# Light Emission due to Peeling of Polymer Films from Various Substrates

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## Synopsis

The intensity of the light which is emitted when polymer films are peeled mechanically from various substrates under varying conditions of vacuum was measured by a photo-multiplier, amplifier, and pen-writing oscillograph combination. The wavelength of the emitted light depends upon the sign of static charge generated on the surfaces of the film and the substrate by peeling. In the PVC–glass sample system, the radiation consists of two bands of light, namely a shorter band (~4900 Å) and a longer one (5200–5900 Å), but in other sample systems (e.g., PVC–copper, PVAc–glass), only the shorter band was observed. The latter band appeared at the higher degree of vacuum. Comparing these bands with discharge spectra of nitrogen gas and using various substrates, it was proved that the light of the shorter band can be attributed to the light of gas discharge and that of the longer one, to the light of glass luminescence. Generally speaking, the intensity of the light of the longer band is weaker than that of the shorter one. Total intensity of light changes with peeling speed and reaches a saturated value. This type of saturation may be interpretable if the streamer process is taken into consideration as a mechanism of electrostatic discharge. Total intensity of light depends also upon the pressure in the peeling chamber. At pressures of $10^{-2}$–$10^{-3}$ mm Hg, the total intensity of light becomes minimum. This phenomenon is interpreted as a change of discharge potential according to Paschen's law under the condition of constant width of discharge gap.

## INTRODUCTION

The phenomena of light emission observed in the peeling process of polymer film from substrates have usually been considered to be attributable to electrostatic discharge, which is one of the dissipation mechanisms of electrostatic charge. Karasev et al.[1] showed that if various polymer films are peeled from glass mechanically in an average vacuum of 1–0.1 mm Hg, then, at a certain threshold of peeling speed, the gas in the chamber luminesces brightly owing to gas discharge. They also recognized that under further reduction of the pressure in the chamber, luminescence of glass is observed instead of gas discharge under the action of the electrons

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driven out from the polymer film* by the strong electric field set up in the space between the two substances. Williams[2] measured the intensity and wavelength of radiation due to spontaneous breakdown between high polymer (polyvinyltoluene) and glass vessel occurring in the cooling after thermal polymerization by pulse-height discriminator and spectrograph, and showed that the light is radiated from the glass and that the intensity of radiation diminishes gradually with time.

As stated above, the light emitted from a polymer–glass system consists of the radiation due to gas discharge and the luminescence of glass, and high energy electrons take part in this light emission process. When two substances are brought into contact with each other, it is assumed that positive and negative charges are generated on the interface and that they are in an electrical equilibrium before separation of the substances, i.e., an electrical double layer is formed. The breakdown of this equilibrium by peeling action sets up a strong electric field between the substances. Hence, electrons existing casually in the space are accelerated by the electric field and ionize the gas, producing many additional electrons. These electrons are attracted to and strike against the positively charged substance. If this is the luminous body, secondary luminescence may be expected to appear besides the light of spark.

In any case, we can assume that the electrical double layer has been constructed previously at the interface of two substances, whatever the mechanism of the generation of the electrical double layer is, and that the double layer is separated by the peeling action. Thus, the peeling action corresponds to the charging of two electrodes placed at a certain distance from each other, as in a condenser.

From the above considerations, it is clear that there are some relationships between the light emission and the electrification of the substances. In this paper these relationships, especially the relationship between the intensity and the wavelength of the emitted light, the relationship between the intensity and the sign of electrostatic charge, as well as the dependence of light intensity on peeling speed (or peeling load) and on the pressure in the peeling chamber, were studied to make clear some of the mechanisms of the dissipation of electrostatic charge.

## APPARATUS AND SAMPLE SYSTEMS

### Apparatus

In order to measure light intensity which is thought to be irreproducible, an apparatus that can provide the conditions of light emission reproducibly and a stable detecting instrument are required. In this experiment, pres-

* Karasev et al.[1] proposed that electrons are driven out from polymers. It may rather be appropriate to assume the existence of electrons between or on the surfaces of two substances (adhered electrons, electrons of impurity, and those existing in the space).
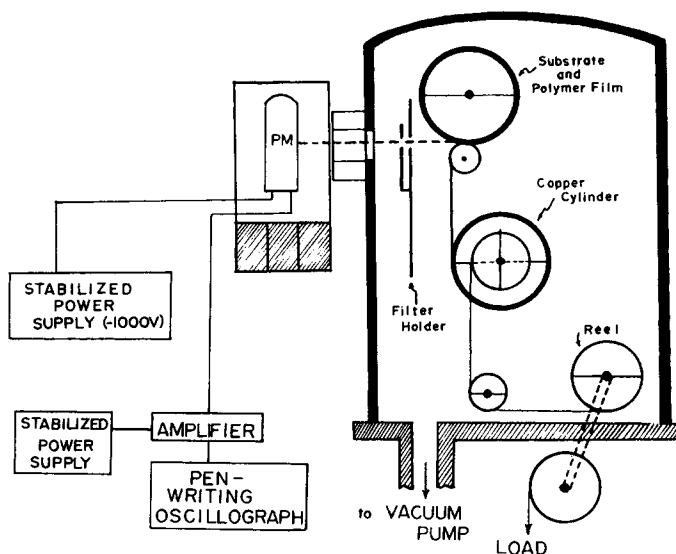
Fig. 1. Block diagram of apparatus employed in peeling under vacuum (right-hand side) and that of detector system (left-hand side).

sure in the peeling chamber and peeling speed (or peeling load) were chosen as the conditions of light emission.

The diagram shown on the right-hand side of Figure 1 shows the apparatus employed in peeling polymer films from various substrates in vacuum. Cylindrical glass and copper substrates were used in order to keep the distance between the point of light emission and the detecting instrument constant. A polymer film adhered to the cylinder was connected to another copper cylinder with a reel. This reel was coupled with another reel by a wire rotating outside the glass bell jar under the action of load. This rotation leads to the peeling of the polymer film from the substrate. The linearity between the load and the force which is conveyed to the film was ascertained using a spring balance. A filter holder with a slit which avoids ghosts was put in front of the sample system. The pressure inside the glass bell jar was changed from atmospheric pressure to $10^{-4}$ mm Hg, measured by a Geissler tube and an ionization gauge.

The block diagram of the detector system used in this experiment is shown on the left-hand side of Figure 1. The emitted light is caught by a photomultiplier tube (Tohshiba MS-9S) and converted into photocurrent. The photomultiplier tube was set in a light-tight metal box together with a dry box filled with silica gel. The minimum detectable light flux was $10^{-10}$ lumens. The output current was amplified by a two-stage difference amplifier and recorded as a function of time by a pen-writing oscillograph (Watanabe Instruments Corp. WR211-3C).

The equipment was calibrated by means of a ferrioxalate actinometer. A mercury lamp and a solution filter (combination of 0.84 g/l. $KMnO_4$

solution, 1 cm; and 375 g/l. $CuCl_2 \cdot 2H_2O$ solution, 0.5 cm) were used to get 4358 Å monochromatic light.  The relationship between the number of photons that entered the photocathode in unit time and the area under the luminescence glow curve recorded on the chart was ascertained.  Hence, we can determine the number of photons that entered the photocathode by comparing the area measured in the experiments with this calibration curve.

## Sample Systems

Cylindrical glass substrates (diameter 60 mm, length 150 mm) were chiefly used, but in some cases copper bases were used.  Poly(vinyl chloride) (PVC) and poly(vinyl acetate) (PVAc) were chosen as polymer samples.  PVC films generally acquire a negative charge when they are peeled from glass, but get a positive charge when peeled from copper substrates. On the other hand, PVAc films charge positively against glass.

The general method of preparing the sample system was as follows.  The substrate was dipped and rotated in a polymer solution.  During the rotation, the solvent evaporated and the polymer was deposited on the substrate.  After desiccation under vacuum, polymer films of an average thickness of 0.05 mm were obtained.  At room temperature, PVAc films could not be stripped smoothly, because the glass transition temperature is significantly lower.  The PVAc sample system, therefore, was prepared as a sandwich.  A piece of thin cotton cloth was wound around the half-dried sample cylinder, and this system was again dipped in the solvent and dried under vacuum for about a week (the evaporation velocity was maintained at a slow rate at first and later accelerated).  In this way a substrate–polymer–cotton cloth base sandwich was obtained.  The thickness of the cloth was about 0.03 mm.  As a result, the PVAc film was easily stripped from the substrate and none of the PVAc film remained on the substrate.

## EXPERIMENTAL

Peeling of polymer films was carried out under the action of load.  As stated above, the force conveyed to the film was linear with the outer load. Dependence of the peeling speed on the outer load for the PVC–glass system is indicated for each pressure in Figure 2.  Similar curves were obtained for the other sample systems.  Thus, it is possible to use outer loads for the purpose of estimating the peeling speed.  The speed of peeling was determined by the width of the luminescence glow curve and the chart speed of the recorder by assuming that light is emitted from the very moment of stripping and that there is no retardation in the radiation process at the beginning and the end of peeling (Fig. 3).

First of all, the wavelength distribution of the emitted light was estimated.  The spectra of emitted light were obtained at constant pressure and peeling speed, using a series of cut filters rather than the spectrograph because of low intensity of the emitted light.  Each filter passes 90% of incident light and cuts off the light of shorter wavelengths with a sharpness
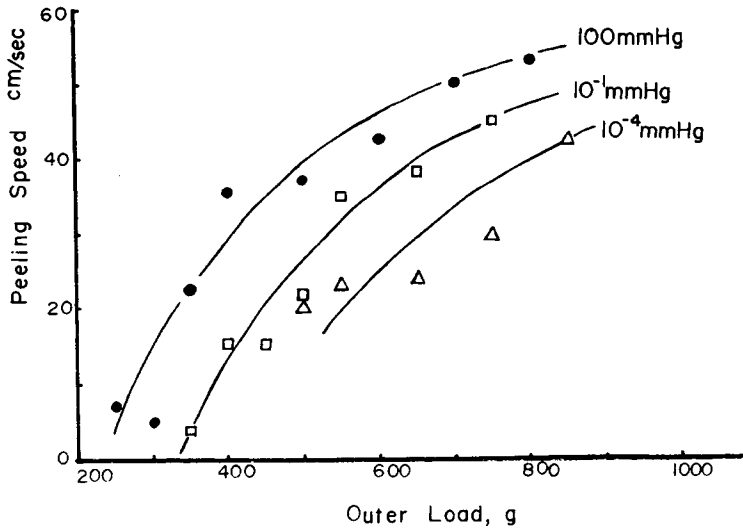
Fig. 2. Dependence of peeling speed upon outer loads for PVC–glass system at each residual air pressure.
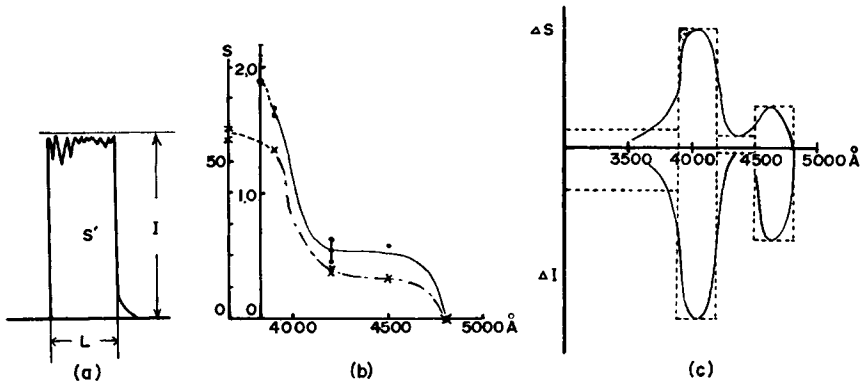


Fig. 3. Example of luminescence curve and of wavelength distribution curve of light intensity. (a) Luminescence curve described by recorder: I, length between baseline and top of luminescence curve; S′, area under luminescence curve; L, width from beginning to end point of luminescence curve. When chart speed is R, L/R is the period of luminescence. Therefore, the area under the luminescence curve recorded in unit time is equal to $S = S'/(L/R)$, that is, proportional to the number of photons that entered the photocathode in unit time. (b) S and I plotted as a function of wavelength characteristic of the filter: Values of S and I on ordinates correspond to those obtained when no filter is interposed; these values are proportional to photocurrent produced when the whole of the emitted light enters the photocathode. (c) Wavelength distribution of emitted light: ΔS is the difference between the values of area at different wavelengths; ΔS is proportional to the number of photons which exist in such a wavelength region. These values are plotted as a histogram, as shown by the dotted line; and from this histogram we can easily obtain a distribution curve (smooth curve). ΔI is obtained similarly.

of 20 Å above or below the wavelength characteristic of the filter. The wavelength distribution of light was obtained measuring the decrease of maximum intensity and area under the luminescence curve when a graduated series of filters were interposed in turn between the photomultiplier and the sample system. The wavelength distribution curves estimated from the area were coincident with those obtained from the maximum height of the luminescence curve (Fig. 3).

The maximum light intensity was measured changing outer load at constant pressure. The variation of light intensity in the pressure range of $10^{-2}$–$10^{-4}$ mm Hg under constant outer load was also investigated.

In this paper the average values of data obtained in five runs of peeling are cited.

Photographic measurement was also carried out to estimate the qualitative aspects of radiation. A Polaroid Land camera was used. Sensitivity of the film was 3000 (ASA).

## EXPERIMENTAL RESULTS AND DISCUSSION

### Photographic Measurement

Total light was photographed using a Polaroid Land camera to investigate qualitative aspects of the light emission. The PVC–glass system was chosen as a sample. The results are not given in this paper because it is impossible to get clear replicas of the positives obtained by the Polaroid camera. From the positives we could see that total intensity and the width of the discharge gap increase with peeling speed at constant pressure. The intensity of the light depends upon the residual gas pressure in the chamber under conditions of constant peeling speed. The width of the discharge gap reaches a constant value at high peeling speed.

### Wavelength Distribution

Experiments were carried out at an average peeling speed of 37 cm/sec. Figure 4 shows an example of the wavelength distributions of the light emitted in a PVC–glass system (in this case, glass charges positively) under the condition of constant peeling speed at pressures of $10^2$–$10^{-4}$ mm Hg. Each curve has two peaks. At the higher residual gas pressure, both of these peaks ($\alpha$- and $\alpha'$-peak) appear in the shorter wavelength region ($\sim$4900 Å); but at the lower gas pressure, $\alpha'$-peak and a new peak ($\beta$-peak, 5200–5900 Å) appear in the longer wavelength region. Table I shows the spectra of the light at each pressure for the PVC–glass system. It is interesting to estimate the origin of these peaks. For the purpose of identifying the sources of the light, the wavelength distribution curves (Fig. 4) and the data summarized in Table I were compared with the discharge spectra of nitrogen gas in the Plücker tube. The discharge spectra of nitrogen gas are given in Table II. These spectra do not result from neutral atoms, but from ionized atoms. From Tables I and II, we can con-
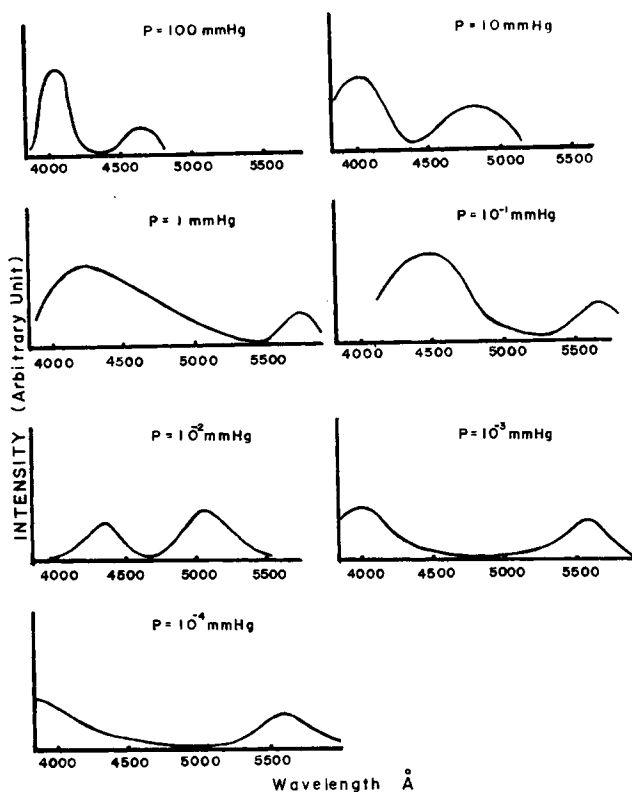
Fig. 4. Spectra of emitted light for PVC–glass system at a constant peeling speed of 37 cm/sec. $P$ denotes the residual air pressure in the chamber:  abscissa, wavelength (Å);  ordinate, intensity (arbitrary units).

clude that the $\alpha$- and $\alpha'$-peaks are attributable to the light due to the discharge of nitrogen gas existing in the chamber.   The existence of these two peaks should be expected in the peeling process which corresponds to the operation of supplying high voltage to the gas in the space between the two

TABLE I
Spectra for PVC–Glass System

| Pressure, mm Hg | Band of shorter wavelength, Å $\alpha$-Peak | Band of longer wavelength, Å | |
|---|---|---|---|
| | | $\alpha'$-Peak | $\beta$-Peak |
| 100 | ~4300 | 4300–4800 | |
| 10 | ~4800 | 4800–5200 | |
| $10^0$ | ~5000 | | 5500–5900 |
| $10^{-1}$ | ~5000 | | 5300–5900 |
| $10^{-2}$ | ~4700 | 4700–5500 | |
| $10^{-3}$ | ~4500 | | 5200–5900 |
| $10^{-4}$ | ~4500 | | 5200–5900 |

TABLE II
Discharge Spectra of Nitrogen Gas

| Band of shorter wavelength, Å | | | Band of longer wavelength, Å | | |
|---|---|---|---|---|---|
| 3955.8 | 3995.0 | 4035.0 | 4601.5 | 4607.1 | 4613.9 |
| 4227.7 | 4236.9 | | 4621.4 | 4630.5 | 4643.0 |
| | | | 4788.2 | 4803.3 | 5001.3 |

TABLE III
Spectra for PVC–Copper System

| Pressure, mm Hg | Wavelength of emitted light, Å |
|---|---|
| $10^{-2}$ | 4200–4900 |
| $10^{-4}$ | 4000–5000 |

electrodes. The $\beta$-peak is thought to be due to the luminescence of glass, because this peak did not appear when a copper substrate (copper in the PVC–copper system charges negatively) was used instead of glass. In this case, only the peaks that correspond to the $\alpha$- or $\alpha'$-peaks were obtained (Table III and Fig. 5).

The mechanism of the phenomenon described above may be understood as follows. In the process of breakdown of the electrical equilibrium between positive and negative charges on the interface, the electric field V due to the charges increases as the distance $d$ between the electrodes (in this case polymer film and substrate) increases, and the breakdown of the gas takes place when the strength of the electric field V attains the initial discharge potential. Electrons emitted in the discharge process are attracted
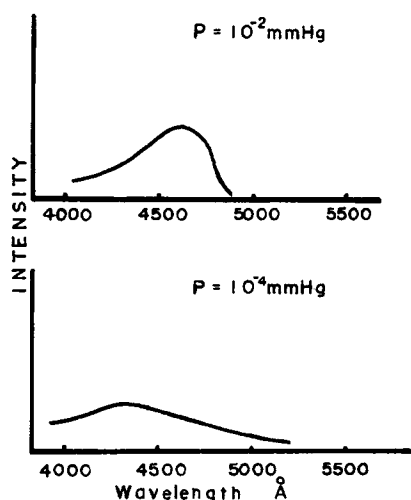


Fig. 5. Spectra of emitted light for PVC–copper system at a constant peeling speed of 40 cm/sec: abscissa, wavelength (Å); ordinate, intensity (arbitrary units).

TABLE IV
Spectra for PVAc–Glass System

| Pressure, mm Hg | Band of shorter wavelength, Å α-Peak | Band of longer wavelength, Å α'-Peak |
|---|---|---|
| 10 | ∼4500 | 4500–4900 |
| 10⁰ | | –4900 |
| 10⁻¹ | ∼4000 | 4000–4800 |
| 10⁻² | ∼4300 | 4300–4500 |
| 10⁻³ | ∼4300 | 4300–4900 |
| 10⁻⁴ | ∼4500 | |

to and strike against the positively charged substance (e.g., glass in PVC–glass system). Thus, if the positively charged substance is luminous, the luminescence may be observed, that is, a phenomenon similar to cathode luminescence occurs.

The spectra of light radiated from the PVAc–glass system are summarized in Table IV and Figure 6. In this case, the glass substrate is electrified negatively. Only the $\alpha$- and $\alpha'$-peaks, which are thought to originate from the gas discharge, appear. It is clear that radiated electrons move to and are trapped on the PVAc film. Hence the luminescence of glass is not observed although the sample system contains a glass base. In the PVAc–copper system, the $\beta$-peak, of course, does not appear (Fig. 7).

The $\beta$-peak does not appear in the PVC–glass system at the higher residual gas pressure because both the mean free path and the range of the electrons become shorter on account of the greater density of gas.
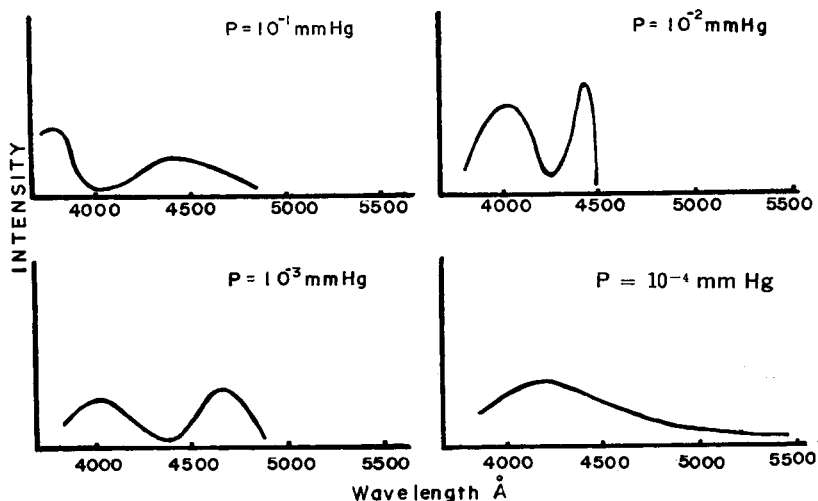


Fig. 6. Spectra of emitted light for PVAc–glass system at a constant peeling speed of 47 cm/sec: abscissa, wavelength (Å); ordinate, intensity (arbitrary units).
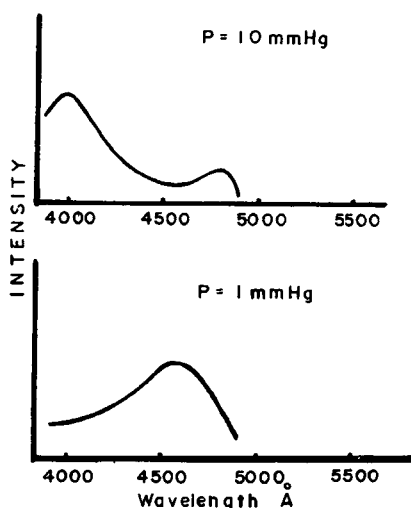
Fig. 7. Spectra of emitted light for PVAc–copper system at a constant peeling speed of 47 cm/sec: abscissa, wavelength (Å); ordinate, intensity (arbitrary units).

From the experimental results, it is concluded that there exist two bands of light radiated in the peeling process of polymer films from glass. The shorter band ($\sim$4900 Å) appears in all cases, but the longer one (5200–5900 Å) depends upon the sign of the charge generated on the surface of the glass base, upon the pressure, and on the kind of substrate.

It is impossible to decide whether the radiation is monochromatic or not. If we choose, however, the value 4300 Å as the wavelength for the $\alpha$- or $\alpha'$-peak and 5700 Å for the $\beta$-peak, the numbers of photons entering into the photocathode are $7 \times 10^{-13}$ photons/sec of mean energy 2.88 eV (4300 Å), and less than $5 \times 10^{-12}$ photons/sec of mean energy 2.17 eV (5700 Å),[*] respectively. (The quantum yield of the actinometer is lower for 5700-Å light than for 4358-Å light used in calibration; therefore the actual number of photons for 5700-Å light is thought to be far smaller than that obtained using the calibration curve.) So we can also conclude that the light intensity due to the gas discharge is greater than that of the luminescence of glass.

## Dependence of Light Intensity on Peeling Speed

Figure 8 shows the light intensity plotted as a function of the outer load for the PVC–glass system. In other sample systems, similar curves were obtained. As seen from each curve, the intensity of light approaches a constant saturated value asymptotically. This tendency seems to be interpretable by comparing the luminescence curves with the curves which show the dependence of residual charge on the surface upon peeling speed

* It is necessary to consider the difference in sensitivity of the photomultiplier for the light of the standard wavelength used to calibrate the actinometer and of the wavelength of the experimentally obtained peak.
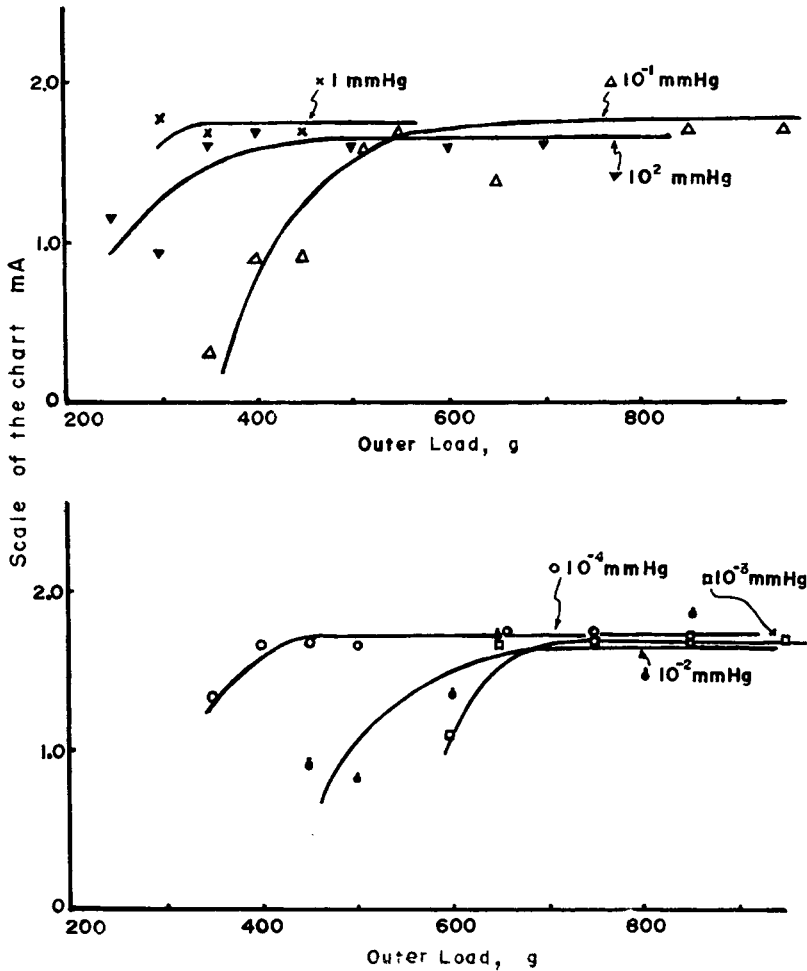
Fig. 8. Light intensity as a function of outer load at each residual air pressure for PVC–glass system: abscissa, outer load $W_{out}$ (g); ordinate, scale of the recorder chart (mA). Residual air pressures in the chamber are as follows: ($\blacktriangledown$) $10^2$ mm Hg; ($\times$) 1 mm Hg; ($\triangle$) $10^{-1}$ mm Hg; ($\spadesuit$) $10^{-2}$ mm Hg; ($\square$) $10^{-3}$ mm Hg; ($\bigcirc$) $10^{-4}$ mm Hg.

(Fig. 9), that is, it is considered that leakage of the charge through the surface of the dielectrics partially diminishes the potential between two substances at the low peeling speed, so that the light intensity decreases.

TABLE V
Peeling Load and Peeling Speed at a Pressure of 100 mm Hg

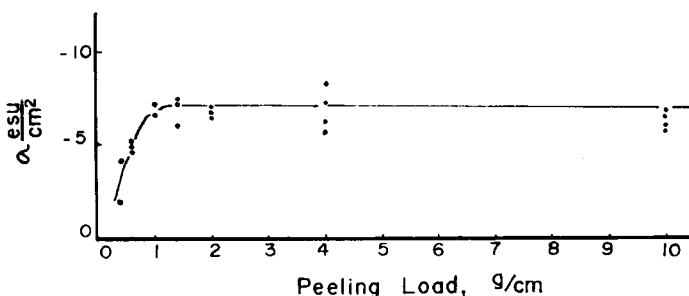| Outer load, g | 250 | 300 | 350 | 400 | 500 | 600 | 700 | 800 |
|---|---|---|---|---|---|---|---|---|
| Force conveyed to film, g | 24 | 42 | 66 | 90 | 137 | 180 | 245 | 360 |
| Peeling speed, cm/sec | 7.3 | 4.9 | 22.4 | 35.4 | 37.0 | 42.5 | 50.0 | 53.1 |

Fig. 9. Dependence of electrostatic charge upon peeling load for PVC–glass sample system. This curve was obtained using a Faraday cage and the vibrational reed electrometer: abscissa, peeling load (g/cm); ordinate, electrostatic charge (esu/cm²).
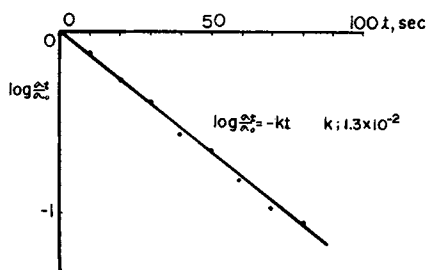


Fig. 10. Decay curve of residual charge on PVC film. This was measured using a Faraday cage and the electrometer. Size of sample film was 11 × 5 × 0.05 mm: abscissa, time $t$ (sec); ordinate, $\log \dfrac{\sigma_t}{\sigma_0}$ ($\sigma_0$ and $\sigma_t$ denote the residual charge at $t = 0$ and $t = t$, respectively). This curve is expressed by the equation

$$\log \frac{\sigma_t}{\sigma_0} = -kt$$

where $k$ is equal to $1.3 \times 10^{-2}$.

However, as we can see from Figure 8 and Table V, the peeling speed at which the radiation takes place is comparatively high. From the decay curve of the charge on the PVC film (Fig. 10), it is obvious that the charge cannot leak at such a high peeling speed. So it is necessary to interpret this saturation phenomenon by introducing the mechanism of discharge. In this case, we can assume that dissipation of charge occurs only through the spark discharge process.

In a general electrostatic discharge, complete breakdown is attained through the streamer mechanism, because there is no supply of electric current and no continuous electron emission. In the electron avalanche, the numbers of electrons and positive ions are largest at the head and increase with electric field $E$ and with the distance $d$ between the two electrodes when the strength of the electric field is maintained at a constant level. The density of the positive ions which are produced by high energy

NEGATIVE ELECTRODE



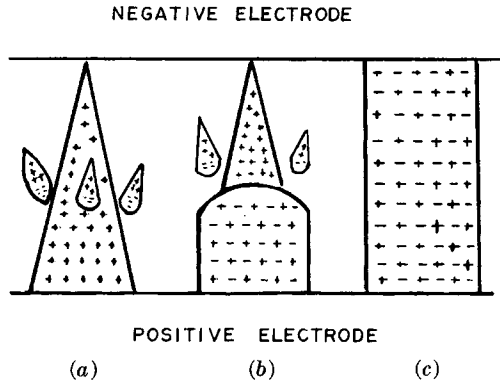POSITIVE ELECTRODE

$(a)$          $(b)$          $(c)$

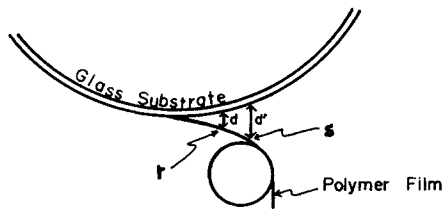Fig. 11. Development of streamer.



Fig. 12. Discharge in the peeling process.

electrons in the ionization process and the sum of $E$ and the potential $Er$ induced by the positive ions become largest in close proximity to the positive electrode.   Such electron avalanches, however, are so weak and positive ion transfer is so slow that only partial electrical breakdown takes place.   In the partial breakdown, many electrons accumulate near the positive electrode, because some photons are not only emitted from the high-density ionized gases, but also ionize the gases.   These electrons are attracted into the potential field $(E + Er)$ and produce small avalanches (Fig. 11a).   As a result, the head of the field advances somewhat to the negative electrode, as shown in Fig. 11b.   Repeating this process, the passage of ionized gases develops throughout the gap (Fig. 11c).[3]   In the case of electrostatic discharge, electron emission from the negative electrode is not continuous, so the streamer soon ceases, dissipating the charge of the surfaces.

The mechanism stated above may be adapted to explain the saturation of intensity.   At the lower peeling speed, the streamer develops only through the shorter gap ($d$ in Fig. 12) without giving rise to a discharge through the longer gap ($d'$), that is, the charge on the surfaces is dissipated at point $r$. In this case, the light intensity is weak in spite of the complete electrical breakdown, because the width of the gap is so small that the number of ionized gas molecules and electrons is small, although the instantaneous electron emission from the negatively charged surface of the dielectrics (quasi-stationary state) is taken into consideration.   (If we assume the
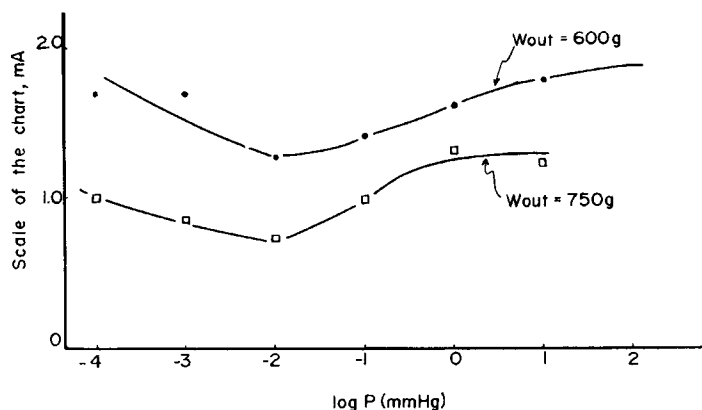
Fig. 13. Dependence of light intensity upon residual air pressure at average peeling speed of 43 cm/sec: abscissa, log $P$ (mm Hg); ordinate, scale of the recorder chart (mA); (●) PVC–glass system; (□) PVAc–glass system.

existence of some extra electrons on the surfaces of the dielectrics which result from impurities or are adhered on the surface, the consideration that there exists an instantaneous electron emission—quasi-stationary state—might be appropriate. But this does not mean that the electrons are emitted from dielectrics themselves.)

In case of fast peeling, the high potential field moves up to the point $s$ before the streamer ceases at $r$ (Fig. 12) and a new streamer is generated in the gap. Thus, a streamer is completed with a decrease of potential at $r$, but a new potential field comes into existence by peeling, and streamers continue to exist in the gaps $r$ and $s$. The number of ionized gas molecules and electrons produced in such a process are large. Considering the instantaneous electron emission, the intensity of radiation becomes large. Increase in width of the discharge gap $d$ with peeling speed is observed by photographic measurement. This width $d$, however, does not increase infinitely with peeling speed but approaches a definite value. The phenomenon of saturation of light intensity is interpretable from these considerations.

## Dependence of Light Intensity on Pressure

The light intensity is plotted in Figure 13 as a function of pressure at a constant peeling speed of 43 cm/sec. Each curve has a minimum value at a pressure of $10^{-2}$ or $10^{-3}$ mm Hg. The luminescence of glass is mixed in the light emitted in the PVC–glass system, but it is very weak, as stated in the foregoing section. The shapes of the curves are similar to those obtained in the PVAc–glass system in which the luminescence is not observed. Thus, we can conclude that the dependence of the light intensity on pressure is determined by the light radiated from gases.

Assuming instantaneous electron emission from surfaces of negatively charged dielectrics (a quasi-stationary state with quasi-γ-mechanism),
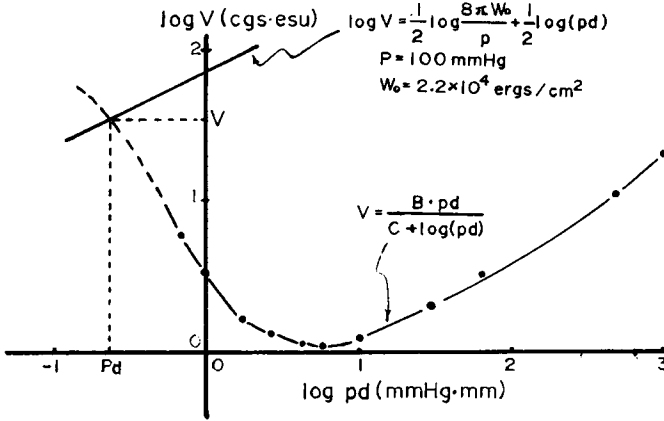
Fig. 14. Paschen curve for air: abscissa, log $pd$ (mm Hg·mm); ordinate, log $V$ (cgs·esu).

Paschen's law would be adaptable for the electrostatic discharge, that is, the following equation is obeyed:

$$V = \frac{B\,(pd)}{C + \log\,(pd)} \tag{1}$$

where $V$, $d$, and $p$ are discharge potential, width of the discharge gap, and residual gas pressure in the chamber, respectively, and $B$ and $C$ are constants (Fig. 14).

The maximum width of the discharge gap was reached at the experimental peeling speed of 43 cm/sec at a pressure of 100 mm Hg. The dependence of the light intensity on the pressure could be explained qualitatively considering that the discharge potential changes with pressure according to eq. (1), because the width of the gap is almost constant at high peeling speed. The intensity of light is proportional to the frequency of interaction between the electrons and the gas. Hence, it is probable that the dependence of the light intensity on the pressure is attributable to the variation of initial discharge potential.

## Discussion of Paschen's Law and the Surface States

Paschen's law was used to explain the experimental results qualitatively in the preceding section, assuming a quasi-stationary state for the electrostatic discharge. This law is applicable practically to the stationary spark discharge and eq. (1) is derived postulating a $\gamma$-mechanism for the negative electrode. On the other hand, in electrostatic discharge, continuous electron emission in a true sense does not exist. It is obvious, however, that the electrostatic charge on the contacting surfaces is generated by electron transfer from one to the other substance. The transfer of electrons is attributed to the existence of extra surface energy levels (surface states). From this point of view, the surfaces of dielectrics would behave the same as

those of metals and the properties of such electrons would be similar to those of free electrons in metal. Of course, the motion of these electrons is restricted more intensely than that of free electrons in metal. But under a strong driving force (e.g., a high potential field) such electrons would be able to leave the surfaces of the dielectrics. If the surfaces of dielectrics have such extra energy levels, electrons are emitted instantaneously and phenomena similar to the stationary state in ordinary discharge take place (quasi-stationary state). Then, strong light emission would be observed when the streamer is completed and positive ions strike the negatively charged dielectrics. Paschen's law may be applicable under such circumstances.

Assuming that the peeling action of elementary sections is replaced by the process of separating two electrodes of a condenser, the work $Wo$ done in separating two electrodes* by a distance $d$ up to the occurrence of discharge is:

$$Wo = \frac{V^2}{8\pi d} = pV^2/8\pi(pd) = 2\pi\sigma^2 d \qquad (2)$$

or

$$\log V = \frac{1}{2}\log\frac{8\pi Wo}{p} + \tfrac{1}{2}\log (pd) \qquad (3)$$

where $p$, $V$, and $\sigma$ are pressure, initial discharge potential, and charge density, respectively.[4] From eqs. (1) and (3), the width of discharge gap, $d$, and the potential $V$ are calculated schematically according to the method of Derjaguin et al.[4] (Fig. 14). For example, if it is accepted that the values of $P$ and $Wo$ are 100 mm Hg and $2.2 \times 10^4$ ergs, the value of $V$ is 8400 volts and $d$ is equal to $2.6 \times 10^{-4}$ cm. From the values of $Wo$ and $d$, $\sigma$ is obtained as $1.35 \times 10^3$ esu/cm$^2$ using eq. (2). If we assume that the generation of charge is caused only by the electron transfer, the density of surface electrons is about $2 \times 10^{12}$ electrons/cm$^2$, and this value is also equal to the number of surface energy levels (surface states). This value agrees approximately with the number of energy states obtained by Bardeen[5] as the number of surface states.

Gonsalves[6] considered the "activated" insulator. On the surface of such an insulator there must be places which can take up electrons and also places which can deliver electrons. If we assume such levels on the surface of dielectrics, it is understandable that instantaneous electron emission can occur as stated above.

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* There is a question whether the work of adhesion is exactly equal to the work of peeling. It would generally be thought that the work of peeling can be partly construed as that of deformation of film. Our observation for the PVC-glass system, however, showed that, in this sample system, the work of peeling was almost entirely the work of separation of PVC film from glass. It appears that the film adhered to the substrate owing to electrostatic force.

## CONCLUSIONS

The light radiated when polymer films are peeled from glass exhibits the following properties, as measured by a photomultiplier:

1. The radiation consists of two bands of light. One is a band with limits of ~4900 Å, the other is a band between 5200 and 5900 Å. The latter band appears when a glass substrate is positively charged.

2. The intensity depends upon the peeling speed. At high speed, a saturation phenomenon is observed.

3. The intensity shows a Paschen-type dependence on pressure.

4. The number of surface states is obtained by Paschen curve and the work of peeling.

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