous composition"* if only *"very quick ways of drawing it out into small wires for use could be found"*.

THE EIGHTEENTH CENTURY

The emphasis on static electricity, where a substantial triboelectrical charge can be built up by sliding contact between materials such as the traditional fur and amber and then discharged in a momentary flow of a very small current, was to remain until the nineteenth century. In the nineteenth century the development and understanding of the science and technology of current electricity generation had reached a sufficient level to provide inductive generation of high voltages.

George Mathias Bose, professor of natural philosophy at Wittenberg, Germany, and a probable co-inventor of the Leyden Jar[2] wrote "*Recherches sur la cause et sur la véritable théorie de l'électricité*" (Wittenberg, 1745) and described aerosols generated by the application of high electric potentials to drops of fluid [4]. He improved the Von Guericke (he of the Magdeburg hemispheres[3]) triboelectrical static electricity generating machine by the addition of a capacitive charge collector – a glass cylinder suspended on silk cords.

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[1] Following feedback received during the writing of this paper the authors suggest that it is a highly appropriate time to draw together the story of those involved in the commercial development of electrospinning, perhaps through the pages of this journal.

[2] An early device for electrical charge storage consisting of an insulating jar coated on the inner and outer surfaces with a conducting foil.

[3] The Magdeburg hemispheres were 500 mm diameter hollow copper hemispheres that were evacuated by pump to low internal air pressure. In Von Guericke's original demonstration, teams of horses were unable to pull the hemispheres apart, although it has been noted that horses show little enthusiasm to pull against a stationary load.

Bose, somewhat of a showman, demonstrated his apparatus by standing a female subject on an insulating platform, charging her up and inviting a man from the audience to kiss her, and consequently both parties received a static shock through the lips. An inventive publicist, he held electrical feasts with static discharges flickering across the table and published his results as poems [5]. He also managed to convey a charge through a six foot jet of water, determining the presence of the charge by shocking one of his luckless assistants with it [6]. Evidently a scientist in demand, he was kidnapped from Wittenberg as a strategic asset during the Seven Years War with Prussia and died two years later, still held hostage at Magdeburg.

Giovanni Battista Beccaria published "*D'ell Electrismo Naturale et Artificiale*" in 1753; the work was translated into English in 1776. Morton [7] noted that Beccaria had observed that a charged fluid evaporated faster than an uncharged one

THE NINETEENTH CENTURY

Manchester silk manufacturer Louis Schwabe (he made the silk for Queen Victoria's wedding dress) invented the extrusion spinneret. His test material was glass, and he spun the fibers to make demonstration pieces of Williams and Sowerby's glass damask which was exhibited at the Manchester Mechanics Institute in 1840 [8].

In June 1842, Schwabe was reported in the *Manchester Courier* as asking for the assistance of the British Association in:

"carrying out experiments which would lead to the discovery of a substance which would form a homogeneous mass possessing the quality of ductility and susceptible of being drawn out through fine holes, or otherwise, into filaments or fibres possessing suitable strength and other properties to adapt it for manufacturing purposes."[9]

Schwabe's effort to produce artificial fibers ended unhappily with his protracted suicide via a draught of sulfuric acid in 1845.

It is unfortunate that a suitable candidate material, nitrocellulose, was discovered only a year later by Christian Friedrich Schönbein. It is said [10] that whilst distilling nitric and sulfuric acids in his kitchen, he spilt his reaction mixture and mopped it up with a cotton apron. Schönbein, an "*energetic, quick-moving, short, stout and eminently friendly man*", was professor of chemistry at the University of Basel at the time, so it is not clear why he should have been doing such a thing in his kitchen. Nevertheless, clearly a tidy soul, and doubtless not wanting to vex Frau Schönbein, he washed the apron, and hung it up to dry above the stove. The nitration process had clearly proceeded to a much greater extent (probably about 13% nitrogen as nitrate) than had previously been observed due to the catalysing presence of sulfuric acid. The sulfuric acid also mops up the water produced by nitration, which would otherwise limit the extent of the reaction [11]. The result was that the apron exploded, leaving negligible solid residue or smoke. Schönbein, realising the potential of this material as a smoke-free explosive alternative to gunpowder rushed to patent rather than publish, and was able to demonstrate his new explosive *schießbaumwolle* ("*guncotton*") by rock blasting at Istein, Germany, in July 1846.

Schönbein's patents provoked a Europe-wide effort to duplicate his material, and presumably work around his patents. In the same year, workers in the laboratory of chemist Prof. Théophile Pelouze – the first worker to nitrate cellulose, but not to the same degree of nitration and hence explosivity as Schönbein – were well advanced in the race. Pelouze employed an aspiring revolutionary poet (author of *Le Prologue de Revolution* and translator of *Promethee delivri* amongst others) Louis-Nicolas Ménard. Ménard devised a mixture of ether (ethoxyethane) as the solvent and ethanol as a diluent that rendered cellulose nitrate into clear gelatinous liquid [10]. That liquid was dubbed "collodion" (from the Latin *collodium* meaning glutinous). Ménard then quit the laboratory forever to become a poet, artist, academic, and political activist. Collodion was used by early photographers as a medium for light active chemicals, and therefore due to the wide popularity of photography, was readily available to the pioneers of electrospinning.

In 1855 George Audemars of Lausanne, Switzerland, patented a method for spinning collodion – extracted from cellulose from mulberry (*Morus alba*) trees. This wood was perhaps selected because it forms the foodstuff for the mulberry silkworm, *Bombyx mori*. At this time silk was an expensive luxury and, as now, there was a clear market for cheaper substitute materials. Audemars' first experiments simply dipped a needle into his solution, and drew it out, pulling a long thread of rapidly hardening collodion behind it [12]. This method was time consuming and produced a product that, being essentially guncotton, was really far too inflammable for use in clothing.

Later on, in 1873 Joseph Antoine Ferdinand Plateau at the University of Ghent advanced the understanding of the behaviour of columns of liquid by describing [13] observations of the breakup of columns of molten iron and mercury. The iron was in the form of wire, which he melted by passing electric current through it, forming molten metal spherical blobs. He extended these observations by constructing an apparatus that enabled him to construct a "wire" of liquid mercury caught between two straight edges. Simultaneous removal of the straight edges caused similar behaviour. He was able to formulate a rule that if the length of the column was more that 3.13 to 3.18 times its diameter then the column would break up into droplets. John William Strutt, more widely known by his inherited title of Lord Rayleigh, acknowledged the insights into the phenomenon from Plateau's work when he published a theoretical model of column breakup [14], showing experimentally using stroboscopic illumination [15] that a column of liquid will break up into droplets when its length exceeds its circumference. Rayleigh gained a Nobel laureate for his co-discovery of Argon, and produced a satisfactory explanation of why the sky is blue. He also conducted some experiments on the stability of electrically charged water drops [16], calculating a theoretical charge to cause a droplet of a certain size to burst. He also worked on explaining the observation that a moderate electrical charge will increase the stability of an ascending jet of water, and that when the charge is increased above some critical level, then the stability is decreased [17].

Comte Louis-Marie Hilaire Bernigaud de Chardonnet, also known as Hilaire de Chardonnet, was working on his ancestral estates at Besançon, France, at the behest of Louis Pasteur to investigate the problems in the silk industry caused by the pébrine parasite[4]. Clearly an independent spirit, Chardonnet spent considerable effort examining the biochemistry of the mulberry tree and the method by which the silkworm produced its thread. He felt that the process could be duplicated artificially and devised a process to extrude collodion through a glass capillary. He took the process a step further and used Joseph Swann's ammonium sulphide technique to reduce the flammability of his material, [10] which was exhibited at the Paris Exposition Universelle of 1889. The process proved difficult to scale up, but was used to produce haberdashery trimmings until the last Chardonnet silk factory (in Brazil) burnt down in 1949 [12].

Charles Vernon Boys was a physicist and talented instrument maker. In 1888, he designed and constructed an improved torsion balance to measure the universal gravitational constant, and in passing, the density of the Earth, a matter he considered as being purely of local interest [18]. The torsion balance needed a reliable and stable suspension fiber. Boys considered using *"the old, but little known-experiment of electrical spinning"*. Boys' apparatus consisted of "*a small dish, insulated and connected with an electrical machine*" [19]. He found that as his stock liquid reached the edge of the dish, that he could draw fibers from a number of melts including shellac, beeswax, sealing-wax, gutta-percha and collodion. He observed and was able to control, by means of melt temperature, the formation of beaded threads. However, his electrospun fibers did not have the mechanical properties required for his torsion balance, and he finally selected fused quartz as an appropriate material. This material was not suited to electrospinning, and so he devised a method of drawing a fiber which involved fastening a fragment of fused quartz to a crossbow bolt, heating the fragment, and firing the crossbow. The resulting fiber was wound on to a wooden former. He achieved quartz fiber lengths of up to 90ft (about 27 metres) and thicknesses estimated to be less than $^{1}/_{100,000}$ inch (254 nm), and certainly below the resolution of any available optical microscope.

Meanwhile, in 1892 at the Jodrell Laboratories in Kew, London, Charles F. Cross and Edward J. Bevan were working as consultants to the cloth industry, looking into the process of Mercerizing – a caustic treatment to improve the lustre of cotton thread. They treated cellulose with sodium hydroxide and carbon disulfide to produce cellulose xanthate and then regenerated the materials by coagulation in sulfuric acid [20]. The first attempt at commercialising the material was as a moulding compound dubbed "Viscoid". Further development by Charles Topham Jnr. added a chemical step allowing the viscose solution to "ripen" by leaving it to stand. He also invented the Topham Box, enabling a fiber (known as "Viscose") to be collected on a bobbin. These names both came from the highly viscous nature of the raw material solution. By the 1920s this regenerated cellulose fiber, renamed Rayon in the USA, was a widely used textile, firmly establishing the market for artificial fibers.

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[4] A disease of silkworms caused by a parasitic infestation by the microorganism *Nosema bombycis*, which was causing severe problems in the French silk industry.

THE TWENTIETH CENTURY

John Francis Cooley, originally of Penn Yan, New York, was a professional inventor and an electrician. His inventions include a rotary steam engine or pump – a progenitor of the rotating cycle later used in the Wankel engine, and an over-ambitious attempt to build a flying machine at Rochester, New York. Only seven years after the Wright brothers, Cooley's machine was over 80 ft (24 m) long with a 42 ft (12 m) wing span and required a crew of two. It never left the ground and was finally seized by court order in respect of an unpaid grocery bill.

Cooley filed the first electrospinning patent [21] in which he proposed four types of indirectly charged spinning heads – a conventional head, a coaxial head, an air assisted model, and a spinneret featuring a rotating distributor. He also proposed the recovery of solvent and the use of a dielectric liquid instead of a gas as the medium. His three electrospinning patents used a Wimshurst type influence generator. He used pyroxylin (nitrocellulose) in ether as his test material, and used his co-axial head to introduce benzole (a mixture of benzene and toluene) onto the outside of the fiber, presumably to stop the premature evaporation of the ether from clogging the nozzle.

William James Morton was the son of James W. Morton, who was a pioneer of anæsthesia [22]. A graduate of Harvard medical school, Morton became a professor of electrotherapeutics and used, as part of his electrical arsenal, X-rays to both diagnose and treat ailments such as alopecia and cancer. His high voltage source was described [23] as *"a Crocker-Wheeler quarter horse power motor with a make-and-break attachment connected with the street arc light wires, a Rhumkorff coil with a four-and-a-half inch spark, a cabinet for tests in opacity and Crookes tubes of various patterns"*. No mention is made as to how Dr. Morton came to an agreement with the electricity company to run his apparatus from the street lamp circuit, but the length of the spark indicates that this induction coil apparatus was capable of producing about 110 kV. His 1902 patent [7] is bolstered by references to obscure publications – a French version of a bibliography published in New York [24], as well as earlier scientists [25] – but is very light on practical details, describing a sort of separating funnel allowing a stream of liquid collodion or pyroxylin (presumably in an ether-ethanol solvent-diluent mixture) to fall in front of a ball-shaped anode and variously a chain, or a reel to collect the fiber as a "*cobweb-like mass*" which ultimately "*may be put to any industrial use*".

In 1912 W.B. Wiegand and B.F. Burton published a paper on the effect of electricity on streams of water drops [26] examining the relationship between surface tension and charge. They note that by using a triboelectrically charged ebonite paddle, "*during the process of atomization, one may observe the formation of a fine jet of liquid*". Burton went on to be a pioneer in electron microscopy, and Wiegand proposed the role of nano-scale particulate carbon black as a reinforcing material.

John Zeleny was a physicist working at the University of Minnesota. He invented an electroscope to measure electric charge, and between 1907 and 1920 published a sequence of papers on electrical discharge from solid and liquid surfaces. He started by quantifying the effect of the shape of a pointed cylindrical electrode and atmosphere (pressure, temperature and humidity) on the discharge current [27] concluding that the diameter of the electrode was the principle factor, rather than the shape of the end. He extended this work to look at the effect of humidity [28] noting that the potential needed to produce a given current flow tends to increase with humidity. He [29] further investigated the discharge from points noting that positive polarity of discharge tended to oxidise the ends of his steel needles to a greater extent than negative polarity, and that a sharp point needed a higher voltage to initiate discharge than a blunt cylinder of equivalent diameter. By 1914 he had started to concern himself with discharges from liquid surfaces [30]. He used a hemispherical drop on the end of a capillary tube, noting the tendency of the hemisphere to distort at high voltage. He used a similar apparatus to observe the flight of liquid drops from the meniscus [31], and then to photograph a fine (4 µm) stream of liquid issuing from the capillary [32]. He also noted the lag between the application of the electromotive force and the reaction of the meniscus [33]. His work on the behaviour of fluid droplets at the end of metal capillaries began the attempt to mathematically model the behaviour of fluids under electrostatic forces.

Professor Kiyohiko Hagiwara of the Imperial University of Kyoto originally graduated in mechanical engineering in 1900 [34]. Prof. Hagiwara worked on silk [35] and artificial fibres. He used electricity to orientate the molecular structure of colloidal liquid Viscose precursor prior to spinning [36] producing what he called a "*lineal or fibrous sol*" noting that this type of sol is similar to the "*stäbchen*" or "rod" sols described in 1923 by Andor

Szegvári and Emmy Schalek in the Kaiser-Wilhelm-Institut für Physikalische Chemie und Elektrochemie at Berlin-Dahlem. By subjecting his Viscose solution to a high frequency electrical discharge as it trickled through a low pressure inert gas discharge tube Hagiwara caused the colloidal components to align and retain this alignment to then stick together. The increased degree of molecular orientation produces a conventionally spun fiber "*free of irregular aggregation of the particles*" and with improved lustre. Hagiwara also ran through his apparatus various other forms of cellulose (including nitrocellulose, and cellulose acetate), gelatine, albumen and a natural silk solution.

Hagiwara [37] [38] extended the process by using an 80 Hz oscillating current. The electrostatic force was used in conjunction with air pressure to increase spinning speed and increase fiber thickness. Hagiwara claimed a side benefit of his process was that ozone evolved as the fiber loses charge in flight decomposes the hydrogen sulphide produced in the coagulation bath to such an extent that special ventilation to protect process workers is not required. This ozone formation provides the first evidence of loss of charge in flight. His 1929 American patent is assigned to Toshiya Iwasaki, founder of Asahi Glass, a member of the Mitsubishi zaibatsu.

W.A. Macky was a meteorologist in New Zealand [39], and as such became interested in the effect of strong electrical fields on the deformation of water drops in flight [40]. His observations were made with the objective of understanding the maximum field strength that can be found inside a thunder cloud. In the course of his observations he noted that filaments of fluid were drawn from his experimental drops, and that this phenomenon is a limiting factor of droplet size within a thundercloud or other strong electric field. His results indicate that for a breaking drop, the flow of current is due to ionised gas or vapour particles rather than the flight of charged liquid particles.

Anton Formhals made significant contributions to the development of electrospinning through his sequence of 22 patents on aspects of the process taken out in America, France, the United Kingdom and Germany between 1931 and 1944. Dipl. Ing Ludwig Rudolph Anton Formhals was born in Mainz on 24th August, 1877. He was a son of Friedrich August Ludwig Karl Formhals (1844–1921) and Maria Elisabetha Formhals, *née* Grünewald (1850–1918). He lived at Wallaustraße 3, where his father had a "*Technisches Geschäft und Eisenwaren*" (an engineering and ironmongery shop). He did some of his research whilst working for the Verein für Chemische Industrie AG, a company making charcoal and organic chemicals, with a head office in Frankfurt. The company was taken over in 1930 or 31 by the company that is now Degussa-Hüls AG[5]. He died in Mainz (Weintorstraße 12) on 28th November 1956.

There is a degree of cross-over and duplication between his patents, as he sought to maximise the protection of his inventions. The Second World War clearly presented a significant obstacle to the commercialisation of his work – his last American patent in 1944 is vested in the Alien Property Custodian. Formhals clearly intended to gather up the fibers for conversion into yarn or staples for further processing – a technical challenge at least equal to that of producing the fibers in the first place. Formhals' first developments [41] describe a machine design based on a saw-toothed rotating fiber emitter. The emitter resembles a circular saw blade and dips into a trough of the spinnable liquid. Charge concentration at the wetted tooth tips causes fibers to be evolved and to fly off towards roller or rotating disc targets. Formhals suggests that the spun fiber can be passed through a coagulating bath if required.

By 1937, he had turned his attention to nozzle design [42] observing that nozzles made by drilling a plain parallel sided hole were prone to blocking. Formhals' design has a conical taper and can be disassembled for ease of cleaning.

His next designs [43] were constructed to produce controlled shorter fiber lengths. This was achieved by interrupting the current flow to the machine's multiple spinning heads. In this case the individual spinnerets were fed from a manifold kept at a constant pressure by a header tank. The fiber was collected on a slatted belt. This design was further refined [44] by the addition of a rotating notched disc counter electrode meshing with the slatted belt to provide more effective removal of the spun fibers from the belt.

A year later Formhals [45] was seeking to control fibers in flight by manipulating the electrical field. His design projects the fiber strand between two parallel wire electrodes that are connected to an alternating supply of up to 100 kV. The variation in electrostatic field resulting from this set up caused the fiber to be deposited in hanks. Formhals also

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[5] http://history.evonik.com/sites/geschichte/en/chemicals/history/degussa/pages/default.aspx accessed on 20th June 2010

proposed co-spinning of fibers with opposite charges to produce a product with no net charge [46], and made serious efforts to devise winding devices to gather up the fiber in a usable form [47] [48].

Charles Ladd Norton was a polymath physicist who was initially educated as an electrical engineer. He worked early in his research career in a group led by Dr Francis Williams at Boston City Hospital using the new Röntgen (X-) rays for medical diagnosis. He would have no doubt gained experience in using high voltage sources to power the Crookes tube used as an X-ray source [49]. His 1936 patent describes melt-spinning using a combined electrostatic (100 kV) and air-jet assist method [50]. He also used deflector plates running at about 2 kV AC, to decrease the regularity of deposition and make the lofted fibers more suitable for insulation or packing. The air blast assist let him use targets up to 20 ft (6 m) away from the point of emission, and the patent notes that the air stream would also remove charge from the product, improving the rate of deposition. Norton's patent is the first to describe melt electrospinning, the use of a means other than electrostatic to generate the initial fiber strand, and the use of auxiliary electrodes to influence the flight path of the fiber. Norton took an interest in the development of fibrous materials to produce fire-proof asbestos roofing shingles and wall boards. It is interesting to note the parallel development described in Games Slayter's 1938 patent for glass fibre production [51], where Slayter describes the formation of glass wool from a melt by an air blast. Slayter's glass wool was commercialised by the Owens-Corning Fiberglas® Corporation, and widely used for fire proof insulation in naval ships. Predating both handsomely is the manufacture of "slag wool" by blowing steam across furnace slag first described in the nineteenth century, and natural formation of basalt fibers known as Pele's hair when the wind blows over molten volcanic lava.

In the late 1930s Nikolai Albertowich Fuchs, at his Aerosol Laboratory in the L. Ya Karpov Institute in the USSR, advanced a theory of ultrafine fibrous materials [52]. However, in 1937 Fuchs was denounced by one of his technicians and arrested. Initially sentenced to 5 years hard labor for counter revolutionary agitation (quoting lines from the poet Pushkin), he was not finally rehabilitated and able to rejoin the institute until 1959 [53]. In 1938 his co-workers Igor' Vasil'evich Petryanov-Sokolov and Natalya D Rosenblum generated electrospun fibres, which they developed into filter materials known eventually as "*Petryanov filters*" – for this work they were awarded the Stalin Prize. Unfortunately, even this honor was not sufficient to prevent Rosenblum from being liquidated[6] [53]. Their work rapidly led to the establishment of a factory in Tver' for the manufacture of electrospun smoke filter elements for gas masks. The material, dubbed BF (Battlefield Filter), was spun from cellulose acetate in a solvent mixture of dichloroethane and ethanol [1]. In the early 1950s the "*Lepestok*" ("*Petal*") particulate filter mask using a Petryanov filter was devised for use in the nuclear industry. The five billionth *Lepestok* unit was manufactured in 2003 [54]. By the 1960s output of spun filtration material was claimed as 20 million m^2 per annum. Russian practice in electrospinning was characterised by the acknowledgement of the Taylor cone as being the rate limiting step in the process. The spinnable material was pumped through the spinneret by force, and an exceptionally high (100 kV) charging voltage applied. The stream of liquid then bifurcates in flight. This leads to a high volume throughput [1].

In 1952 Bernard Vonnegut[7] and Raymond L. Neubauer [55] investigated the production of liquid jets by electrostatic force. They noted the formation of uniform sized droplets and made an estimate of the size of the droplets (about 1 µm) from the observation of the rainbow colors of high order Tyndall spectra in the droplet cloud. They also noted that two like charged droplet clouds would repel each other – the origin of the "tramline" effect often observed in multiple spinning head devices.

Three years later, Vadim Drozin at Columbia University, New York, USA, [56] also examined the formation of streams and droplets by electrostatic force, relating the electrostatic force required to the dielectric constant of the fluid and the radius of curvature of the fluid droplet. He measured limits of operation in terms of specific conductivity, dipole moment and refractive index.

Sir Geoffrey Ingram Taylor started his working life charting icebergs in the north Atlantic following the sinking of the RMS Titanic. In the Great War he worked on the practical development of parachutes. He went on to invent the CQR small boat anchor and was involved in the Manhattan Project and the development of supersonic aeroplanes. In his later years, between 1964 and 1969, he produced a significant advance in the theoretical underpinning of electrospinning. Taylor's work contributed to

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[6] Although there are a number of publications from Russia on polymer research by an N.D. Rozenblyum appearing into the 1970s.

[7] Brother of Kurt Vonnegut, the science fiction writer.

electrospinning by mathematically modelling the shape of the cone formed by the fluid droplet under the influence of an electric field [57]; this characteristic droplet shape is now known as the Taylor cone. He further worked with J.R. Melcher [58] to develop the "*leaky dielectric model*" for conducting fluids.

Peter Karl Baumgarten was born in Vienna in 1926, and came to the USA in 1940, where he worked for E. I. du Pont Nemours & Co. In 1971 he devised a method of photographing electrospun fibers in flight, and in the course of investigating the effect of solution viscosity, surrounding gas, voltage and jet radius on fiber diameter and jet length [59] described the electrospinning process as follows *"Although the spinning process appears as a hazy cloud, micro-second flash pictures proved that only a single fiber is spun at a time and that the filament forms many loops which fall to the electrical ground"*.

In 1981 Larrondo and St. John Manley [60] constructed a melt electrospinner similar in principle of operation to a melt flow index device[8]. A static weight was applied to a piston running in a heated barrel to produce a drop of polymer melt at the spinning tip, and a fiber was drawn from the drop by electrostatic force. The apparatus was used to examine the flow regime of fiber formation by means of the addition of tracer particles to the polymer melt, finding that there is a rotational, as well as extensional, element to the flow of the jet, and that the extensional strain rate increases applied electric field intensity. Using polyethylene and Nylon 12 as test materials they were able to match observations of the deformation of polymer melt drops to a model of performance based on the consideration of the behaviour of a pendant spherical droplet.

In the early 1990s several research groups (notably that of Reneker, [61] who popularised the name electrospinning for the process) demonstrated that many organic polymers could be electrospun into nano-fibres. Since then, the number of publications about electrospinning has been increasing exponentially every year.

CONCLUSION

Like most technological advances, electrospinning was not devised in a few years as the result of direction provided by clear demands from business of the research community. Scientists, engineers and entrepreneurs worked independently towards the general and sometimes overlapping aims of advancing knowledge and making money. The work undertaken by these savants and industrialists provided both theoretical and practical underpinnings for the invention of the process of electrospinning as we know it. At the end of the nineteenth century, both the technological ingredients (high voltage power supplies and soluble polymers), and the commercial drivers (the potential of the emerging artificial fibers industry) were in place to allow the "invention" of the process to take place. It was not until the last half of the twentieth century that the craftsman's empiricism and the scholar's systematic thought [62] were brought together to continue and accelerate development of the electrospinning process.

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