

Fiber Optic FTIR: A Novel PUR/PIR Catalyst Development Tool

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ABSTRACT

Development of new catalysts promoting different phases of polyurethane foam formation (blowing, gelling, cross-linking) is typically done using a series of physical and handmix generated reactivity profile properties. The ability to understand the evolution of chemical species associated with rigid polyurethane/polyisocyanurate (PUR/PIR) foam formation has been historically only inferred based on their final distribution in the fully cured foam using Fourier transform infrared spectroscopy (FTIR) or solid state carbon-13 nuclear magnetic spectroscopy (NMR). Neither technique gives insight into the reactions as they occur. Recently, however, we have refined the usage of infrared transmitting optical fibers as evanescent wave sensors and a mathematical deconvolution technique (iterative target transformation factor analysis) to extract and follow the isocyanate, urea, urethane and trimer concentrations as they occur in both lab scale and machine scale foam production. Additionally, the fiber optic probe used can be placed at specific locations within the growing foam to target the evolution of isocyanate chemistries at the surface or core of the foam. The specificity of the technique, speed of data acquisition, and portability of equipment all make this method ideal as a tool enabling us to fundamentally probe how our catalysts alter the distribution of individual chemical species during the initial moments in foam formation. This paper describes the usage of this unique analytical tool. Further, we demonstrate its utility in understanding the mechanism whereby a

novel new catalyst, Polycat® 48, improves dimensional stability in a HCFC-141b blown appliance formulation. The fiber optic FTIR results for Polycat 48 will be contrasted to a control catalyst blend of Polycat 5 and Polycat 41 in the same formulation.

INTRODUCTION

In rigid polyurethane foam manufacture for appliance, a reaction profile and density are targeted to achieve the desired balance of material performance and processing cost. Given the constraints of the established reaction profile, catalyst formulation plays a pivotal role in making foam with desired flame retardancy, compressive strength, flow properties, insulating value, and dimensional stability. Catalyst package optimization involves balancing the rates of reaction associated with blowing, gelling, and cross-linking or alternatively, the formation of the corresponding chemical species: urea, urethane, and isocyanurate (trimer) /allophanate/biuret, respectively. Fundamental understanding of the relationship between catalyst type, level, activity and the formation of these species results in a more predictive approach to catalyst package formulation. It further provides greater insight into the relationship between physical properties and functionality contribution resulting from catalyst choice.

A well-established method for examining functionalities formed in cured polyurethane foams is Fourier Transform Infrared (FTIR) spectroscopy. Some time after the foam is formed, an FTIR spectrum is obtained from the sample surface or core. By

obtaining individual FTIR spectra at increasing time intervals, foam cure rates resulting from isocyanate reaction with atmospheric moisture can be determined. Further, the relative efficiency of isocyanurate formation can be determined and compared from one catalyst package to the other. However, the path the chemistry took to get to that point occurred long before the spectrum was acquired. Inferences about catalyst performance have to be made by looking at the final distribution of urea, urethane, isocyanate, and trimer. Although FTIR is broadly utilized for foam characterization off-line [1-3] as well as for raw materials quality control (QC) or identification, it does not let us capture the interplay and evolution of these species early in the foaming process.

Another off-line analytical tool used to understand functionality distribution in rigid PUR/PIR foam is solid state carbon-13 (¹³C) magic-angle spinning nuclear magnetic resonance (MAS NMR) [4]. This method enables us to detect and relatively quantify the amount of trimer formed in a foam by looking at the relative amounts of carbonyl in trimer versus urea/urethane environment. However, due to the inability of ¹³C NMR to resolve unreacted isocyanate or differentiate between urea and urethane, this technique gives only partial information.

To better understand foam formation and the role our catalysts play in isocyanate reaction chemistry and polymer morphology development, it is necessary to use dynamic methods. To address the limitations of the existing off-line techniques, an in-situ methodology is required. The development of IR transmitting optical fibers with low optical losses, sufficient mechanical strength, and temperature stability to meet the demanding conditions of many process environments have made in-situ FTIR measurements possible [3,5]. The optical fiber can be positioned anywhere within the foaming cavity, allowing us to monitor the in-situ isocyanate reactions during foam production. By positioning the fiber at various points within the foaming mass, it is now possible to dynamically observe differences in isocyanate reaction chemistries between foam surfaces and interiors. Modern fiber technology is enabling us to leverage the strengths of FTIR including

- ease of use,
- specific functionality fingerprint,
- relatively low cost, and
- specificity of fiber placement

to monitor the evolution of key functionalities during the first few minutes of actual foam formation.

As mentioned, the method uses an unclad optical fiber to both irradiate adjacent sample and detect signal coming from the irradiated foam [3,5]. We can obtain spectra at the rate of up to one spectrum per second as the foam rises, covers the fiber, and continues to cure. Although FTIR is a valuable tool for discrimination between key polyurethane chemical species, it has historically been difficult to accurately follow the various isocyanate reactions due to the formation of spectroscopically similar species. Using a novel mathematical deconvolution technique, known as iterative target transformation factor analysis (ITTFA) [6], to extract individual signals that vary independently over time from a severely overlapping spectral region, we can quickly analyze spectroscopic data obtained from dynamic systems, such as polyurethane foaming reactions. ITTFA enables us to mathematically model spectra for the isocyanate and its reaction products and track isocyanate, urea (free, loosely associated and bidentate), urethane (free and hydrogen bonded) and isocyanurate concentrations throughout the reaction (Table 1 and Figure 1).

This technique has been broadly applied at Air Products and Chemicals to give insight into catalyst performance and influence on final product properties in many polyurethane-based chemistry market segments including elastomers, coatings, microcellular [7], flexible, and all rigid foam areas. The use of this methodology to differentiate rigid foam catalysts by studying in-situ the individual chemical reactions and their timing will be demonstrated.

The example shown will illustrate how fiber optic FTIR was used to understand the mechanism by which a novel new catalyst, Polycat 48, enhances dimensional stability in HCFC-141b blown appliance formulation. The results of this new catalyst will be contrasted against a blend of Polycat 5 and Polycat 41 to illustrate the performance enhancement.

Table 1. Polyurethane Chemistry Frequencies in FTIR Spectrum

Frequency	Functionality
1640 cm ⁻¹	Bidentate H-Bonded Urea
1650 - 1690 cm ⁻¹	Loosely H-Bonded Urea
1705 cm ⁻¹	Loosely H-Bonded Urethane
1710 cm ⁻¹	Trimer (Isocyanurate)
1717 cm ⁻¹	Free Urea
1735 cm ⁻¹	Free Urethane
2270 cm ⁻¹	Isocyanate

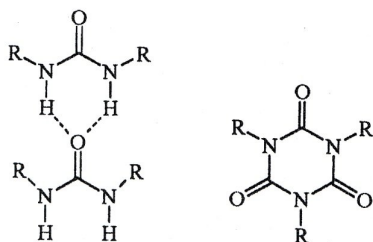


Figure 1. Structures of selected FTIR detected species: bidentate H-bonded urea (left) and trimer or isocyanurate (right)

In addition, future advances being made in this analytical technology area and their potential impact on catalyst development and foam morphology studies will be discussed.

EXPERIMENTAL

Fiber Optic FTIR Method

FTIR spectra were obtained with a Midac Illuminator FTIR source and a Remspec optical fiber MCT detector module. The Midac source was modulated at 40 kHz, allowing a spectrum consisting of four co-added scans at 8 cm^{-1} resolution to be collected each second. Spectra were obtained once each second for five minutes in all cases.

Polymer clad chalcogenide fiber, 500 micron diameter, was cut into sections and the ends were polished with 1 micron alumina. The fibers were subsequently prepared by removing their protective nylon polymer coating with methylene chloride. This was achieved by soaking the fibers in the solvent and wiping them with solvent-saturated cotton pads. The polymer coating was removed to expose the fiber to the reactants.

A generalized instrument configuration is depicted in Figure 2. The foam was handmixed and poured into a corrugated cardboard box. Data collection was started at the beginning of the mix to obtain a consistent start time for each run. In the case of free rise foam, the foam core was sampled by stringing the fiber across the center of a box. The fiber was fixed at each end to the box bottom when sampling surface cure characteristics.

The infrared spectra of the foams during cure exhibit baseline shifts when the foam core is sampled. These baseline distortions are due primarily to light scattering in the fiber as microscopic crystals form within the fiber at temperatures above its glass transition point. It was found that a fourth-order polynomial function could

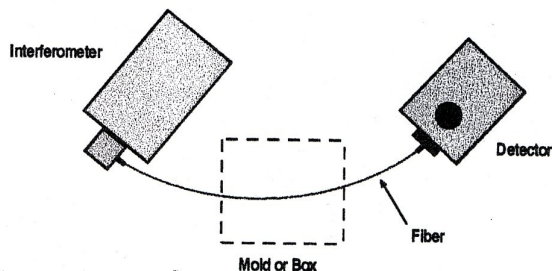


Figure 2. Generalized fiber optic FTIR configuration

be fit to the baseline and subtracted to correct its distortion. This effect is not as extreme in polyurethanes applications where temperatures are lower (foam surface or thin microcellular foam plaques). Additionally, the contact between the foam mass and optical fiber sensor changes as the foam expands and rises, effectively varying the optical path length of the sensor. The RMS intensity of a polyether absorbance band is normalized to compensate for different coverage onto the optical fiber sensor.

Due to overlap of urethane, urea, and trimer absorbance bands in the carbonyl region (1660 - 1875 cm^{-1}) (Table 1), a chemometric method based on principal factor analysis was used to model the component spectra and extract their intensity vs. time profiles. The principal factors were obtained from a singular value decomposition of the data covariance matrix. Model spectra of the individual components were obtained from target transformations of the principal factors. An F-test [8] was performed on the eigenvalues of the principle components obtained from the spectra from each reaction run. This was done to determine the optimum number of principal components for target transformation into model spectra. The first 30 principal factors were obtained from the carbonyl region of the spectra and an F-test statistic and percentage significance level was calculated for each eigenvalue. The results of the F-test on each set of spectra indicated that the carbonyl region could be optimally modeled with two principal factors in each run.

To monitor isocyanate consumption, a broader spectral region including the isocyanate absorbance band can be modeled (as above) or its integrated intensity directly extracted from the 2220 to 2310 cm^{-1} band. The frequency limits indicated for the isocyanate band were selected to avoid spectral artifacts from atmospheric CO_2 and selenium hydride impurities in the optical fiber. In addition, trimer formation is followed by monitoring the 1408 cm^{-1} band directly.

Foam Preparation

For machine studies, an Edge Sweet high pressure machine with impingement mixing guaranteeing intimate mixing between the isocyanate and polyol resin was used to fill an industry standard 200x20x5 cm³ Brett mold. Machine pressures of 2000 psi were used.

The machine was prepared by flushing the polyol resin tank twice for two to three hours each time with 30 lbs of polyol system. Similarly, the isocyanate tank was flushed for several hours with 20 lbs of polymeric-MDI. Tank temperatures were 80°F for both the isocyanate and polyol resin tanks. Once tank temperatures were stabilized, the machine pistons were calibrated to insure proper mix ratios and pump speeds were adjusted accordingly. The mold was heated to 120°F and a paste wax was used to ease foam removal.

Handmix experiments were conducted using the following procedure and the formulation listed in Table 2.

The resin components, including the HCFC-141b, were blended together. The appropriate amount of polyol mixture was weighed into a 32 oz. paper can. Quick addition of a stoichiometric amount of polymeric MDI to the polyol was performed and subsequently all was blended together with a Servodyne Mix Head at 3000 rpms for approximately five seconds. The foaming mixture was transferred to a 10"L x 10"W x 6"H cardboard box and allowed to free rise with the fiber optic FTIR data being recorded for 300 seconds. A 24-inch length of FTIR

fiber was previously prepared and pre-positioned in the final foaming container in the bottom of the box for surface measurements or in the geometric center of the entire foam for core measurements. Fully cured foam parts were cut at the fiber location to ensure proper fiber positioning while foaming occurred.

RESULTS AND DISCUSSION

In rigid foam applications, fundamental understanding of a catalyst's ability to direct the individual elements of polyurethane chemistry is important. By uncovering the catalyst structural drivers for urea, urethane, trimer formation and isocyanate consumption, we can design and screen new catalysts quickly, then focus physical testing methods only on the best catalyst candidates.

In developing new catalysts, we have begun to routinely utilize fiber optic FTIR to shed light on the mechanism for their performance. To demonstrate the utility of the fiber optic method, Polycat 48 was compared directly to an industry standard blend of Polycat 5 and Polycat 41. Polycat 48 catalyst, was the result of an intensive experimental design performed initially on HCFC-141b blown appliance foam. It has found use in many rigid polyurethane foam applications using a variety of blowing agents. It is a balanced blow, gel and trimerization catalyst and, therefore, can be used as the sole catalyst in rigid PUR foam formulations. Fiber optic FTIR data was collected on handmix foams, while physical properties described herein were done on molded foam (refer to experimental section for details of foam preparation). Further, polyurethane chemistries at both the core and bottom surface were monitored using the fiber optic FTIR method to understand catalyst performance differences in both foam regions.

According to the details of the method outlined in the experimental section, the Polycat 5/Polycat 41 control core spectra were used to generate models of the carbonyl region (1350 - 1850cm⁻¹). These model spectra in turn were used to extract the individual carbonyl containing species (urea and free urethane in this case) from the original individual spectra to create the following intensity versus time figures. Figure 3 shows typical model spectra for each of the pertinent species. Although not found to a large extent in this system, trimer identifying features include 1710 cm⁻¹ in the carbonyl region and a confirming band at 1408 cm⁻¹.

Table 2. HCFC-141b Appliance Foam Formulation

Component	Parts Per Hundred
Polyol	100.0
Water	1.50-1.92
HCFC-141b	40.0-45.0
Control catalyst package:	
Polycat 5 / Polycat 41	1.20-1.40 / 0.55-0.65
New catalyst:	
Polycat 48	2.40-2.50
Dabco DC5357 surfactant	3.0-3.5
Polymeric MDI ratio	1.30-1.40

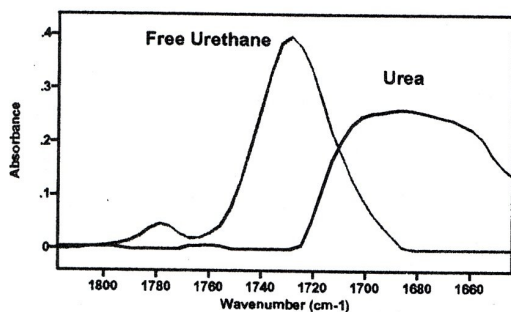


Figure 3. Modeling carbonyl region

In some cases also, a nylon artifact resulting from residual polymer coating on the fiber can be observed, however, most was successfully removed here. For isocyanate, its band is well resolved at 2270 cm^{-1} (Table 1) and intensity changes can be directly extracted by integrating the spectral series following baseline correction.

Figures 4 through 9 show the evolution of isocyanate, free urethane, and urea at the bottom surface and core of the handmix foams.

Isocyanate conversion at the core and bottom surface show significant differences for the Polycat 5/Polycat 41 control when compared to Polycat 48 (Figures 4 and 5). In the core, after approximately 150 seconds, both formulations reach equivalent isocyanate consumption levels. However, the isocyanate consumption rate was slower for the Polycat 48 formulation in the center of the foam mass. There was also less isocyanate consumption for Polycat 48 at the bottom surface. Further, the overall isocyanate reaction is decreased at the surface for both catalysts when compared to the core.

Polymer network build is reflected in the growth of the free urethane band. Figures 6 and 7 show bottom surface and core free urethane evolution. On the bottom surface, both the control and Polycat 48 show similar ultimate network builds, however, the reaction profiles are somewhat different. In the core, Polycat 48 causes a marked delay in gelling resulting in delayed formation of urethane species, but like at the bottom, final polymer network formation (urethane intensity) is similar. The downward slope of the free urethane band (1735 cm^{-1}) is due in part to a shift to hydrogen-bonded urethane (1705 cm^{-1}) caused by foam cure.

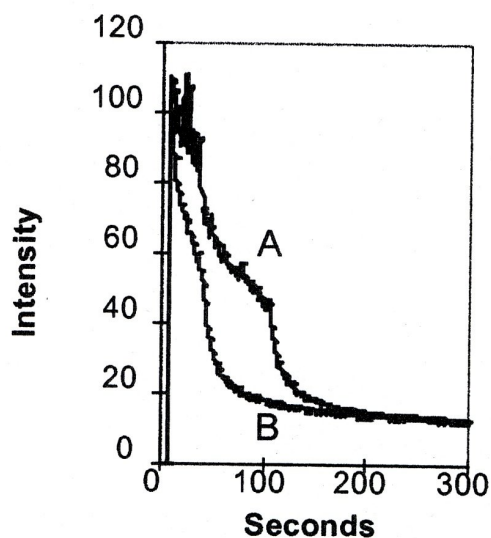


Figure 4. Core isocyanate conversion: A) Polycat 48 and B) Polycat 5/Polycat 41

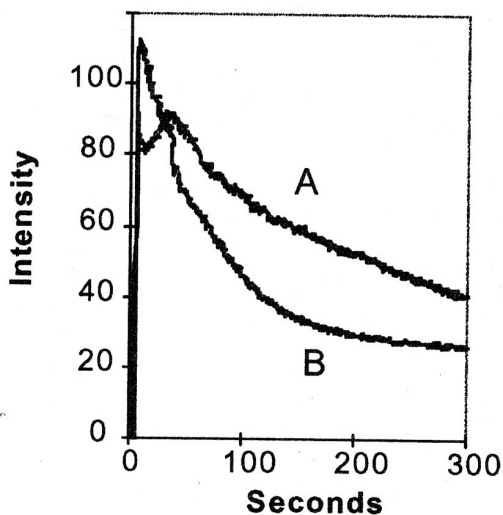


Figure 5. Bottom isocyanate conversion: A) Polycat 48 and B) Polycat 5/Polycat 41

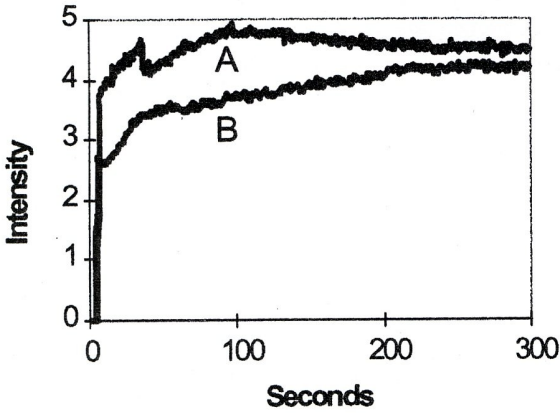


Figure 6. Bottom free urethane: A) Polycat 5/Polycat 41 and B) Polycat 48

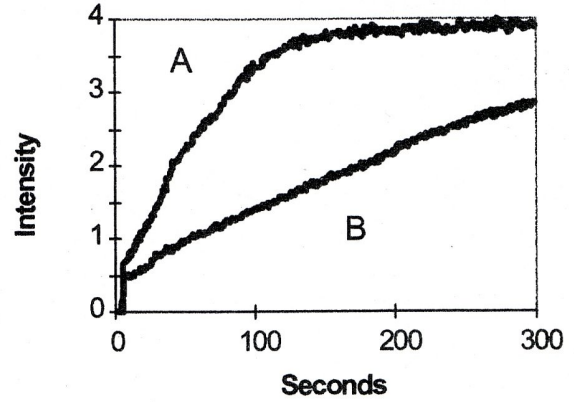


Figure 8. Bottom urea: A) Polycat 5/Polycat 41 and B) Polycat 48

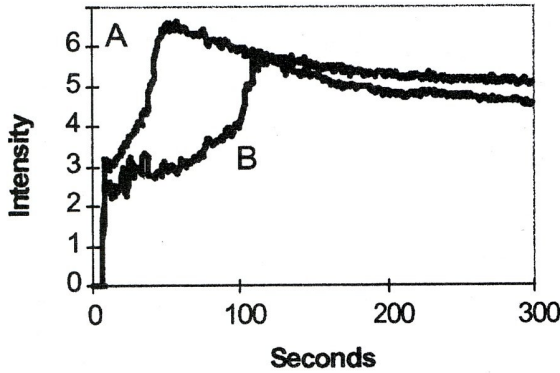


Figure 7. Core free urethane: A) Polycat 5/Polycat 41 and B) Polycat 48

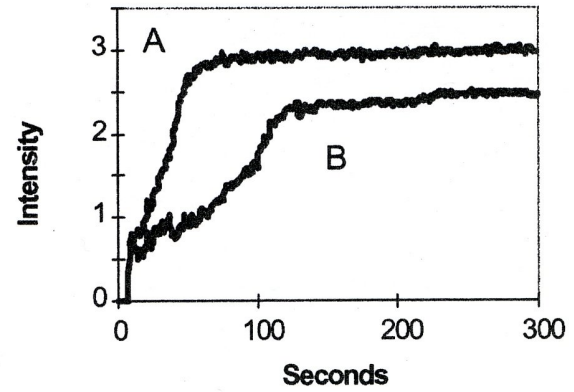


Figure 9. Core urea: A) Polycat 5/Polycat 41 and B) Polycat 48

Figures 8 and 9 show bottom surface and core urea formation, reflecting the blowing reaction rate. Polycat 48 is a significantly weaker blowing catalyst at both surface and core than the Polycat 5/Polycat 41 control.

Although fiber optic FTIR data is not shown, significant levels of isocyanurate were not detected at either the surface or core of the foam.

Based on the above fiber optic FTIR results, the mechanism for enhanced dimensional stability observed for Polycat 48 cannot be attributed to greater trimer formation, or even better overall foam cure (isocyanate consumption). Flow, however,

should be improved due to the delayed onset of polymer network build (Figure 7).

To further determine the mechanism for improved dimensional stability, molded foam was made using a general appliance HCFC-141b/water co-blown formulation (Table 2). A Brett mold was used in conjunction with the Edge Sweets machine to make foams with densities of 1.85, 1.92, 1.96, and 2.01 lb/ft³. These densities correspond to minimum fill, and 4%, 6%, and 8% overpack conditions.

Table 4. Foam Density Distribution						
Overpack	Overall (lb/ft ³)	A (lb/ft ³)	B (lb/ft ³)	C (lb/ft ³)	D (lb/ft ³)	Δ (high - low)
Polycat 5/Polycat 41						
Minimum Fill	1.85	1.52	1.61	1.7	1.8	0.28
4%	1.92	1.78	1.82	1.88	1.94	0.16
6%	1.96	1.84	1.85	1.91	1.99	0.15
8%	2.01	1.87	1.91	1.96	1.99	0.12
Polycat 48						
Minimum Fill	1.85	1.73	1.72	1.82	1.86	0.13
4%	1.92	1.74	1.75	1.77	1.8	0.06
6%	1.96	1.89	1.9	1.91	1.95	0.06
8%	2.01	1.92	1.94	1.95	1.97	0.05

Table 4 lists densities as they were measured along the length of the molded part for two catalyst packages, Polycat 5/Polycat 41 and Polycat 48. The top sixteen inches of each part was sampled. Four inch sections were removed (A from the top and D from the bottom) and their densities determined. Additionally, Δ (defined as the difference between the highest and lowest densities on a single panel) was reported to represent the density uniformity. Finally, the overall panel density or average density is also shown in Table 4. Note that although both catalyst packages have the same overall densities for the indicated minimum fill or over pack conditions, the reported Δ values, overall density spread, vary significantly. Considerably better uniformity in density was seen for the Polycat 48 single-catalyst formulation.

In summary, Polycat 48 is very effective at improving foam dimensional stability at lower packed densities, while maintaining or improving other processing properties such as flow. The combination of the dynamic fiber optic FTIR method with standard physical testing allowed us to understand the mechanism by which Polycat 48 enables more uniform physical properties and less foam shrinkage.

CONCLUSIONS

Fiber optic FTIR has been demonstrated to be a key analytical tool able to uniquely provide dynamic information on the evolving chemistry in many polyurethane applications, but in particular to rigid foams. Its portability, ease of use, and functionality targeted information make it uniquely applicable to both free rise and molded foam applications. The examples shown illustrate the role our catalysts play in imparting dimensional stability, a key physical property, and the impact of this method on that understanding. We are applying this technique more

frequently as we develop novel catalyst structures and as the FTIR technology matures, becoming more economically feasible. Additionally, we are in the process of correlating more fundamental morphological changes to urea and urethane formation as viewed through the eyes of FTIR. Future efforts are underway to gain greater insight into foam morphology, which include at-line or in-situ Raman spectroscopy [9] and a novel on-line process technique called TIRES (transient IR emission spectroscopy) [10]. These key analytical tools will give insight into how catalysts influence polyurethane chemistry, thereby enabling us to tailor-make new catalysts for any end-use application.

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