MATERIALS SCIENCE AND TECHNOLOGY NEWSLETTER

Vol. 9, No. 1 WINTER-SPRING, 2013

Dr. Robert H. Lacombe
Chairman
Materials Science and Technology
CONFERENCES, LLC
3 Hammer Drive
Hopewell Junction, NY 12533-6124
Tel. 845-897-1654, 845-227-7026
FAX 212-656-1016
E-mail: rhlacombe@compuserve.com

POLYMER SURFACE MODIFICATION WITH PLASMAS

EDITORIAL COMMENTS

MST's sequence of symposia for 2013 picks up where we left off in 2011 with the continuation of the POLYMER SURFACE MODIFICATION and SILANE COUPLING AGENT symposia. This year the symposia will be held at Lehigh University in collaboration with the Center for Polymer Science and Engineering at Lehigh. There has been very active interest in both of these topics both from the point of view of academic research and industrial applications and we expect a strong turnout for both of these meetings. Full details of these meetings are available on the conference website at:

www.mstconf.com/surfmod9.htm

www.mstconf.com/silanes9.htm

In addition to the June symposia MST is also offering another presentation of the increasingly popular short course on the CHEMISTRY, PHYSICS AND MECHANICS OF ADHESION SCIENCE. The course will be given again at the Marriott hotel in Newburgh New York located in the scenic Hudson Valley. This course is quite likely the most comprehensive presentation of the multifarious aspects of adhesion science available, ranging from the fundamentals of molecular interactions to the contact angle behavior of liquids and the adhesion stability of all manner of coating and laminate structures. Details of the course offering are again given on the conference website at:

www.mstconf.com/AdhesionCourse.htm

SHORT HISTORY OF PLASMA PHENOMENA

Geissler, Crooks and the Advent of Plasma Processing

Getting back to the topic of polymer surface modification, though the June symposium at Lehigh will cover all aspects of this topic by far the most active area of research and application is the use of plasma technology to modify polymer surfaces. Indeed, with the advent of atmospheric plasmas, this technology has expanded rapidly with applications to coating technology, surface cleaning and even biomedical uses. Thus the editorial essay of this issue will look into the history of plasmas and the evolution of plasmas from scientific curiosities to full fledged applications in industry.

The Early Years

The story apparently begins in 1857 with a novel invention by Heinrich Geissler which was essentially a cylindrical glass tube containing a gas mixture and having electrodes at either end. If a high voltage was applied to the electrodes the gas would light up in a variety of psychedelic patterns glowing in a variety of colors depending on the precise composition of the gas mixture which could contain any number of elements such as argon, neon, xenon, sodium ...etc. Though used mainly as a source of amusement in the late 19th century the Geissler tube had a significant impact on a variety of modern inventions such as flash lamps, x-ray tubes, neon signs and fluorescent lamps to name just a few. Figure (1) displays a sampling of these devices.

The gas pressure in the Geissler tube was relatively high on the order of 0.001 atm so the mean free path of the free electrons which were generated by the high voltage was fairly short and they would quickly collide with other elements in the gas mixture causing them to emit the various light patterns which were observed. Thus the Geissler tube was limited to giving off a diffuse glow as part of a slow diffusion process as the emitted electrons made their way from one electrode to the other.

Moving later into the 19th century by about 1870 William Crooks, working with superior vacuum equipment, got the tube pressure down to about 10^{-6} atm so that the mean free path of the electrons generated by the high extended to the entire length of the tube. In 1869 Johan Hittorf was apparently the first to recognize that something was apparently being emitted from the cathode and was able to travel the entire length of the tube in a straight line. In 1876 Eugen Goldstein was able to prove that what Hittorf was describing were indeed emitted from the cathode and thus they became known as

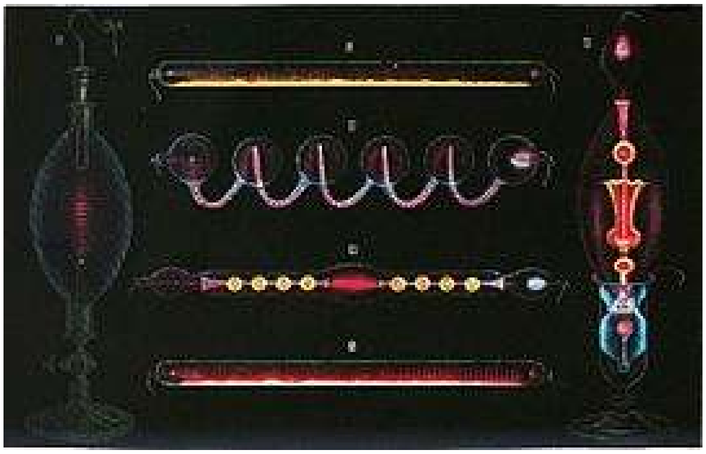

Figure 1: Various Geissler tubes: One of the earliest manifestations of man made plasmas from the mid 19th century. Used mainly for amusement or decoration the Geissler tube lead to a number of important later inventions based on plasmas such as fluorescent lighting and flashlamps.

cathode rays. As with the Geissler tube the early Crooks tubes were mainly used for decoration or amusement. However, in 1895 while experimenting with a Crooks tube, Wilhem Röntgen noticed that unexposed photographic film would be darkened if brought to the vicinity of an operating tube even with substantial barriers of wood, paper or other materials shielding the film from the tube. These experiments eventually led Röntgen to the discovery of X-rays for which he was awarde the Nobel Prize in 1901. Speculation on the precise nature of the entity that was being emitted by the cathode continued into the early 20th century till J. J. Thompson demonstrated by measuring their mass that what was being emitted were charged particles. Thompson was awarded the Nobel prize in 1906 for the discovery of what we today call the electron.

Developing an Understanding, Early Work of Langmuir

Thus by the early 20th century much of the groundwork leading to the discovery of plasmas was in place and it was left to Irving Langmuir to coin the term “plasma” in 1928. Langmuir made great strides in our understanding of plasmas by inventing the Langmuir probe which could be used to measure both the temperature and density of plasmas. Langmuir also apparently came up with one of the first practical applications by using atomic hydrogen to make plasma welds.

By the mid 20th century the nature of plasmas was coming into focus and they were being discovered in a number of natural phenomena such as lightning, auroras, corona discharges and even in astronomical entities such as Supernovas.

Even though the basic nature of all plasmas can be understood as the behavior of a gas of ionized particles attempts to understand their behavior through the use of mathematical models based on the field theories of modern physics have meet with decidedly mixed results. Although the underlying equations governing plasmas are relatively simple, plasma behavior is extraordinarily varied and subtle: the emergence of unexpected behavior from a simple model is a typical feature of what are known as chaotic systems. Such systems lie in some sense on the boundary between ordered and disordered behavior and cannot typically be described either by simple, smooth, mathematical functions, or by pure randomness. The spontaneous formation of interesting spatial features on a wide range of length scales is one of the resulting manifestations of plasma complexity. The features of plasmas can be quite intricate and subtle. For example, a number of features can be very sharp and also spatially intermittent meaning that the distance between features is much larger than the features themselves. This type of behavior is the hallmark of what mathematicians have come to call random fractal behavior. This kind of behavior was initially expounded upon by Benoit Mandelbrot who coined the term fractal as a kind of exotically rough entity. Mandelbrot demonstrated that random fractal behavior also characterizes other complex systems such as stock market prices and weather patterns. Indeed plasmas seem to contain all of the features of random fractal behavior and furthermore tend to exhibit a devilish hierarchy of instabilities as one tries to increase the density and temperature of a plasma constrained by a magnetic field. A direct practical consequence of this behavior is our inability to create plasmas dense enough and hot enough to promote sustained nuclear fusion as it occurs commonly in the sun.

Figure 2 Typical Crooks tube showing fluorescent pattern at end of tube caused by impact of electrons on the glass surface. The sharp outline of the obstructing object indicated that something was traveling in a straight line from the cathode to the anode which were initially called cathode rays.

Large Scale Industrial Applications: The Microelectronics Industry and Beyond

Although our theoretical understanding of plasma phenomena leaves much to be desired, this has not greatly stood in the way of a number of practical applications which were implemented starting roughly in the early 1960s. The microelectronics industry in particular was instrumental in launching plasma technology into the later half of the 20th century. Plasmas were found to be very handy in cleaning substrates, depositing films and in etching patterns in already deposited coatings. Photolithography technology in particular benefitted greatly from the use of plasmas to etch fine patterns in photoresists replacing the old style chemical etchants and replacing them with an "all dry" process. The main advantage plasma processing introduced was the ability to process delicate microcircuit devices in an ultra clean vacuum environment thus also avoiding the need to use and dispose of dangerous chemical solvents which posed a hazard to both workers and the general environment.

Beyond the microelectronics industry, other companies found another important use for plasmas beyond the common substrate cleaning, film deposition and etching of deposited films. This was the ability of plasmas to modify the surface of polymers to enhance their wettability and adhesion to inks, dyes, metals and other polymers. This now brings up the whole topic of polymer surface modification which is the primary focuses of the June 2013 POLYMER SURFACE MODIFICATION symposium mentioned above.

The use of low pressure plasmas for polymer surface modification up to 1994 has been critically reviewed by Liston et al[1]. These authors point out that the main problem with most polymers is the fact that they are low surface energy materials and thus very difficult to decorate or label with commonly available inks or dyes. Thus polymer films are handy for packaging all manner of food stuffs but labeling the container becomes a problem if no ink or dye will wet the polymer surface. Try to write with a pen on nearly any plastic surface and if any mark is made at all it will be found to easily smear or wipe off with the simple swipe of a finger. Special pens are required to write on plastics. The ink in these pens incorporate special solvents that attack the plastic surface in effect solubilizing it locally so that it will accept a dye coating. With plasma treatment, however, the active species in the plasma attack the polymer surface and create active sites such as free radicals which then react readily with nearly any coating material. A further benefit of the plasma treatment is that it affects only the surface leaving the bulk properties of the polymer intact. Thus all the desirable properties of the polymer are preserved such as low cost, ease of fabrication and molding into desirable shapes, low density, flexibility ... etc.

The main drawback of plasma treatment, however, was the need to operate in vacuum. This greatly limited the size of objects which could be conveniently treated and also required the use of cumbersome and costly vacuum chambers and supporting equipment. However, in the early 21st century even this inconvenient obstacle has been overcome with the advent of Atmospheric Pressure Plasmas.

Atmospheric Plasma Jets

The basic operation of plasma jet technology involves the use of a high-voltage discharge (Between 5 and 15 kV in the frequency range of 10 to 100 kHz) to create a pulsed electric arc in an enclosed chamber. A process gas is then allowed to flow through the discharge section thereby being excited into the plasma state. This plasma then passes through a jet head to arrive on the surface of the material to be treated. The jet head is carefully designed to determine the geometry of the exiting plasma stream and is also kept grounded to avoid uncontrolled charge buildup which could cause instabilities in the flow. Depending on the power of the jet and many other parameters the length and width of the beam can be tailored to a large variety of applications.

Even sheet materials having treatment widths of several meters can be treated today by aligning a large number of jets in a row[2]. In doing so the modification of the surface achieved by plasma jets is comparable to the effects obtained with the low-pressure plasma systems mentioned above.

Figure 3 Typical automotive dashboard panel with buttons and switches that must endure many years of poking and handling by both clean and dirty fingers without significant loss of surface finish or imprint readability. (Photo courtesy of Plasmatreat GmbH)

---

[1] "Plasma surface modification of polymers for improved adhesion: a critical review", E. M. Liston, L. Martinu and M. R. Wertheimer, in PLASMA SURFACE MODIFICATION OF POLYMERS: RELEVANCE TO ADHESION, Eds. M. Strobel, C. S. Lyons and K. L. Mitttal (VSP, Utrecht, The Netherlands, 1994) p.3.

[2] See for example the Winter-Spring issue of the newsletter:

www.mstconf.com/Vol4No1-2007.pdf

page 2. "Large Scale Plasma Treatment of Polypropylene"

The key advantage of the atmospheric plasma jet is that by avoiding the use of cumbersome vacuum hardware it can be easily installed without any difficulty in existing production systems. Atmospheric plasma jets are also quite versatile and can be used to coat anti-corrosive layers and adhesion promoter layers without the use of solvents and hence in a environmentally friendly manner.

Plasma jets in the auto industry[3]

The automotive industry provides an illuminating example of the application of plasma jet technology to what would normally be considered the rather prosaic problem of ensuring the durability of automobile dashboard buttons and switches as illustrated by figure (3). The BMW company, for example, requires the paint used for rotary switches to be sufficiently wear-resistant to withstand being turned through 360° no less than sixty thousand times before the paint shows any signs of damage. Standard pushbutton switches, such as are found compact disk units or climate controls, must be able to withstand at least a hundred thousand touches. This corresponds to an assumed usage over a 17 year period –which is regarded by the manufacturer as the total life cycle of the vehicle.

A global supplier of the automotive industry[4] initially tried conventional approaches to cleaning these parts such as power washing with detergent and water or cleaning with CO_2 snow pellets. In both of these cases the small, light buttons and switches tended to be blasted out of their jig molds causing scratching and the molds also tended to trap water. The use of CO_2 also caused parts to be blasted out of their molds and in addition incurred an expense problem due to the extra space required by the gas holding tanks. It became apparent that the traditional technologies were clearly more suited to the treatment of large heavy parts than to the relatively light dashboard buttons and switches. In addition, however, even after successful cleaning, the plastic surfaces had to be somehow activated in order to receive a paint coating since nearly all plastic materials have very low surface energies and are thus difficult to coat with common inks and paints.

Figure 4 Row of 6 rotary plasma jet nozzles capable of surface treating up to 180,000 small plastic knobs and switches per week. (Photo courtesy Plasmatreat)

In light of the above discussion it is clear that the use of plasma jet technology proved to be a godsend for this particular cleaning operation for not only could the delicate parts be easily cleaned but their surface energy would be increased by the plasma action also so that they would be able to receive a coating directly without any further process steps. The result of the suppliers implementation[4] of plasma jet technology was that by the Spring of 2011 a new 25 m long painting line – in which the plasma system takes up only a meter – was up and running. Six patented rotary nozzles (Plasmatreat North America) have since been working in-line around the clock examples of which are shown in figure (4). Each week they clean and activate around 180,000 visible parts made from PolyCarbonate or a PolyCarbonate + Acrylonitrile Butadiene Styrene blend material prior to painting. Parts ranging from simple 2-D components to complex 3-D geometries such as steering wheel covers are treated with equal ease. Thus we see that plasmas which 150 years ago were little more that laboratory curiosities have now entered the world of modern manufacturing as a fully mature and heavy duty technology. As mentioned above we expect that atmospheric pressure plasmas will be well represented in the June symposium on POLYMER SURFACE MODIFICATION

---

[3] The following material is adapted from a most informative article by Inès A. Melamies: "Touched a thousand times" published in KUNSTSTOFFE, 10/2012, page 181-183, Hanser Verlag, Germany.

[4] TRW Automotive Electronics & Components, GmbH, Radolfzell, Germany.