



**CURING OF POLY(ESTERIMIDE) ELECTROMAGNET-WIRE
ENAMEL, ISOMID™:**

**A NUCLEAR MAGNETIC RESONANCE STUDY OF THE INFLUENCE
OF CRESYLIC ACID ON THERMAL CURING**

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Preface

This thesis was completed under the aegis of Schenectady Chemicals Australia Pty. Ltd., and involves the industrial processing of poly(esterimide) electromagnet-wire enamel. Consequently, many technical terms are used to describe methods and phenomena found in the wire-enamelling industry. A glossary of terms has been included to provide a convenient reference, during the reading of this work.

Working for Schenectady Chemicals Aust. Pty. Ltd. over the last six years has been a rewarding experience, and because the work was instigated by this organisation in order to improve the processability of their product, Isomid 860TM, efforts were concentrated toward that end. An understanding of the fundamental reactions, taking place during the thermal curing of IsomidTM varnishes onto copper wire, was considered to be necessary before any constructive changes to the solvent system of wire-varnishes can be undertaken. Hence, it is hoped that the work presented in this volume will contribute to an informed discourse on the functions of the wire-enamelling solvent, cresylic acid.

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Abstract

Nuclear magnetic resonance (NMR) spectrometry has been used to characterise the proprietary poly(esterimide) resin (resin-SC) which is utilised as a varnish, in cresylic acid, to produce high quality dielectric coatings for electromagnet winding wires. These wires must be able to withstand high service temperatures (i.e., upto 180°C , continuously). Although the resin is readily soluble in polar solvents and can easily be characterised by solution NMR techniques, the film that results from thermally curing the varnish is an insoluble and infusible, highly cross-linked polymer, requiring solid-state NMR methods for analysis. Unfortunately, these NMR techniques produce much broader peaks ($\approx 100\text{Hz}$ in width) than the solution techniques, however, useful clues were obtained. Solid-state NMR methods were employed to characterise samples of industrially cured IsomidTM and TerebecTM wire-enamels.

Aromatic residues were detected in both wire-coatings, and were concluded to be aryl-ester derivatives of the polymers formed by reaction with the phenols present in cresylic acid, the varnish-solvent.

Solvent-extraction studies (using CHCl_3 , DMSO, and EG) indicated that the residual solvents were structurally a part of the enamel-films, and are not released until the enamel is heated above $145 \pm 2^{\circ}\text{C}$, the **threshold** temperature. The **extra-resin** substances were thus extracted and detected by UV/visible spectroscopy on the extraction-solvent. Mass spectrometry of scrapings from an Isomid enamel-film also indicated a volatilisation of these substances as the temperature of the

ionising-chamber passed 144⁰C.

Measurements of the water condensed during the esterification of benzoic acid (BA) with EG (in 10-fold excess) within the first 10 minutes of reaction has suggested that the phenols in cresylic acid can acid-catalyse the polycondensation of resin-SC. Two aryl titanate catalysts, tetraphenyl and tetra(*p*-nitrophenyl) titanates, were found to have a similar effect on the condensation-rate, whilst the use of tetra(2,4-dinitrophenyl) titanate greatly increased this rate. On the other hand, the proprietary alkyl titanate, "Tyzor TBT", showed little catalytic activity, possibly due to inhibition by BA. The greater thermodynamic stability of aryl and chelato-titanates suggests that "Tyzor TBT" reacts readily with functionalities of resin-SC and cresylic acid, in the wire-varnish prior to thermal curing. Aryl titanates are readily formed by exothermic ester exchange from "Tyzor TBT" when in solution with phenol, *p*-nitrophenol, and 2,4-dinitrophenol, at room temperature.

Broadband carbon NMR evidence for the chelation of 2-hydroxyethyl benzoate with titanium(IV) has suggested that coordination of the reactive hydroxyethyl chain end-groups of resin-SC can take place upon ester exchange with "Tyzor TBT". The postulated chelato-, or bischelato-, titanate is likely to be the seminal form of titanium in the coordinative catalysis of transesterification; the major polymerisation reaction.

In conclusion, the polycondensation dramaturgy, occurring during the thermal curing of Isomid wire-varnish, is

visualised as acid-catalysis by the phenols which also form aryl-ester derivatives with the poly(esterimide) resin. The aryl esters act as reactive intermediates in polymerisation; these esters are more amenable to nucleophilic substitution than are alkyl analogues such as the hydroxyethyl chain end-groups of resin-SC. The last traces of the phenols (i.e., residual), existing as esters, are released slowly during the late stages of thermal curing. Slow-release prevents nucleation of the volatile solvents, and thereby, blistering due to the formation of bubbles within the mostly cured, plastic enamel-film is avoided.

Therefore, cresylic acid (viz., the phenols) acts in tandem with the titanate catalyst (viz., "Tyzor TBT") to facilitate the polymerisation of the PEI resin (viz., resin-SC), so as to form a smooth, substantially void-free dielectric wire-coating.