

# Innovative Polyurethane Materials for Use in Digital Imaging Equipment

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## Abstract

A family of high density (6–10 lbs/cu.ft.) free rise polyurethane foams has been created as an alternative to more traditional siloxane, epichlorohydrin elastomer and other elastomer-based polymers in laser printer roller applications. A wide range of resistivities, from  $10^5$  to  $10^9$  ohms, can be achieved through patented, innovative modifications to the polymer morphology. Such a low resistivity is very attractive for many digital imaging roller applications. In addition, many of these products exhibit a stable resistivity profile under voltage over extended time.

## I. Introduction

Polyurethane, used as either a molded foam or elastomer, is known for high durability, flexibility and low compression sets. There would be several advantages to a conductive, high-density, “free rise” foam for electro-conductive roller applications:

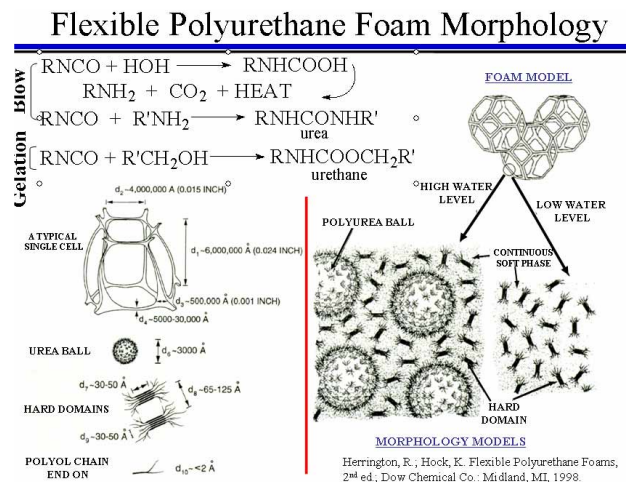
- Lower cost alternative to molded foams and elastomers
- Ease of fabrication and turnaround time
- Wide range of force deflection or hardness properties, without loss in other physical properties
- Excellent lot-to-lot consistency in electrical and physical properties.

The use of low density ( $\sim 1.8 - 4.0$  lbs./cu.ft) “free-rise” foams for toner roller applications is well-documented. These foams have either been post treated with a conductive carbon coating, or in the case of higher resistivity needs, foamed with *in situ* conductive additive such as carbon, quaternary ammonium compounds and metallic salts. Since coatings tend to wear, the *in situ* method has been preferred for consistency of the electrical properties over time. Typically resistivity values in the E10 to E11 range can be expected in this density range with *in situ* conductive foams. There are numerous technical challenges that must be overcome in order to develop higher density *in situ* conductive polyurethane foams with electrical resistivity values in the low E5 range while maintaining good hardness. For this paper we concentrated on the manipulation of the polymer morphology in conjunction with both ionic and carbon additives to manage conductivity.

## II. Discussion

Polyurethane foam presents some unique challenges as well as opportunities in formulating both ionic and carbon conductive materials. During polymerization the developing polymer organizes into two different phase-separated morphologies. This is the result of the reaction between the water and the isocyanate which yields urea (i.e. hard segment domains) and the isocyanate and the polyol (i.e. soft segment domains). The resulting semi-

crystalline morphology [Fig. 1] and how it is formed, has a significant influence on the polymer conductance.



[Figure 1]

## A. Ionic Conductance

It is well-understood that significant ionic motion or flow occurs only in the amorphous regions of the polymer while crystalline regions tend to be nonconducting<sup>1</sup>. It has been taught in patent literature that the lowest electrical resistance achievable in this density range is about  $10^8$  ohms<sup>2</sup>. By optimizing the ratio of the hard to soft segment, or crystallinity, it was possible to obtain this level of conductance over a wide range of physical properties. This was achieved through a proprietary means of chemistry and processing.

Key considerations:

- Overall polymer compatibility, molecular weight and functionality.
- Isocyanate type, functionality and isomer ratio.
- Catalysis used to initiate the hard and soft segment formation.

Table 1 shows the physical and electrical properties of three example foams which contain a metallic salt and were produced by these methods.

[Table 1]

Example Foams: (1) (2) (3)

|                          |                    |                    |                    |
|--------------------------|--------------------|--------------------|--------------------|
| Density (lbs. / cu. ft.) | 7.4                | 7.6                | 8.0                |
| Tensile Strength (psi)   | 23.0               | 50.0               | 118.0              |
| Elongation (%)           | 151                | 141                | 113                |
| Tear Strength (lbs.)     | 1.7                | 2.4                | 2.7                |
| Compression Force        |                    |                    |                    |
| Deflection @ 25% (psi)   | 1.06               | 3.00               | 5.20               |
| Resistivity (Ohm / Sq.)  | 3.0 E <sup>8</sup> | 6.7 E <sup>8</sup> | 2.4 E <sup>9</sup> |

Hardness values are usually reported in Shore units; however, Compression Forced Deflection (CFD) values were reported here. The full CFD curve better characterize how a particular material will function under a load, such as a roller used in digital imaging equipment. Figure 3 shows the CFD curves for the three examples listed in table 1.

[Figure 3]

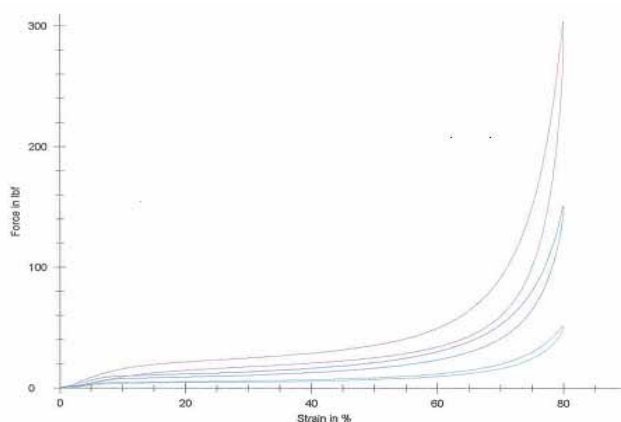
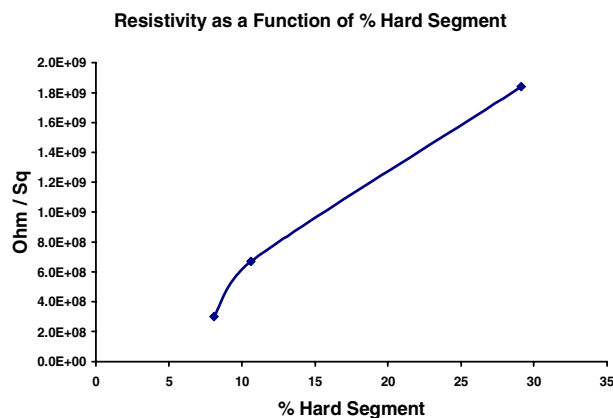


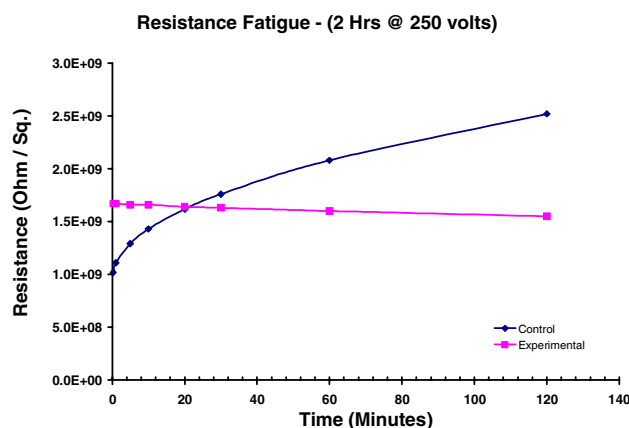
Figure 3 shows the force required to deflect the material to 80% of its original thickness as well as the force being applied as it returns to zero deflection. The area of the curve between the deflection and return is the energy absorbed by the material.

The ability to maintain a given resistivity value while tailoring the force deflection adds design flexibility, i.e., the material can be tailored to the performance characteristics needed. As previously mentioned, the polymer morphology has an influence on the conductance. Figure 4 shows the influence of percent hard segment on the resistivity for the examples in table 1.

[Figure 4]



Another critical electrical property that can be influenced by the polymer morphology, as well as the type of ionic conductive additive, is resistivity fatigue. Good or low resistivity fatigue is the ability to maintain a given resistivity under voltage load over time. In our work we have found that metallic salts tend to be more effective than amine salts in lowering resistance. However, the resistivity fatigue tends to be less than desirable. Again, depending on the polymer morphology, it is possible to use a combination of both amine salts and metallic salts to



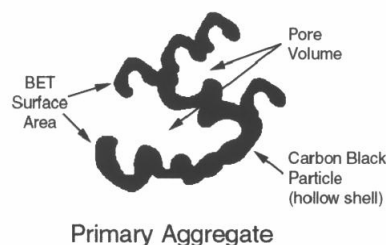
tailor the fatigue response. Figure 5 shows an example of this.

[Figure 5]

## B. Carbon Conductance

Carbon black itself is a semi-conductive material with an intrinsic resistivity of about 0.01 – 0.1 ohm-cm. The most important parameters that influence electro-conductive behavior are surface area, surface chemistry and structure. When dispersed in a polymer at a certain critical concentration the distance between the particles is short enough for cohesive forces to form conductive paths. The particles do not need to be in contact as a small gap of several nanometers wide between them is sufficient to cause electron transport. The electrons can jump from particle to particle, the so-called tunneling effect. As the loading of carbon black in the polymer is increased, virtually no change in resistivity is noticed until a point where enough conductive networks are built to cause electronic tunneling. This point is commonly called the percolation point. Typically the commercially available conductive carbons such as Kejenblack EC series and Cabot's XC series have a very unique, amorphous structure with very high surface area and pore volume. Figure 6 shows an example of structure of Ketjenblack EC. While the structure of these carbon aggregates is good for forming conductive networks they also can present unique foaming difficulties. By their nature they tend to absorb atmospheric moisture as well as have surface chemistries that can contain trace amounts oxygen containing groups like lactones, quinones, phenolics and carboxylics. These chemistries can interfere with the foaming process as well. These difficulties needed to be overcome before good quality foam could be made. In semi-

[Figure 6]

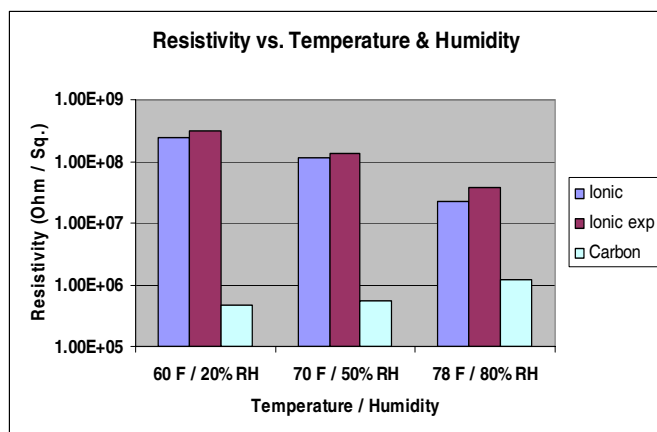


crystalline polymers, such as water blown urethane foams, the carbon aggregates tend to concentrate in the amorphous regions. During the crystallization process a major part of the carbon aggregates are rejected into the interspherulitic boundaries and the rest may be located in the amorphous regions within the spherulites. An increase or refining of the crystalline phase results in a further rejection of the carbon black into the amorphous regions. This raises the relative carbon content in this phase and improves the conductive network<sup>3</sup>. Although the referenced research was based on EVA / HDPE blends, we believed it would apply to our work with semi-crystalline urethane foams. To evaluate the concept, two methods to reorder the crystalline phase were tried:

1. A unique and proprietary post-foaming process.
2. Modifying the EO / PO ratio in the polymer backbone.

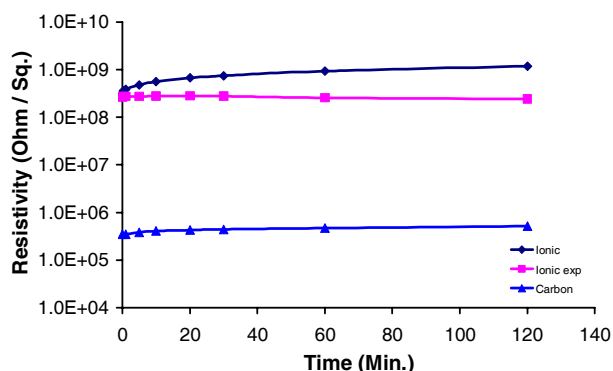
Both of these experiments resulted in significant changes in resistivity. The use of the post-foaming process resulted in a one order of magnitude decrease in resistivity, from E6 to E5 ohm-cm. Altering the polymer backbone had a more pronounced affect. Here the resistivity increased from E6 ohm-cm to E10 ohm-cm! These two experiments clearly show the need to fine tune the polymer morphology to the target or desired product resistivity. The resulting foams had low resistivity fatigue as well as minimal response to temperature and humidity, as shown in figures 7 & 8.

[Figure 7]



[Figure 8]

Resistivity Fatigue



## II. Conclusions

With careful consideration of the polymer morphology as well as the type of conductive additive(s), it was possible to develop a family of high density (6 – 10 lbs. cu.ft.), water blown, urethane foams with tunable electrical properties. Depending on the given application, these foams can be produced having ionic conductance in the range of E8 – E9 ohm-cm and carbon conductance in the range of E5 – E8 ohm-cm. Both systems offer low resistivity fatigue and minimal change in resistivity over a range of environmental conditions.

## References

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2. Poh Poh Gan, Michael Bessette, United States Patent Number 5,855,818, *Electrically Conductive Fiber Filled Elastomeric Foam* (57), 46
3. Stephen H. Foulger, Journal of Polymer Science: Part B: Polymer physics, Vol. 37, *Reduced Percolation Thresholds of Immiscible Conductive Blends*

## Biography

Joe Lovette studied chemistry and mathematics at the University of Delaware prior to joining Foamex's Corporate R&D Group in 1967. He currently serves as a corporate scientist to the Foamex Technical Products group.