SOFTAL ELECTRONIC
Report
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Corona pretreatment to obtain wettability and adhesion

The prerequisite for the printability and adhesion of plastics, metals and paper is the wettability with the printing inks, primers and bonding agents. If aqueous inks, primers and bonding agents are used, the wettability must often be set by pretreatment. Pretreatment with a high-frequency corona is a common method applied in the surface modification of plastic, metal and paper webs. The reasons for the wide acceptance of this method are the good results, the excellent possibilities of control and the easy handling of the equipment used.

This report deals with the essential features of corona discharges. Particular emphasis is laid on the unique possibilities for the surface modification of polymers.

The rule of thumb is that polymers are wetted by a liquid when the surface energy of the polymer exceeds that of the wetting liquid. A comparison with Table 2 shows that polymers are usually wetted by conventional organic solvents but not by water. However, a high degree of wettability is an essential condition for the application of water-based paints, primers and bonding agents which are becoming increasingly popular owing to their environmental compatibility. The required degree of wettability may be obtained by surface treatment by structural and chemical modification of the polymer surface without destroying the volume characteristics of the polymer. Figure 1 shows the effect of the substitution of hydrogen in PE on the surface energy. Corona treatment in atmospheric air increases oxygen and nitrogen concentration thereby increasing the surface energy and wettability of polymers.

Whereas in the case of printing the surface energy must not be set too high, to prevent the ink spreading, in the case of bonding complete spreading is desired to obtain as large a bonding area as possible. Experiments have shown that with complete wetting by the bonding agent a maximum bond is obtained where the polarity of the substrate coincides with that of the coating, so that under certain circumstances it is also desirable to set the polarity as well as the surface energy. However, upon detailed consideration of adhesion in composite systems, mechanical deformation in the proximity of the boundary layer must also be taken into account.

Wetting of surfaces

By wettability we mean the behaviour of a liquid on the surface of a solid. If for example water is applied to a hydrophilic surface, the water will spread forming a uniform skin of water. On a hydrophobic surface the same quantity of water will form a multitude of tiny drops. The angle between the surface of the drop and the surface of the material describes the wetting behaviour. Wetting depends on the chemical composition and structure of the surfaces in question, since the contact angle is defined by the surface energies of the liquid and the solid surface (Young's equation). The entire surface energy and the P fraction which stems from the polar atoms on the surface may be easily determined from the wetting behaviour. Typical values for the surface energy and polarity of polymers are listed in Table 1.

Material		surface energy (dyn/cm)	polarity P
polyethylene terephthalate	PET	43.0	0.02
polyamide 11	PA	43.0	0.02
polyvinyl chloride	PVC	39.5	0.10
polystyrene	PS	33.0	0.05
polyethylene	PE	31.0	0.04
polymethyl methacrylate	PMMA	29.8	0.28
cellulose triacetate		29.0	0.30
polybutyl methacrylate	PBMA	26.0	0.16
polyvinyl acetate	PVAC	24.9	0.32
polytetrafluoroethylene	PTFE	18.5	0.04
polydimethyl disiloxane		14.1	0.04

▲ Table 1

Table 2 ▼

Liquid	surface tension (dyn/cm)	polarity P
water	72.1	0.72
Benzylalkohol	40.0	0.29
Toluol	28.4	0.08
1-Oktanol	27.6	0.23
Tetrachlorkohlenstoff	27.0	0.01
Methanol	22.6	0.39
Ethanol	22.1	0.21

Principle of a corona station

The typical corona treatment station comprises a roller on electric frame potential, guiding the web to be pretreated, and a system of electrodes on high electric potential. The voltage is so high that electric flashover occurs between the electrode system and the roller. A dielectric coating on the roller or the electrodes creates an even distribution of the discharge sparks over the entire length of the station and prevents the formation of strong separate sparks. Using ceramic electrodes, however, detracts from the pretreatment effect (see Figure 2) and so these are only used in practice to treat metals. The typical electrode gap of 1.5 mm is very small which means that direct corona treatment of this nature, where the material to be treated is transported through the electrode gap, is limited to the treatment of web material. The electrode gap is flushed with ambient air to cool the electrodes and to evacuate the ozone which is always formed in an air-operated corona. The physical and chemical effects in the corona are very complex (see insert page 5), but the pretreatment effects can be easily controlled by varying the web speed and the power rating. The equipment is easy to handle and the pretreatment effects are easy to reproduce.

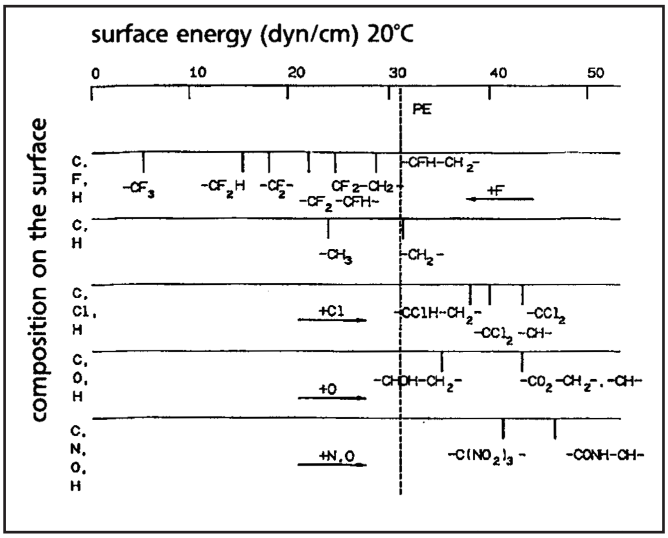


Figure 1
The effect of substitution of hydrogen in PE on surface energy

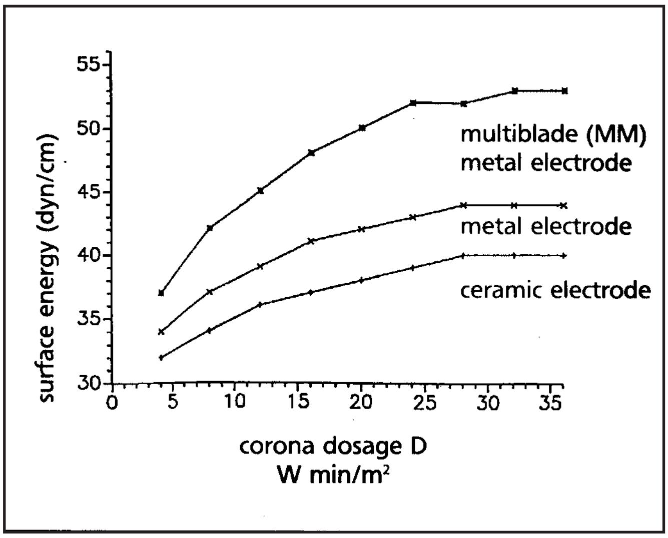


Figure 2
Effectivity of different etectrodes in the pretreatment of potypropylene

The effects of corona on polymers

When the corona strikes a plastic certain chemical reactions are initiated on its surface. These chemical reactions may lead to crosslinking, i.e. new links between adjacent molecule chains or to breaks in the molecule chains. Since the strength of atomic bonds depends on the chemical structure, the pretreatment effect of the corona also depends on the chemical structure of the polymer material to be pretreated, i.e. different polymers require different treatment intensities to obtain the same surface energy. It is known, for instance, that even the degree of crystallinity influences the effect of corona treatment.

The polymer is oxidized very quickly at the breaks in the molecule chains. The oxidation leads to various functional groups on the polymer surface, e.g. hydroxyl, ketone, carboxylic acid, epoxy, ether and ester groups, all of which contribute to an increase in surface energy. At present there is no known process to direct the chemical reactions released by corona treatment in one particular direction. However, it has been demonstrated that the balance between the chain break and crosslinking is affected by the presence of water molecules. This means in practice that the effect of corona treatment may depend on the relative humidity of the atmospheric air.

Owing to the slight degree of crosslinking in the modified surface the mobility of the chemical groups modifying the surface is also high. As a result of this a reduction in the pretreatment effect occurs in many polymers on storage subsequent to pretreatment. Although this undesirable occurrence can be minimized nowadays it still cannot be completely eliminated.

Molten plastic films such as those used in extrusion coating and laminating are oxidized by ozone treatment (SORBEX®) to render thern adhesive.

The corona treatment in practice

The corona treatment equipment comprises a high-power generator and an electrode system. Modern generators produce sinusoidal alternating current up to 20 kV with a frequency in the range of 20 to 40 kHz. A high frequency is favourable for the effectivity of the corona discharge since it produces more, albeit less intensive discharge sparks (see insert, page 5). It also ensures an even corona discharge and improves the service life of the dielectric.

The generator and the electrode system are matched to each other and therefore guarantee a high degree of utilization of the loaded electric energy. In modern generators the required impedance matching occurs automatically which means that there is always maximum coupling of electric energy in the electrode gap, irrespective of the type, thickness or width of the web to be treated.

In order to set a particular surface energy on the material a certain amount of energy must be applied to an area of the material to be treated. On the basis of numerous experiments the following extremely significant equation was found to determine the corona dosage D:

$$\boxed{D = \frac{P}{CB \times v}}$$

P: generator power
CB: corona width
v: web speed

Applying this formula it is possible to define the required corona dosage in a small pretreatment station on a laboratory scale and then extrapolate to production conditions.

The effect of the applied corona dosage depends on the electrode system. Although the wettability of water-soluble inks on plastics presents a certain challenge, it can be achieved for all polymers even under production conditions. The use of high-power electrodes developed in recent years has proved to be successful in this area. One of the most prominent of these high-power electrodes is the multiblade (MM) electrode system. In this system the corona power is distributed over 4 to 10 parallel electrode blades to obtain an even corona with many small sparks. Figure 2 illustrates the greater effectivity of the MM electrode in comparison with simple metal and dielectric electrodes. At the same time the reduction in surface energy during storage after treatment is less in cases where pretreatment was carried out using MM electrodes.

The required corona dosage depends on the surface condition of the polymer in each case and so the following values are only typical values. To obtain a surface energy of 45 dyn/cm the following output is needed with an MM electrode:

PETP	5	W min/m^2
LDPE	7.5	W min/m^2
PP copolymer	12.5	W min/m^2
PP homopolymer	25	W min/m^2

The dependency of the required corona dosage means that the pretreatment equipment must be adapted to the material to be treated to obtain optimum results.

To meet the requirements of the printing and conversion industry a number of corona treatment stations were designed. There are special units which may be integrated into printing machines for sheets, cables, cups or tubes. There are also special designs for UV painting systems, laminating machines, extrusion coating machines and folding box machines. The latter have been developed to improve adhesive properties where bonding is carried out using coldsetting adhesives. Figure 3 shows a unit for the pretreatment of plastic films with multiblade electrodes.

Today in practice corona widths of up to 8 m are treated at web speeds of up to 800 m/min.

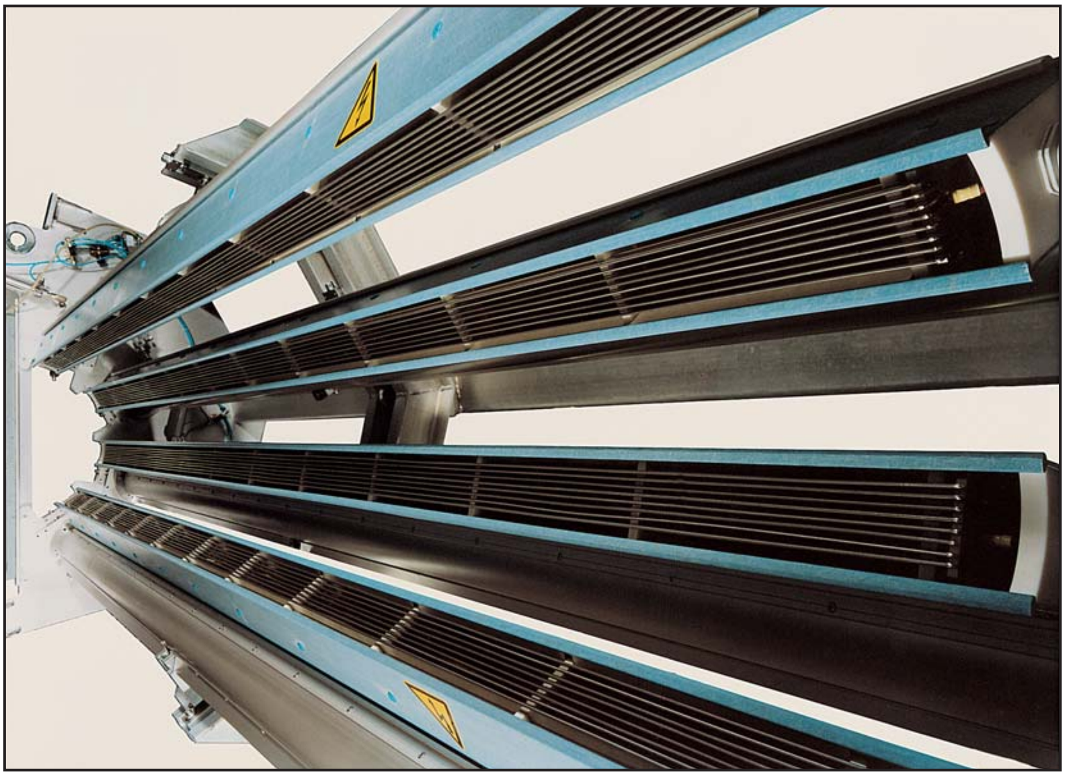


Figure 3: Corona treatment station for plastic films comprising a ceramic-coated roller with (retracted) multiblade electrodes

Figure 4
SOFTAL test inks and test pens (38 mN/m) to measure surface energy

Initial success has also been achieved with indirect corona systems where the material to be pretreated passes by the electrode. In this case a counter-electrode is not required and so this innovative method can be used to treat the outer surfaces of moulded parts of any thickness (e.g. foam rubber, cables, bottles).

SOFTAL has developed the IONAL system for such applications (see SOFTAL Report No. 114).

New developments and future prospects

The application of direct corona treatment where the materials are inserted into the electrode gap is limited to films up to a few millimetres thick. Among the latest developments attempting to overcome this barrier, plasma treatment at reduced pressure has become significant. Furthermore it seems possible with this process to set polarity as well as surface energy using suitable gases as part of the treatment. By adding hydrocarbons or silicon compounds to such plasma, stable semi-organic layers can be deposited on polymer materials. It has been discovered that the surface energy of these materials may be set and that the surface energy during storage at ambient temperature can remain stable (see Figure 5).

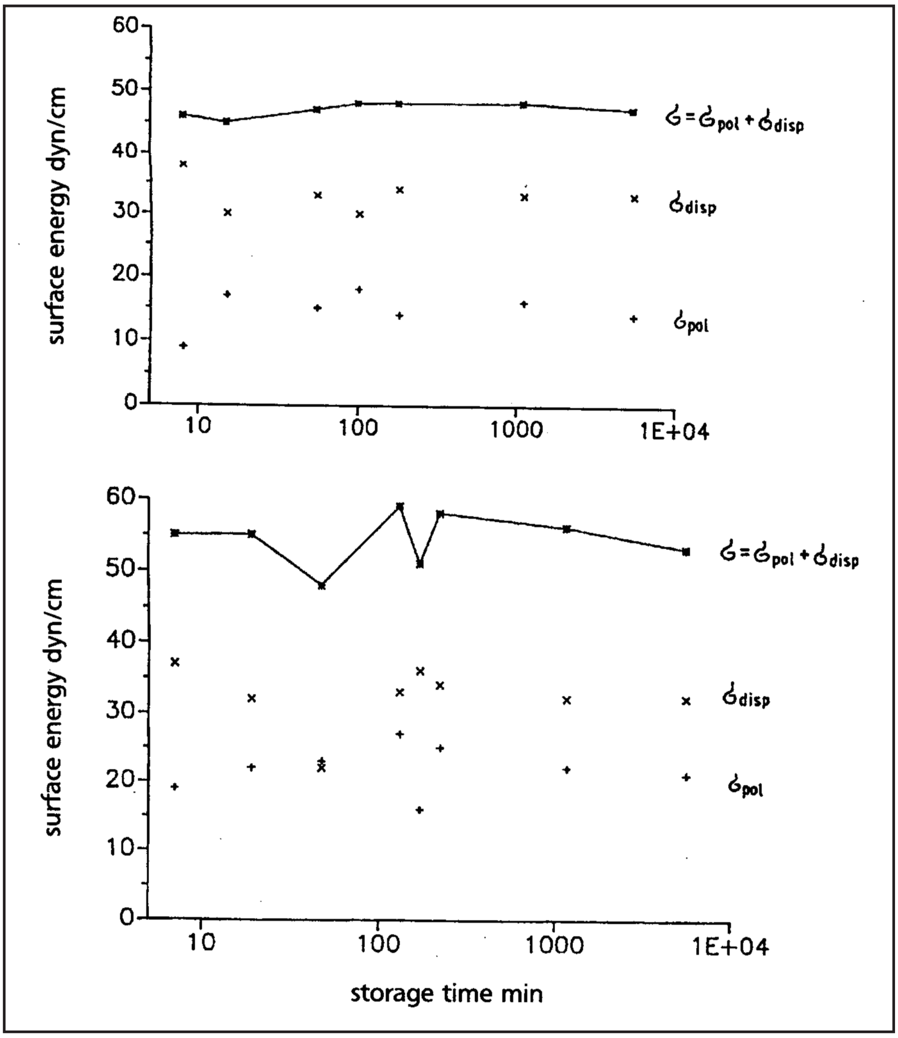


Figure 5
Surface energy of two a-Si:C:N:H layers plasma polymerized at approx. 20 mTorr of hexamethyl disfloxane during storage in air

The basic corona characteristics

Corona discharges occur when an electric current passes through a gas-filled capacitor with asymmetrical electrodes. Figure 6 shows a diagram of processes in a corona discharge in air for a model arrangement (positive wire and negative plate). If the voltage applied is low there is no electric flashover. However a slight electric current still flows because electrons (e^-) are released from the wire owing to the high electric field intensity in that area. The electrons are accelerated in the electric field towards the level electrode and collide with atoms and molecules of the ambient atmosphere. In the process, besides other electrons, an immeasurable number of molecule fragments, new combinations and positive ions (M^+) are produced, which may also be electronically excited (M^*). An area of high ionization is formed in the immediate proximity of the active electrode, which can be seen by macroscope since the electrically excited particles may return to their initial energetic state by the emission of light. In their drift the electrons are captured by neutral atoms and molecules forming negative ions (M^-), so that outside the ionization area the electric current is transported mainly by positive ions. Owing to this electron attachment atomic oxygen and subsequently ozone is formed in the air.

Irrespective of the polarity of the active electrode, the density of the negative (n_{e^-}) and the positive (n_{M^+}) charge carriers is approximately the same in the ionization area. The energy of the ions, 1 to 2 eV, is significantly greater than the thermal energy of the neutral gas particles. Since the corona gas remains cold, the thermal effect of the corona discharge is negligible. Therefore the ionization area is similar to the plasmas which occur with gas discharges at reduced pressures. The drift region on the other hand is characterized by the predominant presence of only one type of charge carrier, depending on the polarity of the active electrode. Whereas the ionization area acts as a chemical reactor, the ion energy (E_{M^+}) in the drift region is too low to set off chemical reactions. If the pressure in the capacitor gap is reduced, the ionization area spreads and the corona discharge becomes a plasma discharge.

If the electric voltage in the arrangement as described is increased, the production rate of ions increases more quickly than the electrode wire can absorb excess charges. The plasma of the ionization area expands and forms a conductive channel, or streamer, to the level electrode. A powerful current may flow: a temporary short-circuit occurs. The peaks of the expanding discharge channels are important for chemical processes in two respects. First, the energy of the positive ions (E_{M^+}) may exceed 100 eV at this point (this energy is very high by comparison with atomic binding energies in solids in the region of 4 eV) and second, the locally high electron energy (E_{e^-}) Of 12 ... 16 eV leads to the increased fragmentation of the surrounding molecules so that chemical processes take place mainly at the head of the expanding discharge channel. For practical application this means that the discharge sparks should be produced as frequently as possible. Since the typical appearance frequency of the streamers is 10 kHz, it is recommended to operate corona equipment at a higher excitation frequency than 10 kHz. Due to the electron attachments the streamer quenches very quickly after approximately 20 ns.

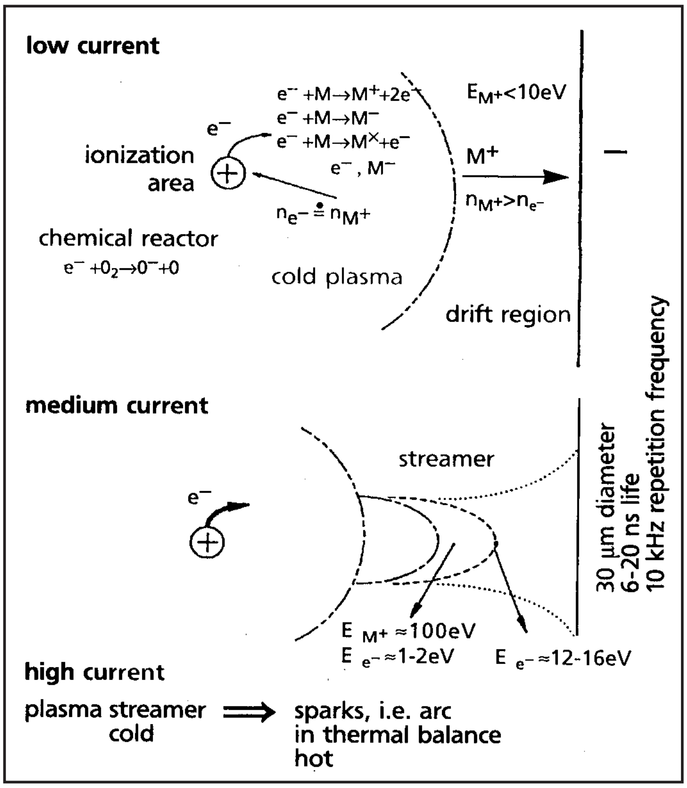
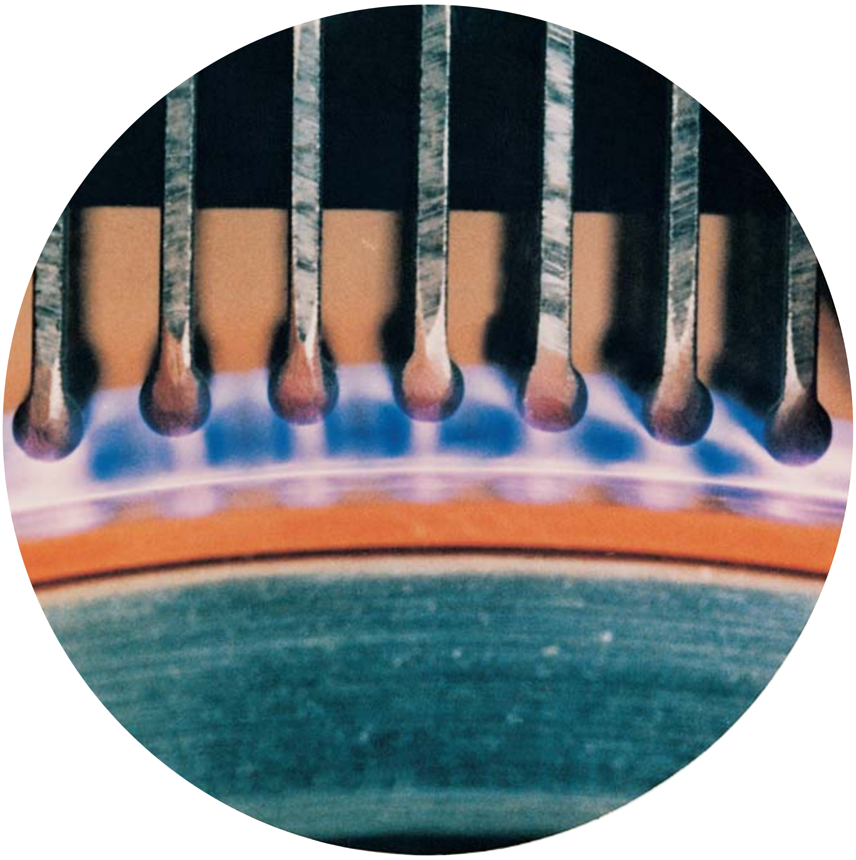
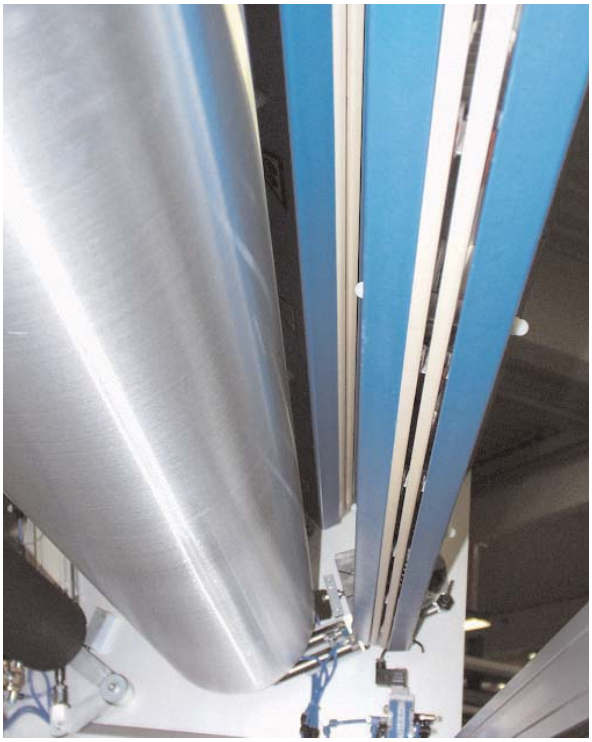


Fig. 6: Schematic diagram of corona discharge processes, positive wire opposite negative plate

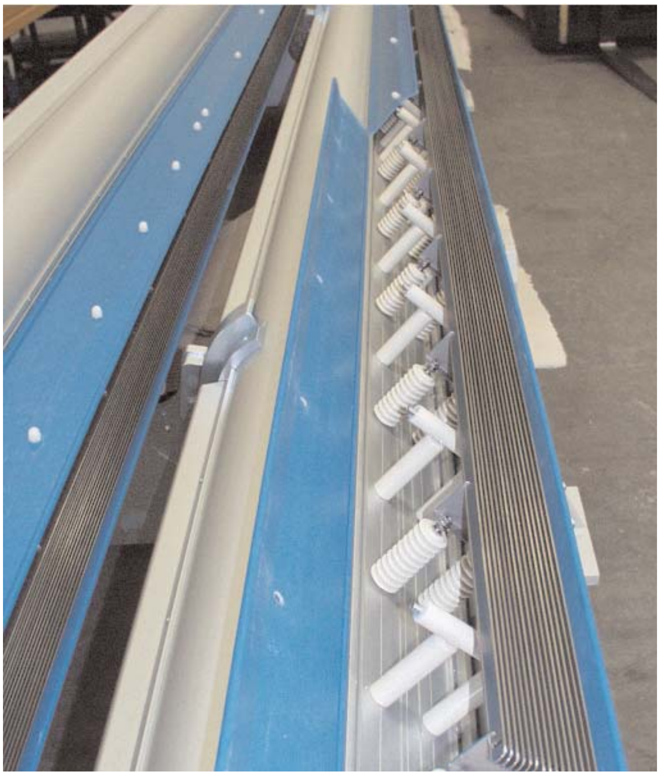
When the corona voltage is increased the electric current also increases and the electrodes are heated at the points where the discharge sparks strike. With the resultant increase in electrode temperature the thermally stimulated charge carrier emission exceeds the field emission. The discharge sparks then produced are thermal arcs which are in thermal balance, that is hot, as opposed to the plasma like streamers. When poly mers are exposed to these hot sparks, a heat treatment of the material occurs which may burn holes in films. In corona treatment the aim is to have as regular a spark pattern as possible and so high currents are only used where they can be distributed over a number of electrodes (multiblade electrode system).



Corona discharge with Multi-blade-electrode (SOFTAL patent), BOPP-film and silicone roller



Electrode system CBAE for single side treatment of conductive and isolating film.



Electrode system CRI for single side treatment of BOPP film.

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