

Tri-Star Technologies 2201 Rosecrans Ave,

El Segundo, CA 90245

Tel: 310-536-0444

Fax: 310-536-9322

Igor.Murokh@tri-starelectronics.com

www.tri-star-technologies.com

In-Line
Plasma
Treatment
of Wire
Insulation
Materials



Igor Murokh, Ph.D.

## **Contents**

3	Abstract
3	Introduction
4	Polymer Surface Modification
7	Dielectric Barrier Discharge
10	PT-1000 Plasma Treatment System
18	Conclusion
19	References

### **Abstract**

Ink-jet based wire marking systems are widely used in the aerospace industry. This paper analyzes the major factors that influence the quality of ink-jet printing. Mark durability and legibility depend upon both marking system parameters and wire surface characteristics. Among these factors are ink type, line speed, ink curing process, chemical nature of the insulation material, physical structure of the surface, wettability, porosity, roughness, uniformity, concentration of defects and impurities, etc. Various methods of polymer surface modification including Flame, UV, Ozone and Corona are compared to Plasma treatment. It is shown, that plasma treatment is the most effective and universal way to improve consistency and durability of marking. PT-1000 atmospheric plasma treatment system based on Dielectric Barrier Glow Discharge phenomenon is described.

#### Introduction

Polymer materials are successfully used in virtually any industry in the world including aerospace, biomedical, semiconductor, automotive, etc. The applications range from thin-film technology and protective coating to the composite materials, fiber optics and many more. Plastics have excellent bulk physical, chemical and weather resistance properties, they are relatively inexpensive and easy to process. However, low surface energy and low wettability of the materials considerably limit their applications when strong bonding is required between polymer surface and adhesive. It is well known that permanent bonding, potting, coating, printing, or the like, on the surfaces of many plastics is impossible without some special pretreatment of the surface. Wire insulation materials are not an exclusion. Beside the inherent "bad" polymer surface properties, wire surface has its own problems imposed by the features of the wire manufacturing. Because the extrusion is a non-equilibrium process, small variations in the baking temperature, line speed, humidity, etc. cause local changes in the surface roughness, porosity, crystallinity, uniformity and other surface characteristics on microscopic and macroscopic levels.

The process does not take place in a clean room environment and therefore, composition, concentration and size distribution of dust particles in the air on the production floor could influence surface properties. Obviously the very surface layers of the insulation are the most sensitive to these variations. At the same time, the surface physical and chemical characteristics define the adhesion strength and other properties of the interface layer that are critical for any further marking, striping or coating applications on the wire surface. This is one of the major reasons, why permanency of the mark printed on the wire or cable even with ideal noninvasive surface marking machine could vary from manufacturer to manufacturer, from gauge to gauge, batch to batch, and even along the same wire segment. To achieve durability and consistency of the wire marking identification described by most military and commercial specifications in the aerospace industry, special treatment of the wire surface is required. The treatment would increase surface "printability" of the wire prior to the marking process and reduce the dependence of marking quality on the local surface properties of wire insulation.

## 1. Polymer Surface Modification

For the last 50 years different polymer surface modification techniques have been proposed and used to alter polymer surfaces without affecting bulk properties of the material. Among these methods are chemical treatment, flame treatment, coronas, low pressure plasmas, IR, UV, X-rays and g-rays irradiation, electron and ion beams bombardment, ozone exposure and others. Plasma treatment is one of the most universal surface treatment techniques [1,2]. Plasma, in general, consists of partially ionized gas or gas mixture. The charged particles (ions or electrons) accelerate in the electrical field to the energies that are comparable or exceed bond energies of the polymer surface. The following phenomena may occur when this particle strikes a solid surface [3]: a. The particle may be reflected, probably being neutralized in the process b. The impact may cause the target to eject electron (secondary electron emission) or atom (sputtering). c.The particle may be trapped into the target (ion implantation, electron trapping)

d. The impact may cause some structural rearrangement of the surface varying from point defects e.g. missing atoms (vacancies), displacement of atoms from their original positions (iterstitials) to the more gross effect such as dislocations, changing crystal lattice, altering stoichiometry, and other order-disorder phenomena.

e. The impact could promote some chemical modification of the surface if plasma gas mixture and/or plasma ions are chemically reactive.

f. All of the above.

A minimum amount of charged particles is always present in the plasma to maintain a discharge. The loss of them on the target and/or by travelling out of the active plasma area is compensated by production of ion-electron pairs during their collisions with neutral molecules in the gas phase and by photoionization. That why most plasmas are also characterized by intensive UV radiation that also could affect the surface modification process [4,5]. The parameters of plasma (frequency, intensity, and pressure) as well as gas mixture could vary depending on the polymer surface properties and surface modification that needs to be done. For example, oxygen plasma treatment increases the surface energy of the polymers [6-10], while fluo-

rine plasma treatment decreases [11-14]. Ammonia plasma is used to modify PTFE surfaces [15-18]. Argon and other inert gases induce crosslinking [19-21]. Plasma treatment is usually fast and affects about 10 nanometers of the very surface layer. The effect of treatment conditions in a glow discharge on the wettability of the PTFE was studied in [22-24]. It was shown that increase of wettability of the film can not be explained either by UV influence or by oxidation of functional groups. A comparison of corona discharge, flame, remote air plasma, ozone and combined UV/ozone treatment of polypropylene and polyethylene terephthalate was done by Strobel et. al. [25]. Authors concluded that corona flame and RFdriven remote-plasma processes rapidly oxidize polymer surfaces attaining XPS O/C atomic ratios on polypropylene of greater than 0.1 in less than 0.5 sec. To reach the same level of the oxidation, UV/ozone treatment required exposure time orders of magnitude greater. It also induces changes much deeper in the bulk structure. The changes in O/C atomic ratio does not exactly correlate with wettability changes, suggesting that other factors might be involved.

On the contrary, Friedrich et. al. [26] have shown a strong correlation between oxygen content and polar component of the surface energy on the polypropylene substrate. They compared low pressure oxygen, corona and spark jet plasmas as well as UV/ozone exposure in terms of improvement of surface energy and adhesion properties for PE, PP and PET. It was found that UV\ozone treatment requires several minutes of exposure time and causes undesirable aging of the bulk polymer properties. At a very short exposure (<0.1 sec), corona produces stable but thin functionalized surface. Longer treatment produces weakly bounded oxidized debris on the polymer surface and significantly reduces the strength of adhesion. This conclusion is in agreement with data obtained in [27] for the polyethylene and polystyrene, which suggest that incorporation of radicals into the surface by adsorption and chemical reaction is in competition with the loss of material due to sputtering of low molecular polymer fragments and plasma chemical etching. The data [18] for PTFE also support a theory that plasma treatment is limited by a weakened boundary layer of the polymer material. Because plasma treatment involves many different mechanisms to affect material surface, it seems to be clear that the result of a

face modification on the one hand, and by the rate of surface etching on the other. The best adhesion results were achieved by the spark jet atmospheric pressure and low pressure oxygen plasmas. The major disadvantages, however, are the non-uniform treatment for the spark jet, and long exposure time and necessity to produce vacuum for the low pressure plasma. Good adhesion results of the spark jet treatment may be partially explained by the mechanical damage of the material surface caused by the nonuniform treatment. Greenwood et.al. [28] found that an atmospheric silent discharge treatment causes a greater level of topographical disruption of the surface. They also have shown that surface oxygenation depends on the chemical nature of the polymer substrate and its reactivity toward the discharge medium. As it follows from the data obtained by AFM and contact angle measurements, changes in the roughness alone can not explain changes in the wettability of the treated surface. On the other hand, surface energy or wettability is only an indicator of whether or not a good adhesion is going to take place on a particular substrate. The ultimate results could only be obtained by measuring the adhesion itself.

long plasma exposure is defined by the rate of sur-

Beside the topographical changes and surface oxidation, plasma treatment also induces local surface charges, which might be another reason for the wettability improvement. Takeda and Murata [29] observed the direct correlation between charging characteristics of the polymer surface and its wettability. After the plasma treatment of HDPE and nylon in argon gas the contact angle of each film decreased and films tended to become more negatively charged. The contact angle and the charge gradually recovered with time and appeared to reach constant values 10 days after the treatment. The process of charging the dielectric substrate to improve wettability using a glow discharge at atmospheric pressure is described in [30]. The method is based on the fact that all insulation materials posses some electret properties. The electret is a dielectric material that retains an excessive electrical charge for a long period of time [31]. This charge is due to ordering of molecular dipoles, or uncompensated local surface or space charges (e.g. electrons trapped into material surface). Glow discharge is a wellknown technique for the electret production, and may be used to charge any dielectric surface. In other words, glow discharge treatment of the dielectric always induces some local charges on the material surface. Although an electrical charge on the surface of quasielectret decays at much faster rate, a momentary increase of wettability induced by excessive charging would provide an improved conditions for such applications as coating, gluing, potting, printing, etc., especially for the in-line processes. As it follows from comparative studies of different plasma systems [26-28], both atmospheric and vacuum plasma treatment cause about the same changes of wettability and adhesion characteristics of the polymer material, when exposure time is less than 1 sec. This result is independent on the specific features of plasma system. From this stand point dielectric barrier discharge at atmospheric pressure seems to be the most effective way for in-line treatment process.

## 2. Dielectric Barrier Discharge

Dielectric barrier discharge is a well-known phenomenon that is widely used in industrial processes such as ozone generation, electret production, corona web treatment, etc. For the last decade this type of discharge has been intensively studied as a basis for the plasma treatment at atmospheric pressure, that opens numerous possibilities both for new industrial applications and for replacement of the old vacuum based processes [32-38].

The dielectric barrier controlled discharge consists of a large number of transient microdischarges in that are distributed statistically on the treated surface. The plasma generation takes place in a gap between two plane electrodes, where at least one is covered with dielectric material. Four phases of the microdischarge could be identified [32] 1. Townsend Phase. The number of charged particles (electrons and ions) increases exponentially without disturbing the applied electrical field.

2. Streamer Phase. The formation of the conducting channel inside the gas Cathode Sheath Phase. The current maximum reaches its value. 4. Quenching Phase. The electrical charge accumulated on the dielectric surface reduces the electrical field in the gap below breakdown threshold and prevents formation of the new ion-electron pairs On the other hand, the in the gas. increases retaining the charge electrical field across the surface and causes the local surface microdischarge. The complete discharge development has duration of several nanoseconds. Electrons are the predominant carriers of the current. The plasma forms randomly distributed filaments of about 100 m diameter with 1.5 mm footprints on the dielectric surface [33]. Due to the short period of the discharge there is no significant heating of the gas within the gap and the substrate. Depending on the parameters of the applied high voltage signal (frequency, duty cycle, waveform, etc.), the filaments tend to appear at the same places leading to the non-uniform treatment. The charged spots remaining on the surface from the previous microbreakdowns are preferential points for the initiation of a new microdischarge with the opposite polarity. To cover the entire surface with microdischarges (homogeneous treatment), a combination of high voltage periods with no voltage periods is used (~1 msec trains of~20 msec HV pulses in a ~1 sec interval). A gap between electrodes may be filled with different gases or gas mixtures depending on the required plasma properties and expected surface transformation. The interaction of the microdischarges generated at near atmospheric pressure with dielectric surface is similar to the plasma-surface interaction at low presIn the former case, however, interaction is localized at the footprints of the discharges and seems to occur at much faster rate. It could be assumed that surface modification under the discharge footprint reaches a saturation level during one cycle. Since footprints are randomly distributed over the surface, increase of the exposure time provides more uniform coverage of the surface with discharges rather than changes an intensity of the surface modification.

Air at atmospheric pressure is the most practical gas for industrial application of in-line material plasma treatment. Other gas mixtures could be blown through the plasma chamber at a slightly excessive pressure if required.

Massines at. al. [34] compared air and helium dielectric barrier glow discharges at atmospheric pressure for the polypropylene surface treatment. Air discharge has clearly filamentary structure. Several pulses of nanosecond microdischarges occur during each half cycle at the applied voltage about 10 kV rms. The overall discharge duration is about 5msec that is much less than a cycle period. An increase in the frequency of the applied voltage does change neither the current nor the duration of the discharge. Therefore, higher frequency leads to more rapid surface treatment.

lium at atmospheric pressure, the discharge changes from filamentary to the homogeneous and covers the entire surface. The discharge duration in helium during a half cycle period is comparable to the one in air, but the current amplitude is much lower. The duration could be easily estimated assuming that plasma quenching is due to the dielectric charging [3]. Local charge densities in the vicinity of the polymer surface for helium and air plasma are about  $4x10^{10}$ and 10<sup>13</sup> charges/cm<sup>2</sup> pulse respectively. The charge Q accumulated in t seconds on the dielectric surface for the current i will be Q=it.That gives t~6.4 msec at the average current density in order of 1 mA/cm<sup>2</sup> for the discharge in helium. The charge density for the air filamentary discharge was obtained based on the metallic "point to plane" discharge data. The discharge duration about 100 nsec gives current density of 16 A/cm<sup>2</sup>. This current would be typical rather for an arc discharge [39] than for the dielectric barrier discharge. A "uniform plane to plane" discharge would have lower current density. It is very difficult to distinguish a real plasma current from the total current in the systems like these, due to significant impedance effects at high frequencies.

When the gap between electrodes is filled with he-

# 3. PT-1000 Plasma Treatment System

The PT 1000 Wire and Cable Treatment System is designed to significantly improve the wettability characteristics of various insulation materials, including polyamides, fluoropolymers, polyesters. The desirable effect is achieved by creating a plasma curtain around the wire and bombarding the dielectric surface with charged particles and high energy UV photons. A solid state programmable generator produces a high voltage high frequency signal that is applied to a cylindrical electrode which is embedded in a protective dielectric chamber (Fig. 1).

Fig.1. PT-1000 System for wire and cable plasma treatment



When a wire is passing through this electrode, voltage is applied above its threshold value, producing an elec

form plasma curtain that completely surrounds the wire. In most cases, this plasma produces a blue color glow that can easily be observed through the opening in the dielectric chamber. The intensity of the plasma treatment is defined as the amount of energy transmitted to the unit area of the wire surface per unit of time, and is dependent on the voltage and frequency of the driving signal. The level of the plasma treatment at a given intensity is proportional to the exposure time (length of an electrode divided by the line speed) and inversely related to the wire diameter. The time dependence is usually exponential, with saturation occurring after long period of exposure (10 sec or more) and linear for short periods of time (0.1 sec or less). To obtain the same quality of treatment for thick wire insulation or to achieve higher wire throughput speeds, the plasma intensity must be increased. Adjusting the electrode voltage of the PT-1000 from 1 to 15 kV can change this intensity. Despite the high potential applied to the electrode, the active currents inside the chamber are extremely low. At normal operating conditions, the average power consumption for the system is only about 100W.

trical breakdown inside the chamber, creating a uni-

dThe threshold conditions as well as the plasma density and composition (concentration of specific ions and electrons) depend on the pressure and nature of the gas in the dielectric chamber, wire diameter, dielectric constant, wire insulation thickness, insulation material properties, etc. A long wire passing through the chamber may be considered as grounded electrode covered with a thin layer of dielectric material. Therefore electrical discharge occurring in the gap between the wire and outer cylinder is similar to the dielectric barrier controlled discharge usually produced in the plane geometry conditions. The theory of discharge taking place between two coaxial cylinders was developed a long time ago for the Geiger-Muller counter [39] in which the axial electrode (anode) is a fine wire and the outer electrode (cathode) has internal diameter of a few centimeters. The detailed description of the phenomenon is given in [40]. The electric field intensity on the surface of the wire is  $E=2V/D_wln(D_c/D_w)$ 

where V is an applied voltage, Dw is a diameter of the

wire, D<sub>c</sub> is an internal diameter of the cylindrical high

voltage electrode.

Breakdown voltage in air at atmospheric pressure for different diameters of the high voltage electrode is shown on Fig.2. It is clear, that different wire diameters might require different electrodes for the most effective treatment. Characteristic oscillogramms of the discharge are presented in Fig.3.

Fig. 2. Dependence of the breakdown voltage in air on the wire diameter for different cylindrical electrodes

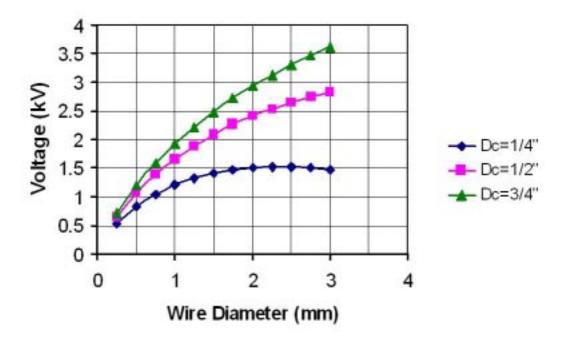
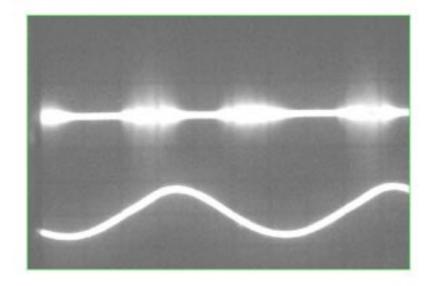


Fig.3. Discharge currents in air at atmospheric pressure at sinusoidal high voltage signal (Vmax=3 kV, f=17 kHz)



The discharge behavior is quite different for positive and negative voltage waves applied to the outer cylinder. In the former case the discharge current amplitude is higher, and the overall discharge duration is shorter. In the negative high field region near the wire positive ions achieve a high energy before striking the wire surface. Secondary electrons liberated from the surface by ion bombardment start outward-moving electron avalanches, that produce many positive ions, which in turn initiate new electron avalanches and so on. The discharge continues until localized positive charge on the wire surface reduces the electrical field below breakdown value. When the wire is positive, the field at the cathode region is too low to support ionization by electrons in the gas, and discharge is maintained by other mechanisms. This corresponds to the fact that in most cases the wire exiting the plasma chamber has an excessive positive charge as measured by electrostatic voltmeter. Tables 1-3 present the results of the marking durability tests made for various types of wires at different facilities. In all cases the marking was done in-line with Tri-Star Technologies Plasma Treatment System. The data clearly show a significant improvement of durability when plasma treatment was used. In case of Tefzel<sup>a</sup> insulated wire the relative improvement could be as high as 1000%

wire passing through the UV oven could also affect marking quality since most inks used in aerospace industry are UV curable. Although the marking durability test is an ultimate acceptance test, it only shows qualitative advantage of the plasma treatment. Quantitative analysis of the effects of plasma treatment on different types of wire insulation requires more objective methods of testing, that would be independent from the features of the marking system. One of these methods is contact angle measurement [41,42]. The results of the measurements on the surface of 22759/11-20 wire made with VCA-2500XE (Video ContactAngle System, ASC Products, Billerica, MA) are presented in Tables 4 and 5. The system utilizes precision optics and a CCD camera in conjunction with image processing hardware and software to perform contact angle analysis and surface energy calculation. From twenty-four to thirty-three contact angles were recorded for each liquid on each wire sample in order to get a statistically valid contact angle value. The contact angle measurements and surface energy calculations consistently indicate an increased wettability for plasma treated samples. The best results were achieved for the plasma treatment in argon atmosphere with small (<1%) amount of ammonia.

(Table 3). UV exposure as well as alignment of the

Table1. Marking durability for the flame and plasma treated wires. (Woven Electronics, Simpsonville, SC)

Insulation Type	ETFE	EIFE	IR ETFE	IRETFE	FEP
Wire Spec	M275000-24TE2U00	M27500-20TO2T14	M27500-24502T23 M23-20186/L	WS 19199/Q-20-1	MIL-C 170
Wire Vendor	-	Thermax	Therma-tics Judd	Delta	Thermax
Trentment Testing	U FI PI	U FI PI	U FI PI U FI PI	U FI PI	U FI PI
Rub (finger)	FPP	F F P*	P P P P P	P P	F F F
Rub (eraser)	FPP	F F P*	F P P F P P	F P*	F F P*
Alcohol	F P P	F P P	F P P P P	F P*	F F P*
1-1-1 Trichlor:	F P P	FPP	F P P P P	P P	F F P*
TMC (freon)	FPP	F P P	F P P F P P	P P	F F P*
Water+	F P P	FPP	P P P P P	P P	F F P*
Acetone	F F P*	F P* F	FPP FFP	* F P*	F F P
Eposolve 301	F P P	FPP	F P P F P P	F P*	F F P*
Masking tape	FPP	F F P*	F P P F P P	P P	F F P*
Thermal shock	FPP	F F P*	F P P F P P	F P*	F F P*
ISO oil	PPP	P P P	P P P P P	P P	F F P*
Pen (40dyne/cm)	F P P	F P P	P P P P P	P P	F F F
Cold shock	FPP	F P P	F P P F P P	F P*	F F P*

Notes All wires where marked with UV cumble ink

U, Untrested, Fl, Flame treated, Pl, Plasma treated

F, fail, P, pass

Rub (finger), 20 strokes of moderate pressure

Rub (eraser) per Mil-M-81531, 4.62.

Alcohol, Trichlor, TMC, Water, Acetone, and Eposolve per Mil-Std 202.

Masking tape, Press on to marking, wait 30 sec, peel off and read marking

Thermal shock per WS 19185

ISO oil, Soak for 48 hr and rub once

Pen, check the spreading on the surface of the wire

Cold shods, 5 min at 40F, bend and rub

Table 2. Results of the rub test with skydrol fluid performed at McDonnell Douglas, Long Beach, CA, per DMS 2325 for the marking identification of Kapton® insulated wire made by M-100 Dot-Matrix Wire Marker.

Conditions	No Treatment	Plasma treatment	Heat curing	Plasma treatment with Heat curing
Sample # 1	12	>30	14	>30
Sample # 2	12	>30	30	>30
Sample # 3	10	>30	26	>30
Sample # 4	14	>30	18	>30
Sample # 5	30	>30	26	>30
Sample # 6	16	>30	24	>30
Sample # 7	22	>30	14	>30
Sample # 8	26	>30	22	>30
Sample # 9	30	>30	30	>30
Sample # 10	30	>30	22	>30

Note: The tests were stopped after 30 rubs.

Table 3. Results of a scrape abrasion test performed at Raychem, Menlo Park, CA, for the marking identification of Tefzel® spec. 55 insulated wire made by M-100J Ink-Jet Wire Marker.

Line Speed	30 ft/min	60 ft/min	120 ft/min
UV exposure	1 sec	0.5 sec	0.25 sec
Average # of cycles Plasma off	7	11	12
Average # of cycles Plasma on	58	>125	48

Testing Method:

Motor-driven, reciprocating cam mechanism, equipped with a reset counter and capable of a 3/8" stroke at 60 cycles per minute with a clamp for holding specimens. The contact surface is a smooth cylindrical steel mandrel, 0.025" in diameter. Applied weight is 500 g. One cycle corresponds to two strokes.

Note: The tests were stopped after 125 cycles.

Table 4. Contact angle (degrees) measurement for the plasma treated FEP insulated wire (22759/11-20)

Plasma treatment conditions	Water Surface tension 72 dyne/cm	Methylene lodide Surface tension 50 dyne/cm	Xylene Surface tension 30 dyne/cm
No treatment	101+/-5	75+/-4	46+/-4
Air plasma	94+/-8	70+/-3	32+/-3
Argon plasma	90+/-4	66+/-5	23+/-5
Argon and Ammonia	82+/-4	67+/-6	20+/-7

Table 5. Surface energy calculation based on contact angle measurement for the plasma treated FEP insulated wire (22759/11-20)

Plasma treatment conditions	Harmonic-mean approximation			Geometric-mean approximation		
	Dispersive Component Dyne/cm	Polar Component Dyne/cm	Total Dyne/cm	Dispersive Component Dyne/cm	Polar Component Dyne/cm	Total Dyne/cm
No treatment	17.3	5.4	22.7	14.3	2.6	16.9
Air plasma	20.5	7.2	27.9	17.7	3.9	21.6
Argon plasma	19.9	9.1	29.0	16.4	6.0	22.4
Argon and Ammonia	23.0	11.5	34.5	19.3	8.40	27.7

Another method was developed at Tri-Star Technologies specifically to measure wettability on the surface of the wires. When a small droplet of liquid falls from the end of glass capillary under the force of gravity, the mass of the droplet is proportional to the surface tension of the liquid and radius of the capillary [43]. Knowing the radius of the capillary and the mass of the droplet right before breaking off the surface, it is possible to determine the surface tension of the liquid. When the droplet falls from the surface of horizontally held wire, the mass of the droplet (at given surface tension of the liquid) depends on wire diameter, surface energy of the insulation as well as on the roughness, porosity and local surface charge. All these factors could affect marking durability. Measuring the critical volume of water droplet (i.e. the maximum mass of the droplet that is able to remain on the surface of horizontally held wire) allows to obtain and to compare some quantitative data describing the overall ability of the surface to accept ink before and after plasma treatment. Fig. 4. illustrates a dependence of critical water droplet volume (CWDV) on the wire diameter and its surface energy. In general, higher surface energy of the material and larger diameter of the wire give higher value of CWDV. Obviously, wire of "zero diameter" retains a droplet of "zero volume". As wire diameter increases, CWDV reaches some maximum value that is determined mostly by the surface tension of liquid rather than surface properties of the solid. Gold coating on the copper-nickel contacts has a high surface energy (>100 dyne/cm) and, therefore, retains bigger droplets as compare to low surface energy fluoropolymers. However, the difference is not as significant as one could expect from the differences in the surface energies. The coating has much smoother and much less porous surface than extruded fluoropolymer wires that seems to compensate high surface energy of the material. Fig.5. presents the results of aging of the plasma treated wire depending on the plasma exposure time. The 16878/6-26 extruded PTFE wire has original CWDV of 13 mL and diameter of 0.65 mm 17 kHz sinusoidal high voltage signal was applied to the cylindrical electrode with internal diameter of 1/4" and 4" length. Total power consumed from the outlet was 35 W. 1 and 0.1 sec exposure times correspond to the 20 and 200 ft/min line speeds respectively. As it follows from the chart the plasma treatment at this setting reaches an equilibrium (saturation level) in approximately 0.3 sec. The effect of plasma treatment achieved on the surface, stored in the open air at normal conditions, slowly decays from maximum CWDV=25 mL to the 22 mL in two weeks. The drop of about 15% in the first two weeks is quite similar to the decay of uncompensated electrical charge on the PTFE surface.

Fig. 4. Dependence of the critical water droplet volume on the wire diameter for the materials with different surface energies

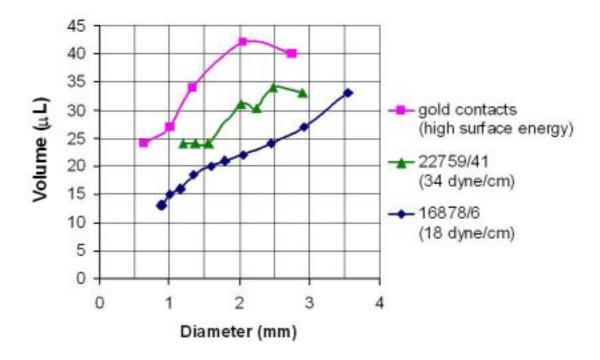
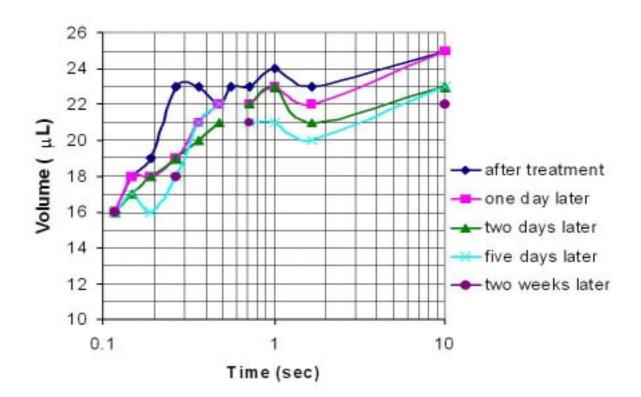


Fig.5. Dependence of the critical water droplet volume on the plasma exposure time for 16878/6-26 wire



CWDV depending on the plasma exposure time for ETFE wires is shown on the Fig.6.The curves have the same shape as the previous one reaching an equilibrium in approximately 0.5 sec. CWDV rises from 26 to 57 mL for the crosslinked ETFE treated in air and from 29 to 53 mL for the regular ETFE treated in argon.

#### Conclusion

PT-1000 plasma treatment system significantly improves the durability of marks placed on the surface of wires and cables insulated with Tefzel<sup>a</sup>, Kapton<sup>a</sup>, Teflon<sup>a</sup>and other difficult to print on materials. The marking on the wires treated with the system passes most military and commercial requirements. The PT-1000 is a stand-alone modular system that easily interfaces and operates with any known wire/cable marking process, including dot matrix, ink jet, gravure wheel and offset. Once processed with the PT-1000, the wire or cable does not require any additional treatment such as alcohol, flame, preheating, etc. The treated surface will retain its improved wettability for some period of time (up to several weeks). The shelf life of this treatment is dependent on storage conditions and type of insulation material.

With fluoropolymers this effect may last up to one year, but eventually it will degrade and the surface wettability will decrease back to its original state. Cables and wires of different outer diameters may require different corresponding electrodes. Since the PT-1000 operates using ambient air at atmospheric pressure, it does not require any special gas mixture or pressure settings. Special gas mixtures may be easily introduced into the treatment chamber if required. The PT-1000 can process many different types and sizes of wires and cables without any damage to their insulation and supports line speed up to 1000 ft/min.

## References

- 1. Chan C.M., Ko T.M., Hiraoka H. Polymer surface modification by plasmas and photons. Surface Science Reports Surf. Sci. Rep. (Netherlands), vol.24, (no.1-2), Elsevier, 1996. p.1-54.
- 2. Egitto F.D., Matienzo L.J. Plasma modification of polymer surfaces for adhesion improvement. IBM Journal of Research and Development IBM J. Res. Dev. (USA), vol.38, (no.4), July 1994. p.423-39.
- 3. Brian Chapman. Glow Discharge Processes. (Interscience, New York, 1980) 406pp.
- 4. Fozza A.C., Roch J., Klemberg-Sapieha J.E., Kruse A., Hollaender A., Wertheimer M.R. Oxidation and ablation of polymers by vacuum-UV radiation from low pressure plasmas. Nuclear Instruments & Methods in Physics Research, Section B (Netherlands), vol.131, (no.1-4), Elsevier, Aug. 1997. p.205-10.
- 5. Matienzo L.J., Zimmerman J.A., Egitto F.D. Surface modification of fluoropolymers with vacuum ultraviolet irradiation. Journal of Vacuum Science & Technology A (USA), vol.12, (no.5), Sept.-Oct. 1994. p.2662-71.
- 6. Friedrich J.F., Geng S., Unger W., Lippitz A., Erdmann J., Gorsler H.V., Woell C., Schertel A., Bierbaum K. Plasma functionalization and reorientation of macromolecules at polymer surfaces. Surface and Coatings Technology (Switzerland), vol.74-75, (no.1-32), Elsevier, Oct. 1995. p.664-9.
- 7. Qiang Zhao, Hsueh Yi Lu, Hess D.W. In situ infrared studies of polyvinyl chloride films exposed to H<sub>2</sub>/O<sub>2</sub>/Ar downstream microwave plasmas. Journal of the Electrochemical Society (USA), vol.143, (no.9), Electrochem. Soc, Sept. 1996. p.2896-905.
- 8. Normand F., Granier A., Leprince P., Marec J., Shi M.K., Clouet F. Polymer treatment in the flowing afterglow of an oxygen microwave discharge: active species profile concentrations and kinetics of the functionalization. Plasma Chemistry and Plasma Processing Plasma Chem. Plasma Process. (USA), vol.15, (no.2), June 1995. p.173-98.
- 9. Petasch W., Raeuchle E., Walker M., Elsner P. Improvement of the adhesion of low-energy polymers by a short-time plasma treatment. Surface and Coatings Technology Surf. Coat. Technol. (Switzerland), vol.74-75, (no.1-32), Elsevier, Oct. 1995. p.682-8.
- 10. Lianos L., Parrat D., Tran Quoc Hoc, Tran Minh Duc Secondary ion mass spectrometry time of flight and in situ X-ray photoelectron spectroscopy studies of polymer surface modifications by a remote oxygen plasma treatment. Journal of Vacuum Science & Technology A (USA), vol.12, (no.4, pt.2), July-Aug. 1994. p.2491-8.
- 11. Satoh M., Matsumoto S., Higashiguchi T., Matsuda M., Muranoi T., Kikuma I., Momose Y., Takeuchi M. Surface fluorination of electrophotographic photoreceptors by plasma treatment for contact charging with a wet polymer roller. Applied Surface Science (Netherlands), vol.92, Elsevier, Feb. 1996. p.635-8.
- 12. Leonard D., Bertrand P., Khairallah-Abdelnour Y., Arefi-Khonsari F., Amouroux J. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) study of SP<sub>6</sub> and SF<sub>6</sub>-CF<sub>4</sub> plasma-treated low-density polyethylene films. Surface and Interface Analysis (UK), vol.23, (no.7-8), July 1995. p.467-76.
- 13. Khairallah Y., Arefi F., Amouroux J. Surface fluorination of polyethylene films by different CF<sub>4</sub> glow discharges: effects of frequency and electrode configuration. Thin Solid Films (Switzerland), vol.241, (no.1-2), 1 April 1994. p.295-300.
- 14. Endo K., Tatsumi T. Plasma fluorination of polyimide thin films. Journal of Vacuum Science & Technology A (Vacuum, Surfaces, and Films) J. Vac. Sci. Technol. A(USA), vol.15, (no.6), AIP for American Vacuum Soc, Nov.-Dec. 1997. p.3134-7.
- 15. Pringle S.D., Joss V.S., Jones C. Ammonia plasma treatment of PTFE under known plasma conditions. Surface and Interface Analysis (UK), vol.24, (no.12), Wiley, Nov. 1996. p.821-9.
- 16. Badey J.P., Espuche E., Jugnet Y., Sage D., Tran Minh Duc, Chabert B. Surface modification of polytetrafluoroethylene by microwave plasma downstream treatment. Polymer (UK), vol.35, (no.12), Elsevier, 1994. p.2472-9.
- 17. Badey J.P., Espuche E., Sage D., Chabert B., Jugnet Y., Batier C., Tran Minh Duc A comparative study of the effects of ammonia and hydrogen plasma downstream treatment on the surface modification of polytetrafluoroethylene. Polymer (UK), vol.37, (no.8), Elsevier, 1996. p.1377-86.
- 18. Kaplan S.L., Lopata E.S., Smith J. Plasma processes and adhesive bonding of polytetrafluoroethylene. Surface and Interface Analysis, Vol.20, (No.5), may 1993, p. 331-6.

- 19. Vallon S., Drevillon B., Poncin-Epaillard F., Klemberg-Sapieha J.E., Martinu L. Argon plasma treatment of polycarbonate: in situ spectroellipsometry study and polymer characterizations. Journal of Vacuum Science & Technology A (USA), vol.14, (no.6), AIP for American Vacuum Soc, Nov.-Dec. 1996. p.3194-201.
- 20. Everaert E.P., Chatelier R.C., Van Der Mei H.C., Busscher H.J. A quantitative model for the surface restructuring of repeatedly plasma trated silicone rubber. Plasma and Polymers, Vol.2 [no.1], March 1997, p.41-51.
- 21. Sprang, N., Theirich, D., Engemann, J. Surface modification of fluoropolymers by microwave plasmas: FTIR investigations. Surface and Coatings Technology (Switzerland), vol.98, (no.1-3), Elsevier, Jan. 1998. p.865-71.
- 22. Goldshtein D.V., Gilman A.B., Shifrina R.R., Potapov V.K. Modification of the surface of polytetrafluoroethylene in a glow discharge plasma in vapors of various organic compounds. Khimia Vysokikh Energii(RUS), Vol. 25, (No.4), 1991, p.361-4.
- 23. Gilman A.B., Goldshtein D.V., Potapov V.K., Shifrina R.R., Prutchenko S.G. Effect of treatment conditions in a glow discharge on the wettability of polytetrafluoroethylene. Khimia Vysokikh Energii(RUS), Vol. 24, (No.1), 1990, p.73-5.
- 24. Gilman A.B., Goldshtein D.V., Potapov V.K., Shifrina, R.R. Wettability change in glow discharge treated PTFE. Khimia Vysokikh Energii(RUS), Vol. 22, (No.5), 1988, p.465-8.
- 25. Strobel M., Walzak M.J., Hill J.M., Lin A., Karabashewski E., Lyons C.H. A comparison of gas-phase methods of modifying polymer surfaces. J. Adhesion Sci. Technol., Vol. 9, (no. 3), 1995, p.365-83.
- 26. Friedrich, J., Wigant, L., Unger, W., Lippitz, A., Wittrich, H. Corona, spark and combined UV and ozone modification of polymer films WeBP23. Surface and Coatings Technology (Switzerland), vol.98, (no.1-3), Elsevier, Jan. 1998. p.879-85.
- 27. Meichsner, J., Nitschke, M., Rochotzki, R., Zeuner, M. Fundamental investigations in plasma modification of polymers. Surface and Coatings Technology. (Switzerland), vol.74-75, (no.1-3), Sept. 1995. p.227-31.
- 28. Greenwood O.D., Boyd R.D., Hopkins J, Badyal J.P.S. Atmospheric silent discharge versus low-pressure plasma treatment of polyethylene, polypropylene, polyisobutylene, and polystyrene. J. Adhesion Sci. Technol., Vol. 9, (no. 3), 1995, p.311-26.
- 29. Takeda, H., Murata, Y. Change in charging characteristics of high polymers due to plasma treatment. Japanese Journal of Applied Physics, Part 1 (Japan), vol.35, (no.9A), Sept. 1996. p.4791-2.
- 30. Murokh I.Y., Kerner A.A. Surface Charging to Improve Wettability, US Patent #5,798,146. Aug.25, 1998, filed Sep.14, 1995.
- 31. Electrets (edited by G.M. Sessler, Springer-Verlag, Berlin, 1997).
- 32. Salge J. Plasma-assisted deposition at atmospheric pressure. Surface and Coatings Technology (Switzerland), vol.80, (no.1-2), p.1-7, March 1996.
- 33. Pochner K, Beil S, Horn H, Bloemer M. Treatment of polymers for subsequent metallization using intense UV radiation or plasma at atmospheric pressure. Surface and Coatings Technology (Switzerland), vol.97, (no.1-3), p.372-7 Dec. 1997.
- 34. Massines F, Messaoudi R, Mayoux C. Comparison Between Air Filamentary and Helium Glow Dielectric Barrier Discharges for the Polypropylene Surface Treatment. Plasmas and Polymers, vol.3, (no.1), p.43-59, 1998.
- 35. Meiners, S., Salge, J.G.H., Prinz, E., Foerster, F. Surface modification of polymer materials by transient gas discharges at atmospheric pressure. Surface and Coatings Technology (Switzerland), vol.98, (no.1-3), Elsevier, Jan. 1998. p.1121-7.
- 36. Friedrich, J.F., Wigan, L., Unger, W., Lippitz, A., Erdmann, J., Gorsler, H.V., Prescher, D., Wittrich, H. Barrier properties of plasma and chemically fluorinated polypropylene and polyethylenetere- phthalate. Surface and Coatings Technology, vol.74-75, (no.1-32), Elsevier, Oct. 1995. p.910-18.
- 37. Leiber, J., Selaff, O., Steffens, F., Rangelow, I.W. New design of a plasma chamber for homogeneous web treatment. Surface and Coatings Technology, (Switzerland), vol.74-75, (no.1-3), 1995. p.49-54.
- 38. Falkenstein Z., Coogan J.J. Photoresist etching with dielectric barrier discharges in oxygen. J. Appl. Phys., Vol. 82, (no.12), Dec. 1997, p. 6273-80.

- 39. Geiger H., Muller W. Physik., Vol. 2, (no.29), 1928, p.839
- 40. Sanborn Brown. Basic Data of Plasma Physics. (AIP Press, New York, 1994) 336pp.
- 41. S. Wu. Polymer Interface and Adhesion.(Marcel Dekker, New York, 1982)
- 42. Modern approches to wettability: theory and applications (edited by M.E.Schrader and G.I.Loeb. Plenum Press, New York, 1992).
- 43. J. de Boer. Atomic theory of heat. Termodynamics. (Pergamon Press, London, 1959).