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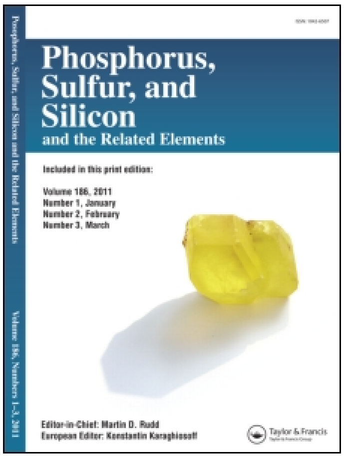

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CHEMICAL ASPECTS OF SELENIUM AS A PHOTORECEPTOR

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Abstract Selenium has been a prime material choice for use as a photoreceptor in xerographic machines because of its high conversion efficiency of visible radiation to charge carriers, its excellent charge transport and its immunity to change during use. Impacts to these properties have been ascribed to structural and chemical variations. The current status is reviewed and new data is presented implicitly demonstrating the subtle chemical variations which have important impacts on trapping kinetics. The role of arsenic and chlorine alloying upon these kinetics is introduced.

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INTRODUCTION

Selenium and its arsenic and tellurium alloys have been used in electrophotography for over 30 years. It is a photoconductive material which has been used to convert a spectral image into a charge replicate. This charge pattern is converted to a physical image through the electrostatic attraction of charged colored plastic toner particles to that pattern. Transfer and fixing of the toned image onto plain paper completes the copying process.

A typical photoconductive transducer, commonly referred to as a photoreceptor, consists of a metallic substrate, such as an aluminum tube, which is chemically cleaned and heated onto which an approximately 50 micron layer of selenium or its alloys is vacuum deposited. Single and multilayer structures are typical depending upon the functional application. The layer resembles a capacitor without 1 electrode.

In a copying machine the photoreceptor is sequentially charged typically using corona charging which forms a transient electrode through air ionization, exposed to light reflected from the medium to be copied, and focussed upon the photoreceptor surface, mechanically and physically acted upon during the development process which also may induce charge exchange, possibly exposed to corona charging or light to reduce the electrostatic attraction to the toner, mechanically acted upon by the paper in the transfer process, electrically, mechanically and/or optically acted upon in the toner removal, cleaning process and, finally, exposed either to light or

AC corona to neutralize or erase the prior image. Add to this the complex chemistry during corona charging and interactions with the many materials and their outgassing products all exacerbated by thermal cycling and long times. The picture painted is intended to portray the very rigorous existence which the photoreceptor must endure and to highlight the forgiving nature of selenium and its alloys.

Taken from a physical perspective, selenium and its alloys sustain a voltage with minimal change during copying cycles lasting seconds, discharge in light exposed areas rapidly (submilliseconds) and exhibit small to negligible memory cycle to cycle. This property set is the key to its being the photoreceptor material of choice for so long. Translating these properties first into physical and then into chemical terms is the intent of this paper.

Physically, one describes selenium as a good insulator[1]; a property which is maintained after alloying. The very low conductivity of these materials is a result of a paucity of free carriers; selenium transports positive charge fairly well having a mobility of approximately 0.1 cm/volt-sec. Slow discharge of the charged device in the absence of photogeneration of charge typically occurs due to charge injection at the substrate-selenium interface or to thermally-induced, charge generation in the layer. The high electric field at which the photoreceptor is operated causes rapid transit of the charge within the layer. That is, the decrease of the potential (measured in volts) which signifies the discharge is charge supply limited. Proper choice of substrate material limits the injection of electrons by creating a high barrier; although electron transport is much slower than positive charge (hole) transport, it is still significant, especially, at the high electric fields experienced. This is important to recognize since these photoreceptors are usually charged positively, i.e. with the free surface partially depleted of electrons and the counterelectrode substrate charged negatively. For selenium, thermally-induced charge in the bulk occurs primarily by excitation of holes (h) from acceptor states (A) into the transport manifold:

$$A \longrightarrow A^- + h$$

and not by excitation either across the band gap or by excitation of electrons from donor states into the conduction band. Hole conduction in selenium is viewed as a hopping process mediated by states approximately 0.3 electron volts above the valence band.[2] At ambient temperatures very rapid communication exists between these states and the valence band. For acceptor states to play a significant role in the discharge of a selenium photoreceptor two conditions must be met: there must be a sufficient number of such states and they must be at an energy for which thermal excitation can occur frequently enough to have an effect. If the energy required to excite the above reaction is low, say of the order of a few tenths of an electron volt or less, then discharge can be very rapid - the extent depending upon the available population. If the energy is

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higher, the discharge will occur during the copying cycle. Changes in temperature of the machine will mediate the extent of discharge. This temperature sensitivity of discharge in the absence of light is perceived as an instability and is undesirable. Too great a discharge is likewise undesirable as it limits the potential achievable with a given charge supply. If this discharge is repeatable device to device and not too temperature sensitive in the range of operation, one can design a machine to cope with this discharge. More generally, it is better to avoid it. The question that is evident is: what is the origin of these acceptor states? Two generic origins are bonding defects and impurities.

Another physically important property is unimpeded transport of charge which has been photogenerated either in response to an image focussed upon the photoreceptor or to light used to discharge the electrostatic image thereby created. Typically, there may be states (T) which trap charge and leave a residual voltage after all the charge on the surface of the photoreceptor has been recombined with counter charges. These counter charges are part of a dissociable electron-hole pair created by absorption of light in selenium, typically within 0.1 micron of the surface. Two types of trap states, namely electron and hole traps, exist:

$$T_e + e \longrightarrow T_e^-$$
$$T_h + h \longrightarrow T_h^+$$

The origin of these states is similar to that of the acceptor states, occupy similar positions within the band gap, but differ in their ability to accept or supply charge. Implicit in this statement is the ability of charge once trapped to be thermally excited into the appropriate charge transport manifold (e.g. band). Hence, a time and temperature dependent release of charge and relaxation of the residual voltage will occur. At any measurement temperature the time characteristic of discharge reflects the energy of the trap state relative to the transport manifold. Therefore, in the simplest view the magnitude of the residual potential and the time for its relaxation describes the trapping probability (the density cross-section product of the traps) and its relative energy, respectively.

In order to put the demands placed upon materials used as a photoreceptor into perspective, a simple illustrative calculation is presented. For this, a 60 micron selenium thick (L) layer with dielectric constant of K = 6.3 is charged to 1000 volts. A 10 percent discharge occurs leaving a uniformly distributed charged acceptor state density. This density, denoted as N, is calculated using:

$$100 = NeL^2/2K\epsilon$$

where ϵ is the permittivity of vacuum (8.85×10^{-14} farads/cm) and e is the elementary charge (1.6×10^{-19} coulombs). Computation gives N = 1.9×10^{13} charged acceptors/cm^3 or 0.6 ppb in selenium. Even if only a small fraction of available acceptors become ionized during use, the initial concentration is still minute. Similar considerations may be used for trapping charge with the added complication of the electric field (E) dependence of charge transport and the implicitly related availability in time of charge to be trapped through the charge velocity, vee, i.e.

$$v = \mu E$$

where μ is the charge mobility, a material's constant. As charge is trapped, the electric field within the layer becomes nonuniform across the layer and as a result the trapping probability likewise becomes nonuniform with trapping skewed toward the surface of origin of the photogenerated charge (assuming an uniform distribution of traps of sufficient initial density).

INTRINSIC DEFECTS

For selenium it was long felt that chain ends may be a significant contributor to its behavior as a photoreceptor. Attempts to resolve its contribution included ESR, x-ray and neutron diffraction and IR and Raman spectroscopy. The ESR data suggested that the chain ends, expected to be paramagnetic due to the presence of an unpaired electron, were less than 10^{15} per cm^3, the limit of detection in the experiment.[3] The chain lengths implied by this are greater than 3 x 10^7 atoms (molecular weight of 3 x 10^9) which is inconsistent with expectations. The spectroscopic data and the attendant interpretation supported a ring/chain distribution model and left open the resolution of the chain end question.[4] The most recent interpretation of that data suggests cis and trans environments for selenium atoms and appears to have superceded the need for a ring/chain distribution but without addressing the chain ends.[5] Structural information derived from x-ray and neutron diffraction have failed in a direct sense to address chain ends. However, when these data are coupled with electrostatic characterization of photoreceptors one can show a qualitative correlation between structure and the density of acceptor states. Specifically, films made at high deposition rates which show indistinct x-ray diffraction peaks compared to those normally seen also have greater discharge due to acceptor state ionization.[6] These films are considered to be more disordered on the basis of the diffraction data, but no specific determination of the acceptor state origin is possible. Films deposited under the more typical conditions show similar diffraction patterns with some difference in the lowest wave number peak. These differences are minor compared to that cited above and have not been correlated to film electrical property differences.

Another historical observation is that the photoreceptor trapping properties are dependent upon substrate temperature during deposition. The dependency is not monotonic and therefore is moderated by more than one mechanism. No model has been posited to explain this phenomena. However, one suggestion is that the approach to an equilibrium distribution of states is incomplete and dependent upon

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the film formation temperature. The ramification of this condition may be most discernable for states low in concentration where small differences, e.g. on the order of factors of two, make significant impacts. These states may be native to selenium or its alloys or may involve impurities.

EXTRINSIC STATES

Selenium for xerographic use has the highest degree of purification to meet stringent specifications. These specifications call for 20 ppm total impurities, but address the level of impurities measured only by spark induced fluorescence; the sensitivity to impurities being dictated by the type of instrument used, i.e. with grating or prism. The specifications are historic and are restricted to elemental species above atomic number 20. They do not necessarily reflect the physical and chemical reality. Selenium is usually thermally evaporated in a vacuum and deposited on the substrate fitting machine requirements. This process in itself acts as a purification in that the higher and lower vapor pressure species relative to selenium selectively deplete from the molten selenium early and late in the evaporation, respectively. Since the process as practiced is not at equilibrium, compositional and thermal gradients exist and mediate the evolution of the vapor species. Most metallic impurities and their oxides, selenides, sulfides, etc. have significantly different vapor pressures at the molten selenium temperatures typically encountered, i.e. by orders of magnitude.[7] Metallic chlorides, in particular, differ and have vapor pressures more equivalent to that of selenium. Another mitigating factor with regard to metallic impurities is that they may form impurity states which are effectively inactive; that is, the energy of the states and/or the nature of their overlap with the charge transport manifold is such to make interaction at these sites negligible. An important consideration addressed by the specifications is the avoidance of accumulation of residue in the evaporative containers which may cause other types of problems, e.g. cosmetic defects in the coated layer which, in turn, may cause copy quality problems.

As has been shown, other, nonmetallic containing impurities are probably very active.[8] This is highlighted in Figures 1 and 2 which illustrate the broad spectrum of selenium available as xerographic grade having nearly equivalent metallic impurities. Figures 1 and 2 contain data for well-rested xerographic photoreceptors made from selenium manufactured by 11 manufacturers from several countries and mining sources and different processes used by 2 particular manufacturers.[9] Figure 1 depicts the hole and electron trapping experienced for these materials. Since hole trapping is less efficient than is the electron trapping for most selenium samples, the residual potential resulting from hole trapping after 50 repetitions of positive corona charging and photodischarge is plotted as a func-

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tion of that for electron trapping after a single negative corona charge and photodischarge in Figure 1. It is evident that selenium which strongly traps electrons relatively weakly traps holes and vice versa with few exceptions. Obviously, different chemical species dominate the trap states for electrons and holes, but what is the reason for the different magnitudes seen for hole trapping? An answer is provided by the relaxation time data. Figure 2 contains a plot for hole trapping of the logarithm of the residual relaxation time taken as first order-kinetics as a function of the residual potential. The measurement of relaxation time terminated after 6 minutes. Three basic types are seen: 1. long times (>360 sec), 2. moderate times (10 to 100 sec) and 3. short times (< 5 sec). This dichotomy in relaxation times measured at room temperature reflect different trap depths relative to the transport manifold and by

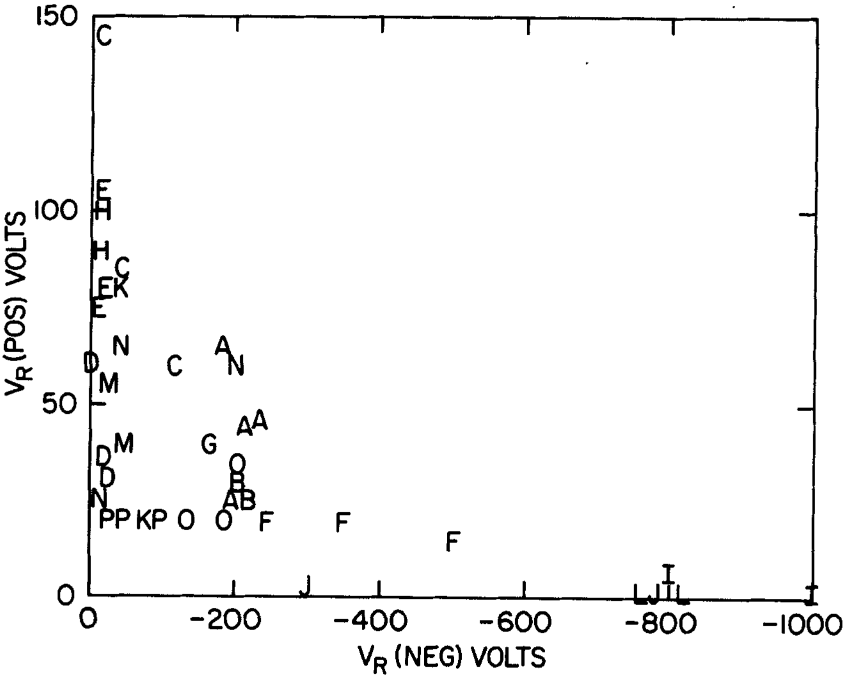

FIGURE 1. Plot of 50 cycle residual potential due to trapped holes as a function of the 1 cycle residual potential due to trapped electrons for xerographic grade selenium photoreceptors from many vendors and purification processes. Note N, O and P are photoreceptors made from 3 different lots each of selenium while multiple points for other lettered samples are for multiple coatings from the same lot.

inference chemical differences. The broad range of residual potentials in the long relaxation time group may reflect the range of trap density. The short relaxation time group's low residual potential may be a result of the rapid relaxation of trapped charge and not provide evidence of the relevant density. No significant differences in the hole mobility were seen for the total set of photoreceptors as measured by the xerographic time-of-flight technique indicating that the manifold of hopping states was basically unaffected by impurities.

Incorporation of arsenic and halogen, chlorine in particular, is common in photoreceptor fabrication. These elements have two notable effects. Arsenic addition at percent levels retards crystallization and thereby provides significantly improved life both in

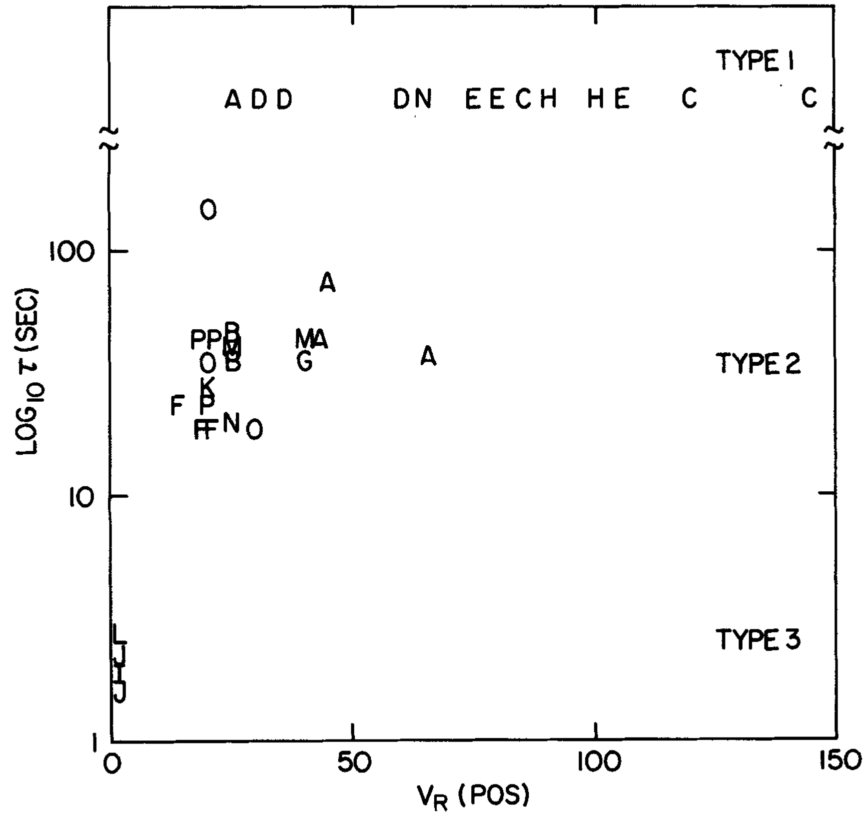

FIGURE 2. Plot of the logarithmic variation of the characteristic decay time of the residual voltage as a function of the 50 cycle residual voltage due to trapped holes.

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machine use and in storage. Alloying also overwhelms the native defect states, probably through chemical modification. Addition of chlorine significantly reduces hole trapping and increases the acceptor state density. These acceptor states have an energy of approximately 1 ev above the valence band and are at a low enough density that at typical concentrations of chlorine (≤100 ppm) little discharge occurs at room temperature. However, significant discharge may occur at elevated temperatures in machines. There is not necessarily a 1:1 correspondence between chlorine concentration and acceptor state density indicating that the reaction kinetics during alloy fabrication and photoreceptor fabrication may play a decisive role. Large concentrations of chlorine typically result in rapid discharge. The various seleniums discussed above were simi-

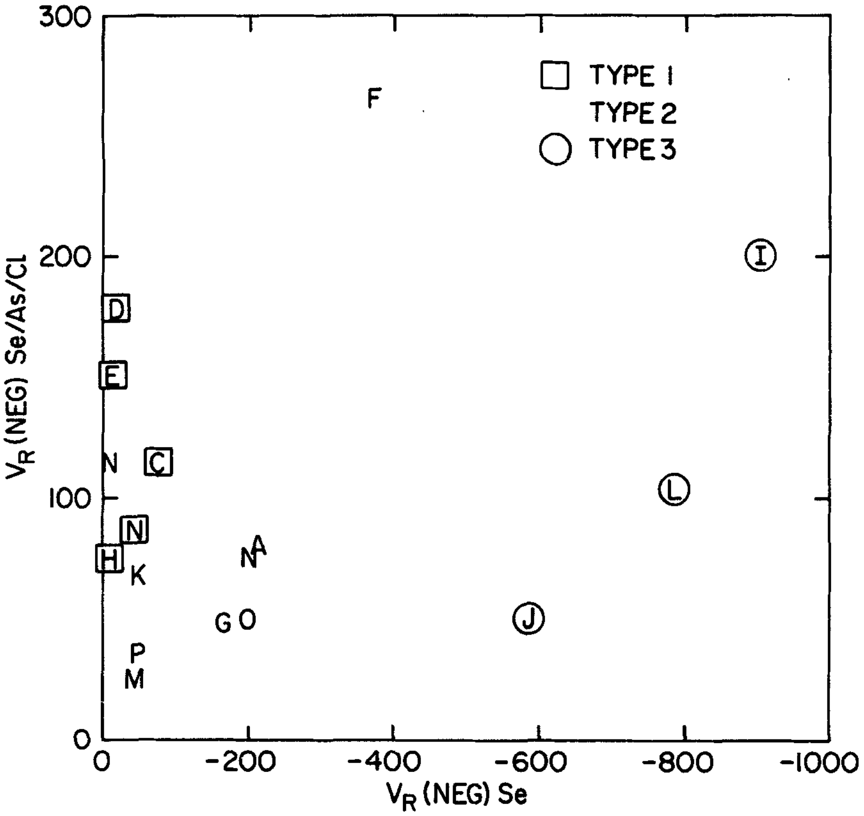

FIGURE 3. Plot of the 1 cycle residual voltage due to trapped electrons for selenium alloyed with 5000 and 20 ppm by weight of arsenic and chlorine, respectively, as a function of that for the parent selenium.

larly alloyed with 5000 and 20 ppm by weight of arsenic and chlorine, respectively, and evaporated after shotting onto substrates. The positive charged photoreceptors showed less residual potential than the parent Se, in general. The exceptions were, primarily, the type 3 which had shallow traps in the parent form and deeper traps when alloyed. With 1 exception all of the alloyed samples had traps from which charge relaxed with time constants between 10 and 100 seconds. Apparently, the deep, slow emptying trap states of Se with type 1 behavior are reactive and altered by the alloying with arsenic and chlorine. The negative residual was significantly changed as shown in Figure 3. Those seleniums which trapped few electrons when alloyed trap more, those which trapped electrons very efficiently trap them much less efficiently. The electron trapping behavior also appears to be similar amongst the alloys.

This description of the phenomena experienced only superficially portrays a more complex picture. It belies also a rich chemistry. This chemistry is both controlled and altered by the time-temperature history of the selenium and alloy fabrication. It is also significantly dependent upon the materials of the fabrication process and those which come into contact with it later. These materials may be organic or may be nonmetallic and at final concentrations which defy diligent efforts of detection. Succinctly stated, depending upon the specific materials' electron affinity they may lead to the formation of electron or hole trap states of widely different relative energies. Alloying with chlorine or other halogen decreases the hole trap density, can increase the electron trap density and increases the deep acceptor state density. Alloying with arsenic decreases the electron trap density and alters the hole trap density. Not described but observed by trapping behavior in a series of alloying experiments is the affinity of chlorine and arsenic. Hole trapping increased dramatically for different levels of chlorine when arsenic content increased above a 1:1 atomic ratio with chlorine.

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