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Triboluminescence and Triboelectrification by the Motion of Mercury Over Glass Coated with Scintillator Dyes

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ABSTRACT

The conversion of mechanical energy into electrical energy and light (triboelectrification and triboluminescence) by the movement of mercury over glass surfaces coated with scintillator compounds was investigated. The motion of mercury over the coated glass involves the build-up of potential differences in excess of 20V; the nature of these triboelectric potentials differs significantly from those observed in the absence of scintillator coating. Twelve scintillator compounds were investigated with the observed luminescence being characteristic of the coating material.

Interfacial processes can generate potentials of varying magnitude, and from a fundamental aspect, these voltage-producing interfacial processes involve energy conversion. Scintillator compounds are characterized by a relatively efficient conversion of one form of energy into another; that is, in the usual experimental situation, the kinetic energy of high energy particles is converted into light energy. The study was concerned with the electrification, *i.e.* the separation of electrical charges, which occurs upon rubbing together dissimilar materials, a process termed "triboelectrification" or sometimes "static electrification." The related optical phenomenon is called triboluminescence (1), the emission of light when certain materials are rubbed or certain crystals are crushed. It has been known for a long time that triboelectrification and triboluminescence occurs when mercury moves over a glass surface in the presence of inert gases. For example, Picard (2) in 1675 observed a "whitish glow" in a Torricelli barometer. He attributed this to some "phosphors" ostensibly present as impurities. The explanation that is in general agreement with present thinking, namely, that a static electric charge builds up, was first put forth by Huksbee (2) in 1705. Recent workers in this field have observed chemical reactions in a triboelectric discharge (3, 4) and have studied the spectra of light generated by the relative motion of contiguous surfaces of mercury and glass (5-7). In related experiments, contact electrification potentials as high as 100V have been measured (8). While many details of the basic mechanism remain obscure, the process involves charge separation at the mercury-glass interface with the subsequent charge recombination reaction being energetic enough (>20 eV) to produce excited states of the inert gases, mercury and even of the silicon and boron of the glass, and to cause decomposition of such molecules as methane. We report here that coating the glass surface with a scintillator compound results in intense luminescence that is color-specific to the coating during movement of mercury over the surface and that this light emission is localized at the scintillator coating and does not extend into the interior volume as has been reported when only mercury and glass are involved (6). Other significant differences that can be attributed to the scintillator coating and potential difference measurements are also discussed.

Experimental

The structures and fluorescence maxima of the scintillator compounds that we used as coating with positive results are shown in Fig. 1. In our previous work involving scintillator compounds (9) we found that the commercially available samples are of a high quality and required no further purification. The FTD, ATD, APD, and BTD samples were sent to us by Prof. Richard L. Taber, Colorado College, who reported them to be extensively purified by column chromatography; these were used as received. The purity of the other compounds that were used as coatings (rubrene, phthalocyanine, $\alpha,\beta,\gamma,\delta$-tetraphenylporphin) was ascertained as described previously (9).

The glass surface to be coated was always cleaned first by rinsing with reagent CH_2Cl_2, hydrochloric acid, distilled water, ethanol, and methylene chloride (spectroscopy grade) several times. The last CH_2Cl_2 rinse was checked using an Aminco-Bowman spectrophotofluorometer and a quartz cuvette to make sure that no traces of luminescent impurities, especially those from a previous coating, were still evident. The glass was almost always coated by contacting it with a

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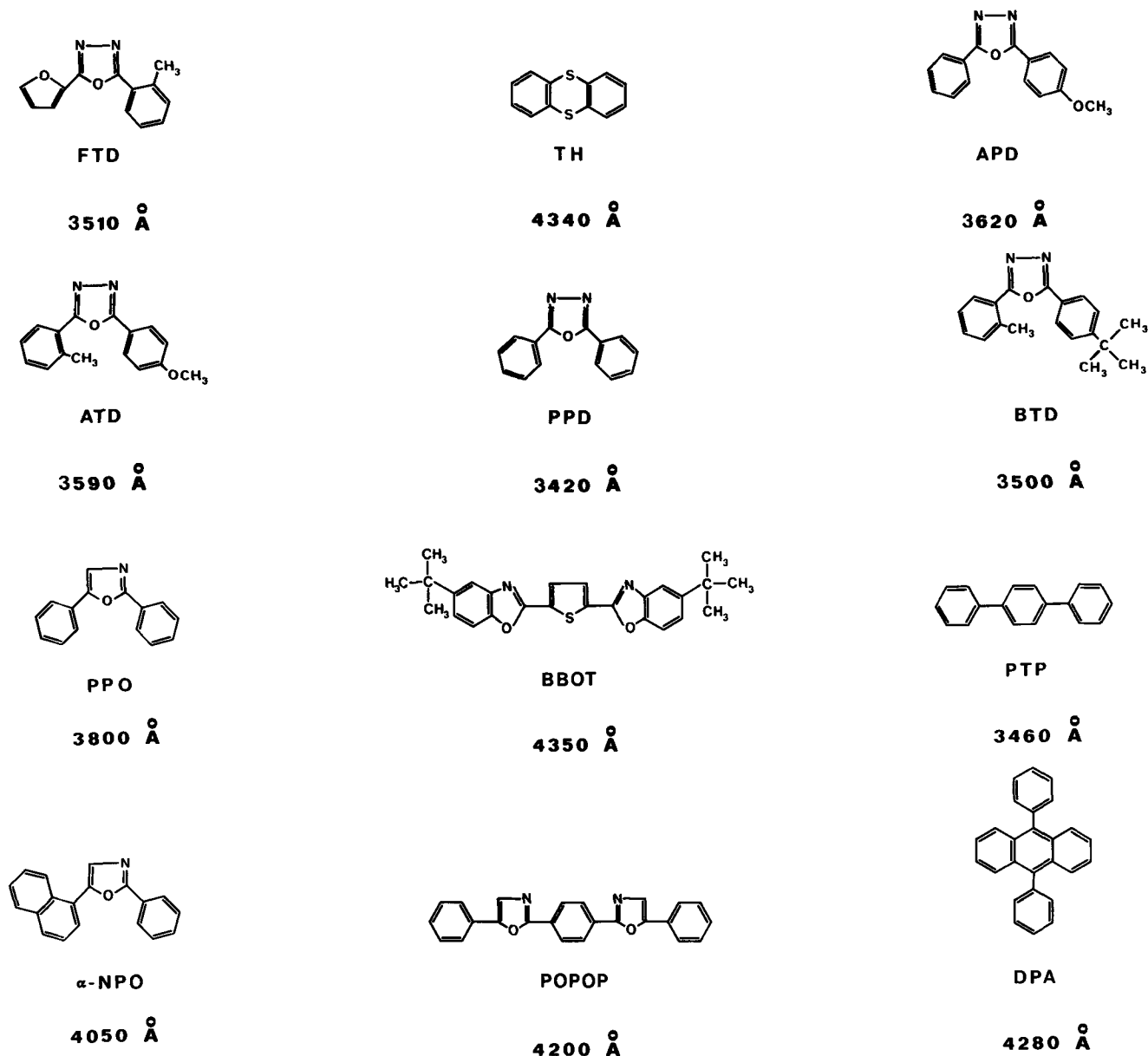Key words: luminescence, static electrification, scintillator compounds.

Fig. 1. Structures of the scintillator compounds that were used as coating. [Principal fluorescence or scintillation emission is indicated by λ (Å)].

CH_2Cl_2 solution saturated with the compound being investigated; using approximately 0.5 ml solution for the length of the tube indicated in Fig. 3; the liquid was slowly rocked back and forth in the horizontally held tube that was slowly rotated until all the CH_2Cl_2 had evaporated. Vapor deposition was also employed as a coating technique. By use of a "heat gun," it was possible to make the coating more homogeneous, melting the coating at either specific spots or along the entire surface. The observations were made either in hermetically sealed cells (Fig. 2) or in a detachable vacuum-line type arrangement using "Swagelock" couplings.

Potentials were measured in an arrangement resembling Debeu's (8) by using either an electrometer (General Radio Company, Type 1230-A) or a solid state operational amplifier (Philbrick-Nexus) in a voltage follower arrangement yielding an input resistance $>10^{12}$ ohms. A Moseley 7005-A XY recorder was used to obtain the potential-time plots shown in Fig. 4 and 5. The electrometer could measure voltages up to 10V, the Philbrick operation amplifier limits ~20V.

The rate of the rise and fall of the distilled Hg column could be controlled by the arrangement shown on the top of Fig. 3, whereby the vacuum pump or a noble gas source was alternately connected to the main coated tube. It was found impossible to achieve a steady rate of rise under our experimental setup, and recorded measurements were confined to the falling Hg column. The He, Ne, and Ar were a high purity, commercially available, grade, used as received. The imbedded electrodes (cf. Fig. 3) were of platinum wire.

Results and Discussion

For a preliminary investigation of the triboluminescence, the hermetically sealed cell arrangements shown in Fig. 2 were employed. These were coated tubes containing a small amount of mercury sealed under vacuum which produced light emission upon moving or shaking the mercury. Such closed cells functioned essentially without change over a period of several months when used intermittently. For a continuous test, a glass wheel, scintillator coated, and containing mercury, was rotated by connection to a motor revolving at 0.5-5 rpm; emission was observed for 48 hr in this arrangement before the test was terminated. In these cells, even the slightest movement of the Hg in the coated tube produced the characteristic luminescence.

We have made quantitative measurements of the triboelectric potentials generated at the scintillator interface by the movement of the mercury using the arrangement indicated in Fig. 3. In this apparatus,
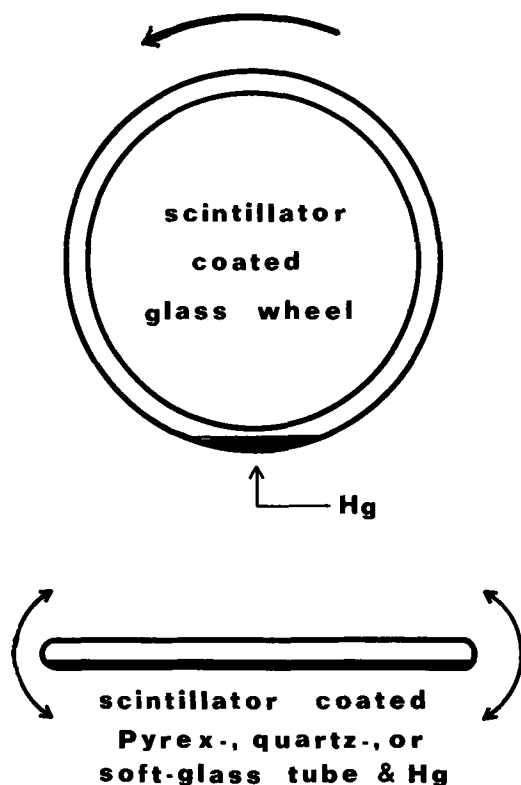
Fig. 2. Triboluminescence could be observed for prolonged periods of time in these hermetically sealed cells; the 9 in. diameter evacuated hollow wheel could be rotated by using an electric stirrer motor equipped with speed control.
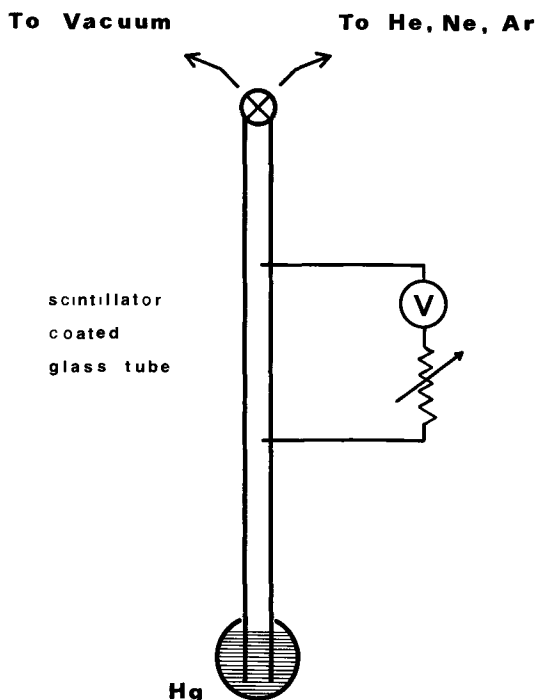

Fig. 3. Triboelectric potentials were measured accordingly (total length of the 6 mm OD tube was 34 in., separation of the imbedded electrodes was 10 in.).

which resembles an ordinary mercury-in-glass barometer except that here the glass has been coated with scintillator compound, the mercury in the reservoir can be made to rise and fall at a given rate in the tube by applying either vacuum or inert gas pressure at the inlet. The potential between the mercury and the glass can be measured by means of the two platinum wires sealed into the tube. In a typical experiment the mercury column, formed by applying a

vacuum to the inlet, is allowed to fall by slow addition of inert gas. Flashes of light are observed at the mercury-coated glass interface. The potential-time behavior (termed here a "potentiogram") between the platinum contacts taken at various ohmic resistance settings of the electrometer is shown in Fig. 4. While the two electrodes remain shorted by the descending Hg column, the reading on the electrometer (or from the operational amplifier in the voltage follower arrangement) is, naturally, zero. There is a sudden increase in potential as the Hg level moves below the top platinum lead (with the lead contacting the mercury positive with respect to the upper glass lead); subsequent variations and the detailed shape of the potentiogram are highly reproducible for a given coating, but vary from coating to coating. This allows "finger-printing" a coating surface, and also checking for any bald spots, striations, etc. The maximum voltage generated by the triboelectrification process could not be determined in these experiments, but we did find it to be in excess of the amplifier limiting voltage of about 20V when the high impedance solid-state operational amplifier was substituted in place of the electrometer in Fig. 4. With the electrometer, the highest resistance setting corresponding to the vacuum tube impedance of the electrometer itself could not be applied for fear of damaging the instrument. Debeu (8) measured maximum voltages in excess of 100V on contact electrification using nickel as the stationary phase, and NaCl or quartz particles as the moving phase; our maximum voltages may well be in the same range.

The rate at which the mercury column was falling had an effect on the generated voltage; lower voltage readings occur at the slower flow rates probably because of leakage of the built-up charge, lateral migration processes inside the scintillator coating, etc. Tentative evidence of such losses is found in the generally declining shape of potentiograms as the Hg column moves farther away from the upper platinum electrode, making the effective scintillator column length being monitored by the electrometer increasingly longer.

The light pulses are quite irregular in their time distribution, and no correlation could be observed between certain positions on the coated tube and light emission either. The typical pulse length was between 0.2 and 0.5 sec; the rise time and decay characteristics have not been measured. By comparison to calibrated light sources with the aid of the photodiode we used in electrogenerated chemiluminescence quantum efficiency measurements (10) the number of photons emitted per cm^2 in these experiments is estimated to be certainly greater than 10^{15} in a pulse.
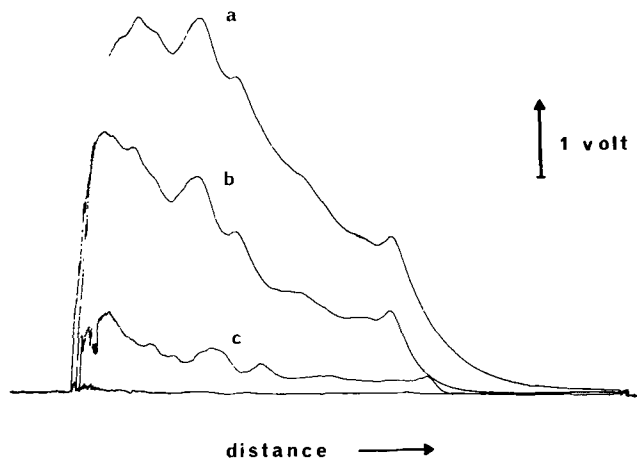

Fig. 4. Potentiogram of the triboelectrically generated voltages with apparatus of Fig. 3; constant recorder sensitivity is indicated by the "1 volt" scaler. The resistance settings of the electrometer were (a) 10^{11}, (b) 10^{10}, (c) 10^9 ohms. The rate of fall of the Hg column was 3 in./min.

Significantly different results are obtained in the same cells under similar conditions when the scintillator coating is removed. As Fig. 5 shows, now complete discharges occur, involving breakdown of the gas in the bulk volume. When a large number of potentiograms are examined, it is unmistakable that the voltage build-up and discharge pattern is quite random, in sharp contrast with the potentiograms taken in the presence of a scintillator coating, where the potentiograms are highly reproducible and also "fingerprint" minute details of the coating surface. In all the experiments when the type of glass varied, we found no specific or obvious differences in behavior. On the other hand, when other fluorescent (nonscintillator) compounds, such as rubrene, TPP, or PC were used as coatings, no intense orange or red triboluminescence resulted.

While a detailed mechanism of the phenomenon can obviously not be presented on the basis of the experiments here, these results combined with previous studies of static electrification and solid-state luminescent processes allow some possible schemes to be presented. The process of contacting mercury with glass causes the mercury to become positively charged and the glass negatively charged as a result of electrons from the mercury moving into unfilled surface states of the glass (6). The separation of the mercury and glass surfaces initiates a discharge, and based on the fact that emission from He has been observed under these conditions as well as decomposition methane and other hydrocarbons, the excitation energy produced by this discharge is greater than 20 eV (7). Thus, one mechanism for the luminescence of the scintillator would involve energy transfer from excited state species of the mercury or inert gas to the scintillator coating. However, the lack of lumines-

cence of certain fluorescent dyes and the relative independence of the emission on the type or pressure of inert gas makes other mechanisms worth considering. The discharge process could lead to highly energetic electrons; the interaction of these "soft β-rays" with the scintillator could produce emission. Yet a third mechanism is suggested by experiments on charge injection into aromatic crystals (11, 12). In these experiments, the direct injection of electrons and holes into crystals, or injection via insulator crystal electrodes and solutions, leads to electron-hole combination in the crystal and light emission. The charge separation across the scintillator coating could lead to this kind of process in these experiments.
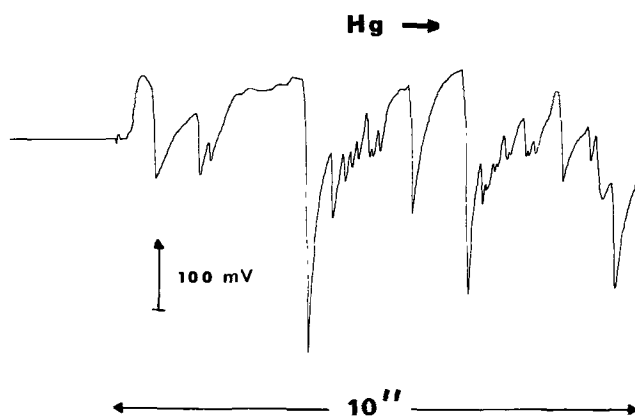
Acknowledgment

Fig. 5. Potentiogram of triboelectrically generated voltages under the same conditions as Fig. 4, except that the scintillator coat was completely removed; the resistance setting of the electrometer was 10^{11} ohms.

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