

PHOTOCONDUCTIVITY MEASUREMENTS USING A SIMULATED ELECTROSTATIC RECORDING DEVICE

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Summary

Measurements of photoconductivity on thin polymer films are described using an electrostatic recording device built in our laboratory from components actually utilized in a commercial photocopier. The voltage applied to the surface of thin films may be measured using an electrostatic voltmeter and photodecays may be easily monitored by a digital-type storage oscilloscope which when coupled to a BBC microcomputer, via the RS423 input, gives an accurately stored decay profile of the charge with time on the millisecond scale. In this paper, the construction of the equipment and its operation are described and some measurements are presented which support its practical viability under various conditions.

1. Introduction

The use of organic photoconductors in the xerographic copying industry is growing rapidly. However, if such systems are to compete successfully with the inorganic types, such as selenium, then their performance and long-term stability need to be improved. Good theoretical knowledge of conduction mechanisms is therefore required. Equipment used to measure photoconductivity can be expensive, particularly that based on the spinning disc technique. In this paper we wish to describe the construction of an instrument using parts from a commercial small-scale photocopier. We believe that measurements obtained with our equipment closely simulate the conditions actually employed in commercial photocopying equipment. Thin films of doped polymers are solvent coated onto aluminized polyester films which are then mounted onto a rotating drum. The surface is charged using a high voltage discharge unit (corotron) and then exposed to a mercury vapour discharge lamp. The surface voltage is measured with a vibrating reed

electrostatic voltmeter linked via an oscilloscope to a BBC microcomputer which prints out the voltage decay profiles.

Electrophotographic materials can be quite complex but may consist of single or dual layers and in both cases the function of charge generation and transport are usually performed by different materials. Typical charge generation materials (CGMs) are organic pigments such as phthalocyanine or perylene, and the pigmented system used depends on the region of photosensitivity required and the spectral output of the photocopier lamp. The charge transport material (CTM) can be either an n-type semiconductor such as 2,4,7-trinitrofluorone for transporting electrons, or a p-type semiconductor such as poly(vinylcarbazole) (PVK) or an aromatic hydrazone for transporting holes. A polymeric binder is required for the CGM and CTM (except where PVK is used as the CTM), typical examples being styrene-acrylate resin or polycarbonate.

In dual-layer devices the transparent charge transport layer (binder plus active material) is coated over a thin charge generation layer, whereas in single-layer devices the two materials are mixed.

The mechanism of photoconduction is complex and still the subject of much dispute, but it essentially relies on the generation of charge carriers in the pigmented polymer film on irradiation. The most favoured mechanism involves the formation of a charge transfer complex [1] and its Onsager-type dissociation [2]. The charge transfer complex is thought to involve a singlet excited polymer molecule (D^*) and a pigment/dye or impurity centre (A).



In the experimental examples given here single layers only are used, PVK is used as the binder and 2,7-dibromoanthanthrone is used as the photosensitive pigment (Fig. 1). Dual layer systems may also be measured with this equipment and, as yet, we have encountered no problems in this respect.

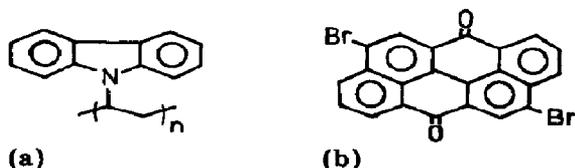


Fig. 1. (a) Poly(vinylcarbazole); (b) 2,7-dibromoanthanthrone.

2. Experimental details

2.1. Materials

Commercial grade PVK (BASF, F.R.G.) was used for film preparation. The pigment 2,7-dibromoanthanthrone (ICI PLC) was added to a solution of the PVK in dichloromethane (10% w/v). This was shaken with glass beads to ensure uniform dispersion. The mixture was then coated onto

aluminized polyester using wire-wound draw bars. After the solvent had evaporated the films were dried in an oven at 100 °C for 30 min and then left overnight for 24 h to allow charge carriers to recombine before taking a measurement. In the experiment on particle size, to avoid metal contamination the pigment was ball milled using ceramic beads.

2.2. Instrument components

The electrostatic recording device was constructed using components from a commercial photocopier. Films cast onto aluminized polyester sheets are mounted onto an earthed steel drum. Electrical contact between the aluminium base electrode (coating on polyester) and the drum is made by a spring steel clip mounted on the drum (Fig. 2). The films are electrostatically charged under a corotron (single-wire device Fig. 3) and then discharged using a mercury vapour discharge lamp (100 V). The charge is

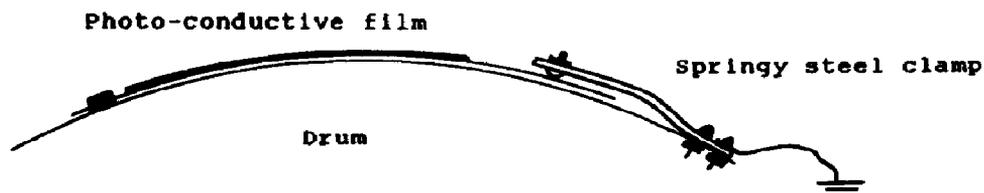


Fig. 2. Clamping and mounting arrangement of polymer films on a stainless steel drum.

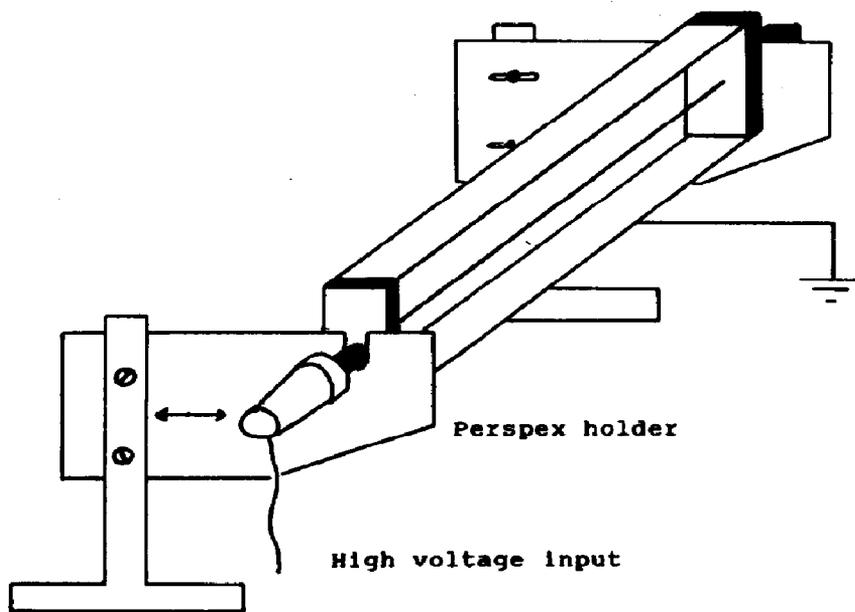


Fig. 3. Corotron charging wire.

delivered via a Matsushita Electric Transformer (outputs 100 V and +5.8 or -4.9 kV). The voltage is measured using an electrostatic voltmeter (Xerox 600T1620) linked to a digital storage oscilloscope (Gould 20 MHz type 1425). A hard copy of the decay profile can then be obtained via a BBC microcomputer. Initial voltage measurements were recorded by coupling the voltmeter to a Thurlby Intelligent digital multimeter (1905a).

3. Results and discussion

3.1. Operation of equipment

The steel drum (20 cm in diameter) is mounted with a rod passing through the centre so that it can be rotated through 180° . The corotron is fixed in such a way so that the distance between the drum and the wire can be altered. The latter allows various surface voltages to be applied. After charging the sample the drum is rotated so that the film is then under the electrostatic probe and the lamp for irradiation. The power for the lamp and the corotron is obtained using the photocopier transformer with outputs of 100 V and +5.8 or -4.9 kV respectively. The component set-up is shown diagrammatically in Fig. 4. The film is positioned on the drum and rotated under the corotron (position 1) for 10 s. The electrostatic probe is switched on after this period and the oscilloscope is triggered. The drum is rotated so that the film is under the probe and the lamp is then switched on. The voltage-decay profile is then stored in the oscilloscope and a hard copy can be obtained via an RS423 interface into a BBC microcomputer. The voltage calibration is carried out by charging the film up and recording the

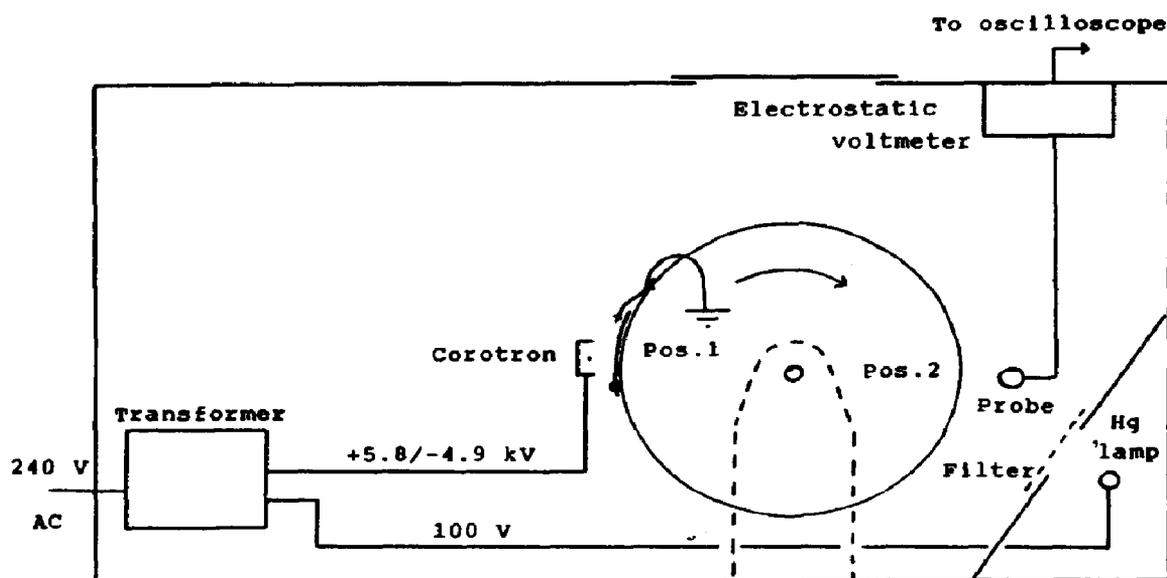


Fig. 4. Measurement positions and major components in the electrostatic charging unit.

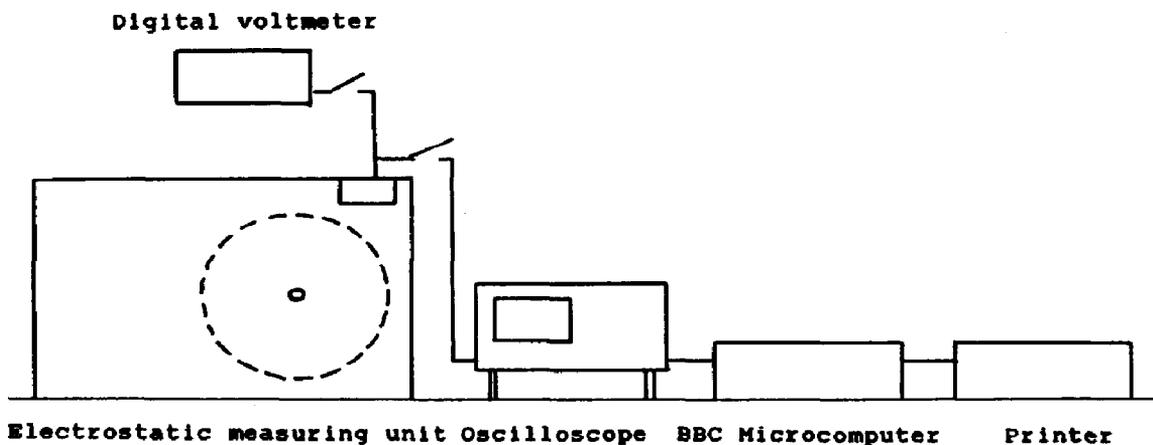


Fig. 5. Diagrammatic layout of the main measurement devices.

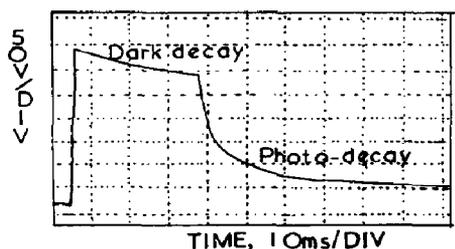


Fig. 6. Typical printout of an electrophotographic decay process showing voltage *vs.* decay time: slow dark decay followed by a rapid photodecay.

voltage from the digital voltmeter. Response times, expressed as half-lifetimes and dark-decay rates may be obtained directly either from the oscilloscope or the computer printout copy. A diagrammatic layout of all the components is shown in Fig. 5 and a typical voltage decay profile (printout) is shown in Fig. 6. Very fast response times on the millisecond time scale are easily measured.

3.2. Comparison of positive and negative charging

Films ($4 \mu\text{m}$ thick) containing 10 wt.% pigment were charged positively and negatively using the above equipment. The positive films were found to have a photoresponse twice as fast as the negative films, where the photoresponse is given as the time taken to discharge the voltage to half of its original value (40 ms compared with 80 ms respectively).

This observation is similar to that for the perylene-PVK system [3] and can be accounted for in the following way. PVK is a hole transport medium and hence transportation of electrons is limited to the pigment. For positive charging, carriers need to be formed near the surface so that electrons can neutralize the charge, and the hole is then conducted through the bulk of the film. Alternatively, for negative charging, carriers need to be produced near to the base electrode (Fig. 7). On illumination it is expected

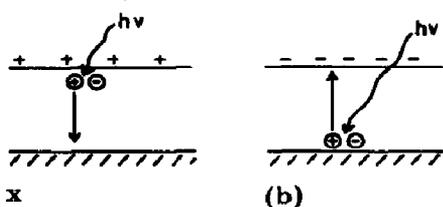


Fig. 7. (a) Positive charging; (b) negative charging.

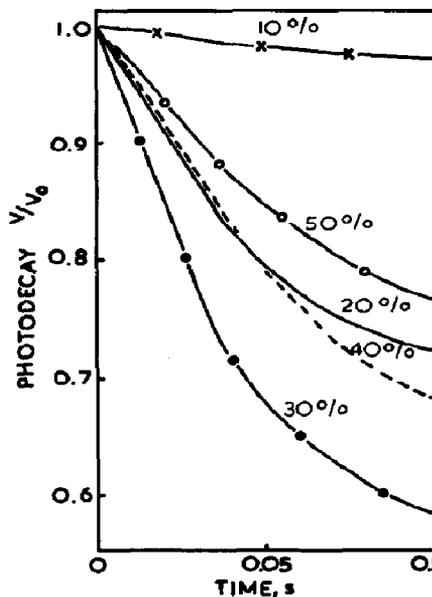


Fig. 8. Effect of pigment concentration on photodecay (film $8 \mu\text{m}$ thick): —x—, 10%; —○—, 20%; —●—, 30%; —○—, 40%; —●—, 50%.

that the bulk of carriers will be produced near to the surface and therefore the photoresponse will be faster for positively charged films.

3.3. Effect of pigment concentration

The effect of increasing the pigment concentration on the photodecay rate for a positively charged film is shown in Fig. 8. The decay rate increases up to 30% concentration of pigment, after which the rate then slows down. The initial increase is explained by an increase in the number of carriers produced, and a screening effect which reduces the depth that the light can penetrate into the film, and thus carriers will be produced nearer the surface. As explained above for positively charged films, carriers need to be produced near the surface. The decrease after 30% is therefore due to a decrease in the hole mobility with reduced PVK concentration.

Other workers [3] observed a maximum decay rate for a similar perylene-type PVK system at 5 wt.% concentration and accounted for this result on the basis of a transfer of carrier generation from the bulk to the surface of the film. This decrease in the rate of decay at pigment concentrations greater than 5% is probably due to a combination of the two effects of reduced hole mobility and transfer of bulk generation to surface generation. The dark decay is seen to increase with increased pigment concentration (Fig. 9), the initial surface charge acceptance decreases and at 100% pigment there is little retention of charge. The increased dark-decay rate is explained by an increase in both the thermally generated carriers and the electron mobility owing to increased particle-particle contact.

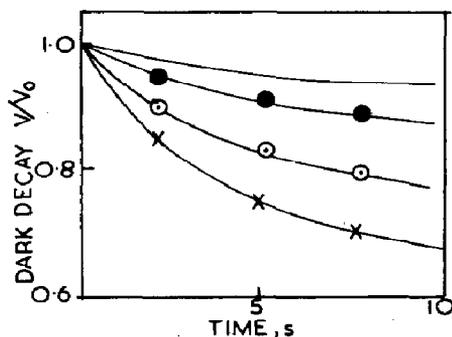


Fig. 9. Effect of pigment concentration on the dark decay (film $8 \mu\text{m}$ thick): —, 30%; —●—, 40%; —○—, 50%; —X—, 70%.

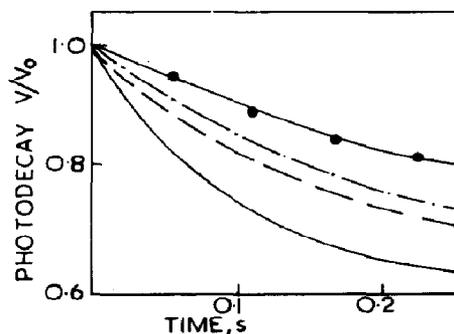


Fig. 10. Effect of milling time on the photodecay (20% pigment, film $4 \mu\text{m}$ thick): —●—, 0 h; - - -●- - -, 4 h; - - -○- - -, 5 h; —, 6 h.

3.4. Effect of ball milling the pigment

Ball milling reduces the pigment particle size and this was confirmed using electron microscopy. In Fig. 10 the photodecay rates are seen to increase with increasing ball milling time whilst the dark-decay rate decreases with increased milling time (Table 1).

TABLE 1

Effect of milling time on the dark decay (decay expressed as per cent voltage loss in 5 s for 20% pigmented films $4 \mu\text{m}$ thick)

| Milling time (h) | Per cent voltage loss in 5 s |
|------------------|------------------------------|
| 0 | 39.1 |
| 4 | 34.6 |
| 5 | 32.6 |
| 6 | 31.9 |
| 7 | 31.1 |

The increase in photodecay rate is certainly associated with greater pigment surface area leading to greater polymer-pigment contact and thus enhancing the quantum yields. Conduction of electrons may also be reduced owing to the increased number of pigment polymer interfaces as the particle size is reduced and this may also account for the reduction in the dark decay.

4. Conclusions

Close simulation of the electrophotographic process can be obtained by constructing equipment using components from a commercial photo-

copier coupled to external measurement devices and output to a micro-computer. The results demonstrated here for the electrophotographic properties of 2,7-dibromoanthanthrone in PVK support the findings of other workers [2, 3] under a wide variety of experimental conditions, thus supporting the practical viability of the equipment.

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