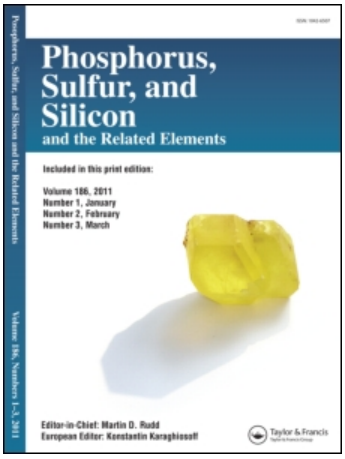

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Lawrence Gettleman

To cite this Article Gettleman, Lawrence(1999) 'Polypohosphazene Fluoroelastomer for Denture Liners and Facial Prosthetics', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 205 — 208
To link to this Article: DOI: 10.1080/10426509908546218
URL: http://dx.doi.org/10.1080/10426509908546218

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 205-208
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Polypohosphazene Fluoroelastomer for Denture Liners and Facial Prosthetics

LAWRENCE GETTLEMAN

Department of Biological & Biophysical Sciences, School of Dentistry, University of Louisville, Louisville, Kentucky 40292 USA

Firestone PNF®-200 and later, Ethyl Eypel®-F were compounded with di- and tri-functional acrylates, $BaSO_4$, peroxide activator, and pigment to make a hot water-curing polyphosphazene liner for removable dentures. Advantages include permanent softness (durometer A = 35), energy absorbance, fungus resistance, and bonding to PMMA dentures. Uses may also include facial prosthetics which replace parts of the face lost due to cancer, trauma, or birth defects.

Keywords: polyphosphazenes; fluoroelastomers; denture liners; extraoral maxillofacial prostheses; denture prosthetics; interpenetrating polymer networks

INTRODUCTION

There are more than 35 million people in the US who have no teeth, and millions more who have lost some teeth whose replacement may require the use of removable dentures. When teeth are lost, the bone that supports them resorbs, resulting in a meager base of bone to support removable appliances. Bone loss continues over time, so the elderly are often handicapped by the inability to retain false teeth (complete dentures) comfortably.

Partial dentures are made of cobalt-chromium metal frameworks lined with a poly(methyl methacrylate) base which rest on the fragile oral mucosa; complete dentures are made of PMMA entirely.

The use of a soft rubber liner under the denture base makes the denture more comfortable and may engage anatomic undercuts to make it more retentive. Traditional materials include plasticized acrylics and silicone rubber. The former lose their plasticizer and harden, usually within weeks or months, and the latter are difficult to finish and bond to the denture base, and are fouled by fungal growth in many patients in a matter of months.

INDUSTRIAL POLYPHOSPHAZENE: Firestone's PNF®-200

Funded by the National Institute of Dental Research in 1980 at Gulf South Research Institute in New Orleans, several industrial rubber materials were examined, with Firestone's PNF®-200 chosen for further development.[1] The material was discovered by Prof. Harry R. Allcock of The Pennsylvania State University and is a fluoroalkoxy-substituted polyphosphazene of approximately 50,000 units, with the substituent groups of C3-C9 fluoroalcohol units. To make the denture liner material, 100 parts of PNF-200 gum rubber is compounded with 18 parts trimethylolpropane trimethacrylate and 2 parts of ethyleneglycol dimethacrylate, 1 part lauroyl peroxide activator, 15 parts $BaSO_4$ radiopaque filler, PMMA beads, and red pigment.[2] This makes a one-part dough which can be compression-packed into gypsum molds against a new or relined PMMA denture base and is cured in water at 74°C for 1½ hours followed by boiling. It is also microwave-curable for more rapid dental laboratory processing.

Toxicity testing of this material at the University of Tennessee at Memphis and the University of Texas at San Antonio provided evidence that the phosphazene material was as safe or safer than existing denture liner products in acute toxicity screens, hemolysis, and in hamster cheek pouch irritation tests. DMA tests were also run, showing high storage modulus for this material.[3] Clinical trials at Northwestern University and at Charity Hospital (LSU, New Orleans) on more than 40 patients demonstrated the material's effectiveness as a denture liner up to 29 months compared to a silicone rubber product in the same patients.[4] US Food & Drug Administration approval was received in 1987 via the 510(k) process. Gulf South Research Institute ceased operations in

1987 and licensed its rights to the denture liner development to LouisianA Research & Development, Inc. (LARD).

INDUSTRIAL POLYPHOSPHAZENE: Ethyl's Eypel®-F

Firestone sold its phosphazene business to Ethyl Corporation in 1985, with production of an identical fluoroalkoxy-substituted phosphazene beginning in 1988. A strong argument was made to Ethyl's specialty polymers division in Baton Rouge to allow the use of their product in the biomedical market, given the experience of A.H. Robbins Co. with the Dalkon Shield IUD a few years earlier (Robbins and Ethyl are both headquartered in Richmond, VA). It was pointed out to Ethyl that marketing resilient denture liners had never resulted in lawsuits, the prostheses were removable, Ethyl already produced generic drugs, and the son of the chairman of the board was a physician looking for ways to commercialize Ethyl products in the biomedical field.

DENTAL POLYPHOSPHAZENE: Hygenic's Novus®

Ethyl was convinced to sell gum rubber to LARD's sublicensee, The Hygenic Corporation of Akron, OH, a dental and physical exercise products company. Hygenic compounded, packaged and marketed the resilient denture liner under the trade name of Novus® in February, 1989. Properties include durometer A of 35, tensile strength 1.65 MPa, elongation 18%, bond strength to PMMA of 3.42 kN/m, and tan δ of 1.4 at body temperature.

The denture liner was the first use of a polyphosphazene material as a biomedical product. It was sold primarily in the United States, with some sales in Europe. Several hundred thousand liners were made in the six-years after the product was introduced. Fewer than ten adverse reports from patients were received by Hygenic, most due to errors in processing the denture liner. The phosphazene system therefore holds promise for many other biomedical applications, including the facial prosthetics and the artificial heart.[5]

In 1993, Ethyl Corporation announced that it would no longer produce Eypel-F and Eypel-A (their arylalkoxy-substituted phosphazene) due to changes in their market position at the end of the Cold War. Hygenic ceased sales of Novus in 1995, as there were no other sources of the raw material.

A grant was received from the National Institute for Dental Research to support further developments of phosphazenes at the

University of Louisville. Until the announcement that Ethyl would cease production, a number of new uses were explored such as use in facial prosthetics, artificial limb prosthetics, in dance or athletic footwear, and as an autopolymerized version of the denture liner. Several patent applications were submitted with the collaboration of Leonid Rappoport, PhD, through the University and its technology transfer agent, Research Corporation Technologies, Inc. The patents were not supported by RCT due to their assessment of less than $10 million potential, an indication of market conditions. It seems that phosphazenes have not yet arrived.

The new availability of phosphazene polymers through Penn State University should make a substantial change in the future of polyphosphazene technology. It is a "designer polymer" which may be customized by substituting any pendant chemical groups from the main chain. The polymer system may be called upon to fill many requirements, with few restrictions. With its -P=N- backbone, it is as different from organic polymers as the silicones, and may become the silicone polymers of the 21st century.

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