The corona discharge, its properties and specific uses

M. Goldman¹, A. Goldman¹ and R. S. Sigmond²

¹CNRS École Supérieure d'Electricité, Gif-sur-Yvette, France ²The Norwegian Institute of Technology, Trondheim, Norway

Abstract - The main properties of corona discharges are reviewed, with emphasis on the features which make them unique for use as non-equilibrium chemical reactors: Their stability and ease of operation over a wide range of gases and pressures, including atmospheric; their sharply confined ionization regions where hot electrons interact with cold gas, inducing reactions without back reactions; and their extended low field drift regions which act as gaseous electrolytes, inducing electrochemical reactions on surfaces.

Present and future applications are discussed: Synthesis of ozone and ammonia, promotion of flames and combustion, surface treatment, and electrical insulation improvement.

INTRODUCTION

Gas discharges have been used for industrial chemical purposes ever since Birkeland's "electric gun" (really a linear motor) short-circuited during a crucial demonstration in Oslo around the turn of the century. The resulting DC arc was blown out in a gigantic fan by the magnetic field, dispersing the assembled dignitaries and all hopes of defense contracts. However, it also gave Birkeland the extended but thin slab of hot plasma he needed to convert air to nitrogen oxides, by heating a passing air flow to around 3000 K in the arc zone, with subsequent fast cooling to prevent back reactions. Backed by the business man S. Eyde and French capital, this was the start of the Birkeland-Eyde process and the Norsk Hydro Company that now dominate European fertilizer manufacture. The purpose of the present paper is to question whether Birkeland would have been still more lucky if his cannon had developed extensive electrical corona.

What are the reasons for using ionized gases as media for chemical reactions? Some applications use the plasma solely as a source of heat, and in these cases coronas cannot compete. Apart from these cases, all use of ionized gases for bulk reactions or for surface treatment exploits the non equilibrium (non-thermal) properties of these media. Here coronas excell, as no other discharge form has sharper internal divisions, both geographically into zones, and species-wise into electron, ion and neutral populations of very different energy distributions.

In the following some fundamental aspects of corona discharges and their interactions with the surroundings will be discussed briefly. A more thorough introduction to the subject will be found in refs. 1-2. After that, we turn to some applications related to chemistry.

BASIC CORONA PROPERTIES

Types of coronas and corona conduction

A corona discharge is, by definition, a gas discharge where the geometry confines the gas ionizing processes to high-field ionization region(s) around the active electrode(s). The corona geometry is named positive, negative, bipolar, AC, or HF, according to the polarity of the active electrode(s), while the current conduction in any corona region is called unipolar or bipolar dependent on whether one or both ion polarities are of importance. Figure 1 shows a typical positive point-to-plane corona, with some commonly used terms.

However, all discharge forms have ionization regions, and thus the really distinguishing feature of coronas is the existence of a low field drift region connecting the ionization region(s) with the eventual low field, passive electrodes. In this drift region, ions and electrons drift and react with neutrals, but with too low energy to ionize and too low density to react with other ionized particles. In unipolar conduction coronas, the drifting ions/electrons will always be of the corona polarity (i.e. no plasma!) and their space charge field will be the dominating factor in determining both the corona current/voltage characteristic and the current density distribution in the discharge gap. Electrically, the drift region then behaves as a large, non-linear resistor in series with the ionization region, often making external stabilizing resistances superfluous.

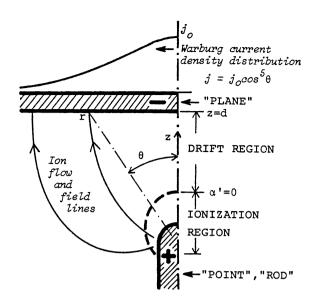


Fig. 1. A typical point-to-plane corona geometry, here shown with positive point, and some commonly used terms (ref. 3). The surface α ' = 0 marks the outer limit of ionization region, where the production of electrons by ionization just balances the loss by attachment.

In air and most other gases containing electron attaching molecules, two very different types of DC (and low frequency AC) coronas are found:

1. Unipolar conduction coronas, variously called positive glow coronas, negative Trichel pulse coronas, and negative glow coronas, all have ionization regions that stay concentrated very close to the active electrode. Also, at microampere currents and above, they either burn stably or, more often, in short pulses of such high repetition rate that the ion flow in the drift region is practically continuous. The predominant ions are of the corona polarity, that is, positive ions in positive coronas and negative ions in negative. The part of the drift region current in negative air coronas carried by electrons is usually small below $10\text{-}20~\mu\text{A}$ total current, because of electron attachment. At higher currents, the space charges make the electric field distribution more uniform. This, and the higher applied voltage, sharply increase the drift region field, increasing the electron/negative ion ratio. Note that the rapidly pulsed nature of the ionization region processes is very important for the corrosion of the negative point electrode. This may affect the drift region and the plane electrode by sputtering (ref. 4) or evaporation of point metal or corrosion products (refs. 5,6).

A plasma chemist may be well advised to look upon the unipolar drift region as an overgrown boundary sheath connecting the ionization region (often a plasma) with the low field electrode.

2. Streamer (bipolar) conduction coronas occur at higher point-to-plane currents, especially at positive point polarity. Under these conditions, the ionization region produces a conducting plasma faster than the plasma can be absorbed by the point electrode. Consequently a conductive plasma filament of some 30 µm diameter grows out of the point towards the plane, carrying the plasma producing ionization region ahead of it with velocity around 10 m/s (values for atmospheric density air). When this streamer hits the plane, a cathode spot is produced, the gap field is redistributed along the plasma channel, and this channel either dies out (by electron attachment) or later converts to a thermally ionized spark channel. A positive streamer hitting a plane cathode will subject it to a pulsed glow discharge treatment, bombarding it with positive ions of energies that may exceed 100 eV (measured at 10 kPa air by retarding potential analysis of extracted positive ions. Scaling laws predict no change with increase in pressure). This is in sharp contrast to the mainly thermal energy ion influx to the plane in unipolar current coronas.

Note that both corona forms may coexist: A 50 μ A positive corona might consist of 20 μ A continuous unipolar current, diffusely distributed over the plane (see below), with 30 μ A of streamers, repetitive at 10 kHz, hitting the plane just opposite the point (ref. 7).

Nearly a century of observations all agree that the unipolar current density in positive and negative point-to-plane coronas is distributed over the plane according to the so-called Warburg law (refs.8-11):

$$j(\theta) = j_0 \cos^5 \theta \tag{1}$$

$$j_{0} \sim 1/(2 \cdot d^{2}) \tag{2}$$

with tg θ = r/d and where I is the total corona current and d the gap length. The field and ion flow lines are somewhat, but not much, pushed apart by space charge repulsion. The observed distributions j (θ) usually fall quite abruptly to zero around $\theta \sim 65^{\circ}$, due to the fact that ions drift

along the field lines and that field lines ending outside $\theta \sim 65^{\circ}$ usually originate on the point surface outside the ionization region. The Warburg distribution is sketched in Fig. 1.

In point-to-plane unipolar current coronas, as well as in wire-cylinder or wire-plane ones, space charge fields will tend to make the total field increasingly uniform at increasing currents. It can be shown (ref. 12) that the unipolar current I at a given voltage U_{0} cannot exceed the saturation limit

$$I_{\text{sat}} \sim 2 \mu \epsilon_0 U_0^2/d$$
 (3)

where μ is the ion mobility and ϵ_0 = 8.85 pF/m the permittivity. For ions in air at atmospheric density, this gives

$$I_{sat}$$
 (μA) \sim 4 U_{o}^{2} (kV^{2}) / d (mm). (4)

If currents above this are observed, they are either partly bipolar (Eqs. (3) and (4) invalid) or electron-carried (μ for electrons must be used).

The space charge dominated currents driven by high potentials (in the 5-10 kV range) make corona discharges nearly perfect galvanostatic ion and electron current generators, on the macroscopic level.

An important feature of the point-to-plane coronas is the so-called *electric wind*. As the charged particle flow in atmospheric density coronas is completely viscous (collision dominated), virtually all momentum and energy extracted by the ions from the electric field are transferred to the neutral gas molecules. A fairly strong, axial gas jet results (refs. 13,14), often employed to blow out candles in demonstration experiments and to carry ions to grammophone records for removal of excess surface charge. However, this jet also transmits up to half the discharge power to the plane (ref. 15), in the form of heat and of chemically very potent excited atoms and molecules.

Our electrochemical view of the point-to-plane corona discharge may be summarized by Fig. 2, illustrating schematically the various reaction regions and channels in the corona gas and on the surrounding conducting and non-conducting surfaces. The importance of synergy between the neutral, activated species and the charged species will be further discussed below.

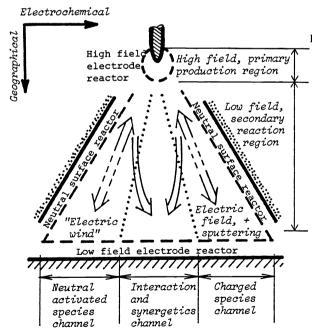


Fig. 2. Schematic diagram illustrating the main reaction regions and reaction channels of a corona electrochemical reactor (ref. 16).

Two intermixed streams of energetic particles emerge from the ionization region where they are produced: Neutral, activated species, carried by the electric wind, and charged species, carried by the electric field. The activated neutrals interact with the gas, the neutral (insulated or insulating) surfaces, and the low field electrode. Charged particles interact with the gas and with the low field electrode. The low densities preclude significant interaction between the two streams and their reaction products, except at the low field electrode surface, where important synergetic effects appear.

Energy, momentum and mass transport in unipolar coronas

 \overline{A} . Let us first look at a positive, unipolarly conducting 10 kV point-to-plane corona of gap 10 mm in atmospheric density air carrying the saturation current of 40 μA . The ionization region is stable at the point electrode; we assume no streamers.

For each electron-ion pair created in the ionization region an electron will impinge on the anode point and a positive ion will reach the plane cathode. On its much longer way (both in distance

and in potential) the positive ion will absorb energy and momentum from the electric field, and transfer them to the gas and to the plane electrode. Further, the ion might attach to or react with neutral constituents of the gas, and thus cause a transport of these to the plane. The relative importance of these effects can be estimated as follows:

- ** Total electric energy input per ion W = U.q = 10 keV
- ** Kinetic energy of the drifting ion, at most:

$$W_i = 1/2 (m_g + m_i) \cdot V_d^2 + 3/2 kT_g$$
 (the Wannier formula) (5)

where m_g , m_i are the gas molecule and ion masses, T_g the gas temperature, and $V_d = \mu \cdot E = (\mu n_g) \cdot (E/n_g)$ is the ion drift velocity. In our atmospheric air corona, with $\mu n_g \sim 5.10^{21}$ and $E/n_g \sim 40.10^{-29}$, we find $W_i \sim 0.06$ eV. The ion carries mainly its ionization energy. Likewise the directed momentum of the drifting in the foundate has indicated. tum of the drifting ion is found to be insignificant.

** The momentum transferred to the neutral gas causes the electric wind. Approximating the corona by a planar system of the average current density j_i and the average "reduced field" E/n_g , we find for a unit volume of gas :

Force $F_e = q n_i E$, i.e.acceleration $a = \frac{q n_i E}{m_g n_g}$. Time for the gas to cover the gap distance $l = t_g$,

$$t_g = \sqrt{2 l/a} = \sqrt{2 l m_g n_g/q n_i E}$$

Directed kinetic energy aquired by the gas:

$$W_g = q n_i E I$$

Energy spent by the electric field over this period:

$$W = U \cdot j_i \cdot t_g = I E j_i t_g$$
for $n_i : n_i = j_i/q \mu E$

Inserting for n_i:

we obtain $\frac{W_g}{W} = \frac{q \, n_i \, E \, l}{l \, E^2 \, n_i \, q \, \mu \, T_g} = \frac{t_i}{t_g} = \sqrt{\frac{j_i \, l}{2 \, (\mu n_g)^3 \, (E/n_g)^2 \, m_g}}$ (6)

Inserting $j_i\sim 40~\mu A/cm^2$, $E/n_g\sim~40.10^{-21}~V~m^2$, $\mu~n_g\sim~5.10^{21}~(Vms)^{-1}~,~m_g=~29\times~1.67\times10^{-27}~kg$ $\frac{"g}{w}$ = 1,4 % going into directed gas motion.

The resulting gas velocity is

$$V_g = \sqrt{2 1 a} = \sqrt{\frac{2 1 j_i}{m_g \mu n_g}} \sim 6 \text{ m/s}.$$

We can thus conclude that more than 95 % of the electrical energy input to a unipolarly conducting positive corona goes to the neutral gas, and only some percents of this energy goes into directed gas motion. The overwhelming part of the energy goes into gas heating, as positive ions hardly can excite neutrals in the low field drift region.

- B. A change in corona polarity, from positive to negative (non-streamer) corona in air, will cause one fundamental change. Considerably higher unipolar current can be passed, because an increasing proportion of the electrons will escape attachment in the increasing electric field and carry current without adding much space charge. These electrons will also cause excitation and dissociation of neutrals much further out in the gap than possible with positive ions.
- C. The ion flow to the passive electrode represents a transport of charge and of particles. In humid air, for instance, most ions will be hydrated, resulting in a selective water transport. What is the importance of such a selective transport relative to that of transport by diffusion and by electric wind?
- ** H_2O flux to the electrode at 40 $\mu A/cm^2$, singly hydrated ions :

$$J_{Hi} = j_i/q \sim 2.5.10^{18} \text{ molecules/m}^2 s$$
 (7)

** By thermal movement, at 50 % RH at 20°C ($n_{H_2O} = 3.10^{23} m^{-3}$)

$$J_{Ht} = n_{H_20} \overline{V}/4 = 4.4.10^{25} \text{ molecules/m}^2 \text{s} \sim 2.10^7 J_{Hi}$$
 (8)

This shows that charge, not chemical species nor energy, is the important quantity that unipolar corona ions transport to the passive electrode. Chemical species, excitation energy and thermal energy are primarily transported by the electric wind. All corona corrosion phenomena must be viewed in the light of these facts.

<u>D.</u> Finally, let us consider how the above picture changes when a substantial part of the corona current is carried as bipolar, repetitive, non-sparking streamers.

Firstly, the ionization region in front of the streamer head is not overly different from a stationary ionization region, except for its rapid movement through the gas. Secondly, the residual streamer channel behind the head is a true, collision dominated cold plasma, but not so dense as to make charged particle collisions of great importance (ref. 17). The total number of ions in that channel, and the field in which they move, are also comparable to what is found in a non-streamer drift region. Thus the ion energy balance should be not very different from inside a unipolar conduction corona. The main difference, then, is the transient presence of free electrons in the channel, of energies sufficient to excite and dissociate neutrals, even in a positive corona. In air and CO₂ most of the free electrons will disappear by dissociative attachment, forming chemically important neutrals

$$e^{-} + O_{2} + O^{-} + O$$
 (9)

$$e^{-} + CO_{2} + O^{-} + CO$$
 (10)

Optimization of coronas as non-equilibrium chemical (bulk) reactors
The conclusions to be drawn from the preceding sections are:

- $\underline{\mathbf{I}}$. The drift regions in unipolarly conducting coronas are useful as stabilizing series resistors, but hardly for anything else. Nearly all electrical energy spent there is used to heat neutral gas, with very little formation of chemically active species, especially in positive coronas. Any such production must take place in and near to the ionization region. Gas is pumped through that region by momentum transfer from the drifting unipolar ions, thus preventing accumulation of reaction products with subsequent back reactions.
- 2. The non-sparking repetitive streamer coronas have ionization regions that very rapidly traverse the corona gap. A given volume of gas thus experiences a short burst of activating electrons in the 12-16 eV range (refs. 18,19), followed by a somewhat longer stay with (ref. 20) 1-2 eV electrons in the residual channel. These electrons may also do some chemically useful work like dissociation (eqs. 9-10). Eventual unipolarly conducted current outside the channel is probably only a waste of energy, as is the residual current in the channel after the active electrons have disappeared. Thus, in the cases where energetic electrons are the ones utilized in the desired reaction, the corona should be fed by voltage pulses not lasting longer than the transit time of a streamer plus the free electron phase of the streamer channel. This has the added benefit of permitting much larger streamers, as the short duration of the voltage pulses prevents that the residual streamer channels develop into sparks. (Sparks mean arc channels in approximate local thermal equilibrium, where back reactions readily occur).

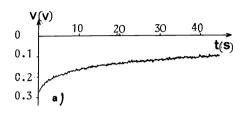
Electrochemical surface reactions in coronas

As early as 1893, Thomson (ref. 21) commented upon the similarities between current conducting gases and liquid electrolytes. In both types of media the current conducting mechanisms are fundamentally interconnected with chemical processes, while electrochemical reactions are induced at the interfaces between the media and metal electrodes. For the case of high temperature plasmas, this was again pointed out by Millet in 1967 (ref. 22). However, the electrochemical aspects of metal surfaces interacting with the drift (low field) regions of corona discharges have only recently received serious attention (refs. 23,24).

As any chemist knows, the interface between a metal and an electrolyte is a much more complicated system than the simple equipotential surface usually assumed by the gas discharge physicist. This is illustrated by Fig. 3a, showing the slow decay of the potential of a cleaned copper surface after 12 s exposure to a $7 \,\mu\text{A/cm}^2$ negative corona in air. The surface layer is clearly a dielectric, and its composition and properties turn out to depend on the metal, the gas, the ion current and polarity, and the nature and amount of neutral, excited species in the electric wind. The curves of Fig. 3b illustrate how a corona discharge can be used both to induce electrode surface changes and to aid in their measurement. These curves were obtained by repeatedly (and automatically) (ref. 25): a. Placing a gold sample as the low field electrode under a corona discharge for a time Δt_a , during which a charge ΔQ is passed; b. Moving the sample under a contactless surface

voltage probe for a time $\Delta \, t_b$, during which the measured potential V falls ΔV . In Fig. 3b each short vertical line represents a registration of the fall ΔV during phase \underline{b} , plotted at an abscissa value equal to the summed charge $Q = \Sigma \Delta Q$ received during all the phases \underline{a} . The hysteresis-like curve shapes are obtained by reversing the corona polarity, thus subjecting the samples first to anodic oxidation in a negative corona, then to cathodic reduction in a positive corona, and again to anodic oxidation in the negative corona.

After each change in polarity the gold surface rapidly reaches a stationary state, in contrast to oxidizable metals, such as copper or nickel. The potential difference between the oxidation and reduction plateaus (~ 1.3 V), and the equivalent capacitance of the layer ($\sim 400~\mu F/cm^2$) are comparable to voltametrically measured values for gold in aqueous acid solutions (refs. 26,27).



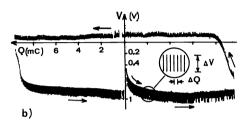


Fig. 3. Surface potential characteristics for corona exposed metal surfaces.

- a) Potential decay of a cleaned copper surface after 12 s exposure to 7 μA/cm² negative corona in air.
- b) Oxidation/reduction V(Q) diagram for a gold surface, obtained by repeated exposures to negative/positive coronas in air

Each vertical bar is the record of the surface potential decay after the surface has received a new increment of charge $\ \Delta \ Q$ by corona exposure.

With less noble electrodes than gold, another similarity to aqueous electrochemistry appears: Corona corrosion, uniform or pitting. Negative coronas in air of more than 10-20 % relative humidity will rapidly form a semi-liquid layer on anodic metal surfaces, containing water and NO ions from the air as well as dissolved impurities. Powered by the corona ion current, this layer seems to behave like any other aqueous electrolytic cell, as illustrated by Fig. 4. For instance, with aluminium as the anode, pronounced pitting occurs. Under dry conditions, on the other hand, negative air coronas cause only uniform anodic passivation of this metal, building up surface layers charged to several hundred volts. Positive coronas do not seem to pit aluminium.

CORONAS EFFECTS AND USES

Chemical synthesis

Many chemical products can be synthetized by corona discharges, but ozone is so far the only one of industrial importance. It is used for the treatment of water, preserving its natural taste and avoiding the smell of chlorine, and for other applications utilizing its large oxidation power. for instance in textile and paper industries.

The streamer type coronas used for ozone generation generally use air or oxygen filled short gaps where one of the electrodes is covered with an insulating layer in order to prevent streamer-arc transition. The relevant features of these so-called silent discharges for ozone production are:

- High energy electrons, providing a high yield of atomic oxygen for the main reaction : $O + O_2 + M \rightarrow O_3 + M$ where M is a molecule, often oxygen, carrying away the excess energy;
- Low gas temperature, necessary to avoid thermal dissociation of the ozone molecules already produced;
- High working pressure, around atmospheric.

Research is still needed to improve both chemical and energy yields, still too low (~ 2 % and 6% respectively in dried air). Progress might be obtained by different ways:

- There is no clear evidence that a unipolar conduction current does not flow in the silent discharge considered, in parallel with the streamers. This should be reduced to a minimum, as mentioned

earlier. For this, an externally pulsed discharge could bring improvements, but entails the use of more complex power supplies. Work is proceeding along these lines (refs. 28,29).

- Ozone is produced via excited and atomic oxygen, and oxygen dissociation can be catalyzed in several ways. Addition of SF_6 (ref. 30) or He (ref. 29) to air, or surface catalysis (refs. 31,32), all seem to involve excitation of nitrogen molecules, which in turn can dissociate and excite oxygen with high efficiency (ref. 33).

The catalytic effect of selected surfaces in production of activated nitrogen in coronas might also be used for chemical synthesis of other products, as ammonia (ref. 31). Yields for production of nitrogen oxides are still much too small for industrial exploitation, however.

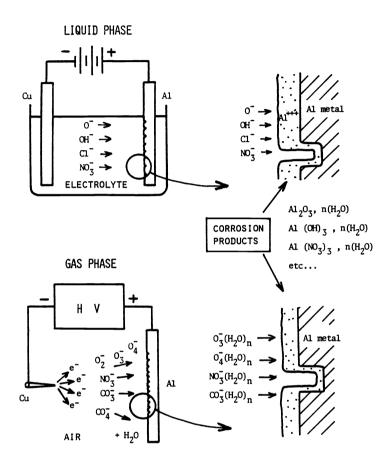


Fig. 4. Schematic representation of the pitting activity of negative ions, leading to comparable effects on aluminium anodes in an electrolyte and in a gaseous plasma (ref. 24).

Surface treatment

Coronas are widely used as chemical reactors for surface treatment. Their oxidation and reduction effects, passivating or corroding, have already been mentioned in the section dealing with the electrochemical behavior of the discharge. Depending on the material to be treated and the desired surface properties, the optimal corona gas composition, discharge parameters and operating procedure may be very different.

An industrially very important application is the surface treatment of polymers, in particular to increase their wettability and their adhesivity to ease printing, painting, sealing, coating, etc. This is achieved simply by corona discharges in ambient air. Discharge products transfer their activation energy to the polymer by breaking chains and creating radicals. These will rapidly react with the further impinging particles, with the environment, and even with gas coming from the bulk material. Polar bonds and hydrogen bonds formed in this way will increase the polymer's surface energy. The bonds most frequently encountered are C - O, C = O, C - O - O', C - OOH (ref. 34)

and, in smaller amounts, NH, NO, NO $_2$, NO $_3$ (ref. 35). The effect of the corona treatment increase with time and current until a saturation state is reached (ref. 36) (Fig. 5); then oxidation processes are counterbalanced by decarboxilation processes, as revealed by ejection of CO, CO $_2$ and H $_2$ molecules emitted from the surface (ref. 37). The chemical changes in the surface are often accompanied by changes in the structure, generally with a loss of crystallinity (ref. 35), that must be ascribed to the large number of short chains remaining on the surface. Other corona induced phenomena which may contribute to or affect the surface evolution are:

- Density variations, for instance a decrease induced by oxygen grafting or an increase due to cross-linking by active nitrogen, causing surface deformation or change in porosity;
- Migration phenomena, changing the surface topography;
- Sputtering phenomena, localized at the impact point of streamers.

If gap length of an air or oxygen corona is reduced so that the drift region becomes very small, the oxygen grafted on polymers rapidly diminishes (ref. 36) (Fig. 6a) due to increased etching. However, the induced surface energy (wettability, etc) is not reduced (Fig. 6b), even if the mechanisms involved must have changed.

The efficiency of a corona surface treatment also depends on polarity. Negative coronas generally appear to be less efficient than positive coronas, both for oxidation and etching. Contributing factors are that the energy delivered to the surface by charge neutralization is lower for negative ions than for positive ones and that the streamers generated in positive coronas submit the surface to concentrated bursts of high energy ions.

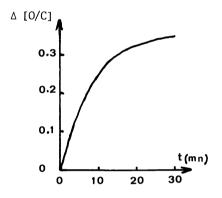
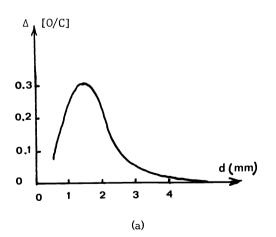


Fig. 5. Variation of the amount of oxygen fixed at the surface of polyethylene terephtalate films as a function of time (ref. 36).



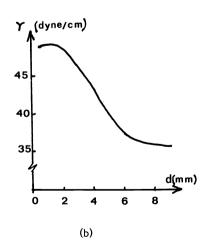


Fig. 6. Variation of the amount of oxygen fixed at the surface of polyethylene terephtalate films (curve a) and of surface energy (curve b) as a function of gap length (ref. 36).

The use of coronas to improve the wettability and adhesivity of polymer and other surfaces is well established. However, more recent work shows that coronas also may be used to reduce these quantities, typically by surface polymerization induced by coronas in fluorinated gases of pressures up to atmospheric. For instance, good results have been obtained on paper and textile materials by corona treatment in a $C_2 \ H_2 \ F_2$ atmosphere (ref. 38).

Finally, let us note that coronas have bactericidal effects. Exposure to air coronas will stop the growth of bacteria cultures, as recently demonstrated on Escherichia Coli.

Coronas and electrical insulation

It is a paradox that many of the gases which are used with high efficiency in corona chemical reactors and plasma etching also are among those most widely used for high voltage electrical insulation. Air, SF_6 , and SF_6 - N_2 mixtues are good examples. It follows that coronas usually are carefully avoided in enclosed high voltage apparatus. However, it is all the more important to know their chemical effects, especially as they also might be directed to improve insulation.

In these insulating gases, with their small but important impurities like $\rm H_2O$ and $\rm CO_2$, coronas will form a complex series of intermediate and final products. Typical are $\rm O$, $\rm OH$, $\rm O_3$, $\rm N_2O$, $\rm NO_2$, $\rm HNO_3$ in air (ref. 39), and $\rm S$, $\rm SF_5$, $\rm SO_2F_2$, $\rm SOF_4$ and $\rm SF_4$ in $\rm SF_6$ (ref. 40). These will in turn react with insulator and metal surfaces, and a general deterioration of the breakdown voltage and the overall system performance usually results. However, recent investigations show that coronas may be put to good use also here, be it as pretreatment or for insulation repair. For instance, traces of organic compounds like methylethylketone added to $\rm SF_6$ promise at the same time to increase the system breakdown voltage by corona stabilization (ref. 41), and to form corona-polymerized protecting coatings on damaged surfaces. Such corona-formed insulating coatings can also serve to render harmless the conducting particles that always occur in gas insulated systems and drastically reduce their performance (ref. 42).

Even when they are only considered as harmful, an intimate knowledge of the physical and chemical properties of coronas is necessary to prevent them in cheap and reliable ways. Knowledge of the ionization and electron attachment properties of gases over a wide range of energies has permitted the "tayloring" of gases for specific applications, usually combining high dielectric strength with other desireable properties (ref. 43). Mixtures of SF and N_2 , for example, are more cost effective than SF alone. The nitrogen slows down fast electrons more efficiently than SF does, to the low energies where attachment to SF becomes efficient. In other cases, gases which trap fast electrons are added to complement the SF, resulting in mixtures which can be better than any of the separate constituent gases (synergy) (ref. 44).

Related applications

Radicals chemistry. The radicals which represent one category of the species activated by corona can by themselves find some uses. One example is given by T. Inomata et al (ref. 45) who have investigated the possibility to improve combustion by the products of a silent discharge.

Diagnostic techniques. Mobilities of ions created by corona discharges can be used for gas diagnostics, for instance to detect and measure gas contaminants. Such apparatus, called "plasma chromatograph", is already commercialized, and usually works with a radioactive source for gas ionization. Time of flight methods are then used for mobility measurements. Alternatively, a similar method developed in the laboratory of two of the authors (M.G. and A.G.) uses corona to ionize the gas, while a varying retarding field is used to obtain the mobility spectrum of the ions (ref. 46,47).

Inversely, the variations of the discharge current due to variations of the mean mobility of the ionic species can also serve for detection of gas contamination. Fire detectors based on this principe are already industrially developed.

Electrostatic applications. The fact that unipolar corona drift regions contain ions of one sign only, and no plasma, is the obvious reason for their extended use as chargers in electrostatic apparatus, like precipitators, paint guns, fertilizer projectors, separators, xerographic copiers, voltage generators, and even lightning protectors. On the other hand, charges generated by other means, typically by triboelectricity, may easily cause coronas and sparks of their own, causing a considerable number of explosion accidents each year. A knowledge of coronas, their transition to sparks, and their interaction with the chemical environment is essential to further progress in these fields.

REFERENCES

- R.S. Sigmond and M. Goldman, in <u>Electrical breakdown and discharges in gases</u>, NATO ASI series, <u>B89b</u>, E.E. Kunhardt and L.H. Luessen (eds), Plenum Press, New York (1983).
- A. Goldman and J. Amouroux, in <u>Electrical breakdown and discharges in gases</u>, NATO ASI series, <u>B89b</u>, E.E. Kunhardt and L.H. Luessen (eds), Plenum Press, New York (1983).
- 3. M. Goldman and R.S. Sigmond, IEEE Trans.Electr.Ins. EI-17, 90 (1982).
- 4. G. Buchet and A. Goldman, in Proc. 1st:Int.Conf. on Gas Discharges, p.459, IEE Conf.Publ. No.70, London (1970).

- 5. R. Le Ny, Thèse Docteur 3e Cycle, Univ. Nantes, France (1981).
- 6. R. Le Ny, in Electrostatics 1983: Proc. 6th Conf. on Electrostatic Phenomena, p.173, Inst. of Physics Conf. Series No.66, Bristol, UK (1983).
- 7. G. Buchet, M. Goldman and A. Goldman, C.R.Acad.Sci.Paris 263B, 356 (1966).
- 8. E. Warburg, <u>Wied.Ann.</u> <u>67</u>, 69 (1899).
- 9. E. Warburg, in Handbuch der Physik 14, p.154, Springer, Berlin (1927).
- 10. A. Goldman, E.O. Selim and R.T. Waters, in Proc. 5th Int. Conf. on Gas Discharges, p.88, IEE Conf.Publ.No 165, London (1978).
- 11. Y. Kondo and Y. Miyoshi, Jpn.J.Appl.Phys. 17, 643 (1978).
- 12. R.S. Sigmond, <u>J.Appl.Phys.</u> <u>53</u>, 891 (1982).
- 13. R. Fieux and M. Boutteau, Bull. de la Direction des Etudes et Recherches d'E.D.F. France B2, 55 (1970).
- 14. R.S. Sigmond, in Proc. 7th Int.Conf. on Gas Discharges and their Applications, p.140, Peregrinus, London (1982).
- 15. A. Goldman, in Proc. 3rd Int.Conf. on Gas Discharges, p.275, IEE Conf.Publ.No. 118, London (1974).
- 16. R.S. Sigmond and M. Goldman, in Electrostatics 1983: Proc. 6th Conf. on Electrostatic Phenomena, p.81, Inst. of Physics Conf. Series No.66, Bristol, UK (1983).
- 17. R.S. Sigmond, J.Appl.Phys. 56, 1355 (1984).
- 18. G. Hartmann, C.R.Acad.Sci.Paris B275, 311 (1972).
- 19. G. Hartmann, in Proc. 3rd Int.Conf. on Gas Discharges, p.634, IEE Conf. Publ. No. 118, London (1974).
- 20. E. Marode and G. Hartmann, C.R.Acad.Sci.Paris B269,748 (1969).
- 21. J.J. Thomson, Recent Researches in Electricity and Magnetism, p.189, Oxford Univ. Press, London (1893).
- 22. J. Millet, Rev.Gén.Elec. 76, 45 (1967).
- 23. A. Goldman and R.S. Sigmond, J.de Physique 40 C7, 443 (1979).
- 24. R.S. Sigmond, A. Goldman and D. Brenna, in Proc. 6th Int.Conf. on Gas Discharges and their Applications, Part 1, p.82, IEE Conf. Publ. No. 189, London (1980).
- 25. R. Haug, Report Lab. de Physique des Décharges (1981).
- 26. E. Lenoir, Mémoire de DESS, Univ. de Paris XI (1982).
- 27. S. Trasatti, Electrodes of Conductive Metallic Oxides, Elsevier, Amsterdam (1980).
- 28. L.M.L.H. Hosselet, Electrochimica Acta 18, 1033 (1973).
- 29. C. Yamabe, H. Akiyama and K. Horii, in Proc. 7th Int.Symp. on Plasma Chemistry, Eindhoven, The Netherlands (1985).
- 30. M. Kogoma, H. Okamura, H. Sugimitsu, T. Moriwaki and S. Okazaki, J.Chim.Phys. 81, 513 (1984).
- 31. M. Miyamoto, H. Sugimitsu, M. Kogoma, T. Moriwaki and S. Okazaki, to be publ. in J.Chim.Phys. (1985).
- 32. M. Goldman, M. Lécuiller and M. Palierne, in Gaseous Dielectrics III: Proc. 3rd Int.Symp. on Gaseous Dielectrics, p.327, L.G. Christophorou (ed), Pergamon Press, New York (1982).
- 33. S. Okazaki, H. Okamura, M. Miyamoto, M. Kogoma and T. Moriwaki, in Proc. 7th Int. Symp. on Plasma Chemistry, Eindhoven, The Netherlands (1985).
- 34. D. Briggs, in Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy, D. Briggs and M.P. Seah (eds), Chapt. 9, Wiley, Chichester (1983).
- 35. O. Demuth, Thèse Docteur Ingenieur, Univ. de Paris VI (1984).
- 36. J. Amouroux, M.F. Revoil and M. Goldman, in Proc. 5th Int.Symp. on Plasma Chemistry, p.388, Edinburgh, UK (1981).
- 37. C. Laurent, C. Mayoux, S. Noël and N.I. Sinisuka, IEEE Trans. Electr. Ins. EI-18, 125 (1983).
- 38. A. Goldman, M. Goldman, J.Amouroux and F.Arefi, in Gaseous Dielectrics IV: Proc. 4th Int. Symp. on Gaseous Dielectrics, p.306, L.G. Christophorou and M.O. Pace (eds), Pergamon Press, New York (1984).
- 39. T. Ito, M.S.A.A. Hamman, M. Schiomi and T. Sakai, Proc. IEEE Annual Conf. on Electrical Insulation and Dielectric Phenomena, p.227, Pocono, USA (1981).
- 40. R.J. Van Brunt, T.C. Lazo and W.E. Anderson, in Gaseous Dielectrics IV: Proc. 4th Int. Symp. on Gaseous Dielectrics, p.276, L.G. Christophorou and M.O. Pace (eds), Pergamon Press, New York (1984).
- 41. A. Goldman, I.D. Chalmers and J.L. Dorémieux, in Proc. 4th Int. Symp. on High Voltage Engineering, p.32.07, Athens, Greece (1983).
- 42. M.O. Pace, J.L. Adcock, L.C. Frees and L.G. Christophorou, in Gaseous Dielectrics III: Proc. 3rd Int. Symp. on Gaseous Dielectrics, p.307, L.G. Christophorou (ed), Pergamon Press, New York (1982).
- 43. L.G. Christophorou and S.R. Hunter, in Electron Molecule Interactions and their Applications, Vol. 2, Chapt. 5, Academic Press, New York (1984).
- 44. S.R. Hunter and L.G. Christophorou, <u>J. Appl. Phys.</u> <u>57</u>, 4377 (1985).
- 45. T. Inomata, S. Okazaki, T. Moriwaki and M. Suzuki, Combustion and Flame 50, 361 (1983).
- 46. A. Goldman, R. Haug and R.V. Latham, <u>J. Appl. Phys.</u> 47, 2418 (1976).
 47. Y. Teisseyre and N.L. Allen, in <u>Proc.</u> 8th Int. Conf. on Gas Discharges and their Applications, Oxford, UK (1985).