

Solving Problems Critical to the Business and Research Chemist by Utilizing NMR Spectroscopy

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The presentation will center on distinct issues encountered in an application for the paints/coatings industry and an application for the tire industry.

A film made with acrylate resin and various components including γ -methacryloxypropyl trimethoxysilane, $[\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(=\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3]$, was formulated by our customer to deliver a hard, shiny clear coat, on automobile surfaces. The film hardens via hydrolysis and the crosslinking of the trimethoxysilyl group ($-\text{Si}(\text{OCH}_3)_3$) with water vapour and silanol functionalities. At the customer's plant, two clear coat films were catalysed with different acids (pK_a 0.7 and 1.85), and each demonstrated different adhesion properties. The better performing film (pK_a 0.7) passed the motor vehicle safety standard test while the other failed. As a possible way to evaluate these differences, we recalled earlier studies wherein it was discovered that $\{^1\text{H}-^{29}\text{Si}\}$ cross polarization magic angle spinning (CP/MAS) NMR spectroscopy could be used to study the crosslinking of the trimethoxysilyl T-groups. Solid state NMR spectroscopy permits the observation of an unaltered, undissolved film. Accordingly, the goal of this study was to investigate the two clear coat films through $\{^1\text{H}-^{29}\text{Si}\}$ CP/MAS NMR spectroscopy and discover the mechanism through which one film failed while the other film was able to meet the required standard.

When tire makers introduced a silica filler in conjunction with a silane coupling agent as a means of reducing rolling resistance in the tire tread, it became important for Momentive to determine the sulfur distribution in bis(3-triethoxysilylpropyl) tetrasulfide, $[(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2)_2\text{S}_4]$. The combination of ^1H and ^{13}C NMR results showed the distribution of sulfur species ($\text{S}_1\text{...S}_7$) in the nominal tetrasulfide silane. The chemical shift region in ^{13}C NMR spectrum for methylene carbon bonded to sulfide ($-\underline{\text{C}}\text{H}_2\text{S}-$) was deconvoluted and the results compared with the peak areas from supercritical fluid chromatography (SFC) data. The NMR and chromatographic data were in good agreement.