

# Catalysts for Improved Spray Foam System Stability and Reactivity with Low GWP Blowing Agents

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## **ABSTRACT**

Polyurethane spray foam has emerged as an insulation material of choice for improving energy efficiency in the construction market. The high R-values achievable, coupled with fast, on-site application have helped fuel the growth of spray foam globally. However, formulations for closed-cell spray foam have traditionally contained hydrochlorofluorocarbons (HCFC's) such as HCFC-141b, or hydrofluorocarbons (HFC's) such as HFC-245fa and HFC-365 as auxiliary blowing agents. Although these blowing agents offer excellent insulating values and handling properties, there have been increasing concerns in the public with respect to the high ozone depleting potential (ODP) of HCFC's and high global warming potential (GWP) of HFC's. These concerns are addressed under the Montreal and Kyoto Protocols, respectively, and call for the eventual replacement of these blowing agents with new options that have both low ODP and low GWP. Air Products and Chemicals, Inc. has previously developed catalysts for spray foam with improved stability, reduced emissions, or reduced odor compared to the prior generation of catalysts. The current paper will describe our latest catalyst developments designed to provide both excellent system stability and reactivity for closed-cell spray foam systems incorporating low GWP blowing agents such as HFCO-1233zd(E).

## **INTRODUCTION**

Improving energy efficiency is a growing interest in the construction market as energy costs rise and consumer awareness of energy issues increases. Increasing insulation and reducing air leakage are proven methods for improving energy efficiency. Spray foam insulation has emerged as the material of choice to insulate and air seal structures in a single application, thus significantly reducing the energy consumption of buildings. Formulations for closed-cell spray foam with densities of 2 to 2.5 pounds per cubic feet (pcf) often contain hydrochlorofluorocarbons (HCFC's) or Hydrofluorocarbons (HFC's). HCFC and HFC molecules have excellent insulating values and have been used extensively as blowing agents in the past decade for both wall and roof applications. However, there have been increasing concerns in the public with respect to the Ozone Depleting Potential (ODP) or Global Warming Potential (GWP) of HCFC blowing agents such as HCFC-141b, and HFC blowing agents such as HFC-245fa and HFC-365mfc [1]. These concerns are addressed under the Montreal and Kyoto Protocols, respectively, and call for the eventual replacement of these blowing agents with new options that have both low ODP and low GWP. As a result of these environmental concerns, spray foam polyurethane foam formulators are developing systems based on new blowing agents which are both low ODP and low GWP.

Air Products and Chemicals, Inc. has previously developed catalysts for spray foam with improved stability, reduced emissions, or reduced odor compared to the prior generation of catalysts. The current paper will describe our latest catalyst developments designed to provide both excellent system stability and reactivity for closed-cell spray foam systems incorporating low GWP blowing agents such as HFCO-1233zd(E).

## EXPERIMENTAL METHODS AND FORMULATION

The general screening formulation utilized for all results presented in this paper is shown in Table 1. The control catalyst package included 1.0% of Polycat® 30, an amine catalyst with balanced blow/gel selectivity, and Dabco® T120, a tin gel catalyst that is hydrolytically stable and provides a fast reaction and good back-end cure [2]. A summary of the commercial catalysts used in this study is shown in Table 2. Dabco PM300 is an emulsifier with some cell stabilization, and is useful in ensuring that the blowing agent and other reagents remain compatible and in the same phase during the aging studies [3]. Dabco DC193 is a silicone polyether surfactant that provides excellent foam stability and has been shown to give good performance in flammability testing of the finished foam [4]. The blowing agents used in this study are 1,1,1,3,3-trifluoropropane (HFC-245fa available from Honeywell as Enovate®), and trans-1-chloro-3,3,3-trifluoropropene (HFCO-1233zd(E) available from Synquest Laboratories product 1300-7-15, and Honeywell as Solstice® LBA).

### Handmix Foam Preparation

A polyol pre-mix was prepared by blending the polyols, flame retardant, emulsifier, surfactant, catalysts and water together in a Nalgene® container. After gentle shaking to blend the components, the desired amount of blowing agent was weighed into the container. The container was then tightly closed and shaken until the reagents were well mixed. If the premix was to be used in an aging study, the total weight of the closed container was recorded and then re-recorded after aging to ensure there was no inadvertent loss of blowing agent or other reagents during the aging study. For the accelerated aging studies, the completely formulated B-side was stored in an oven at 50°C for 1 week and 2 weeks, and then allowed to cool to room temperature overnight before being used to make a foam test. To make a handmix foam, equal weights of the polyol pre-mix and the isocyanate were combined at room temperature in a 1 quart paper cup at room temperature and immediately mixed for 2.5 seconds at 12,000 RPM using a Laboratory Dispensator made by Premier Mill Corp, as shown in Figure 1. Foamate® machine (Format Messtechnik GmbH) sonar and software equipment was used to obtain foam rise profiles, and the foams were cut apart to examine cell structure, as shown in Figures 2 and 3.

### Machine Foam Preparation

A polyol pre-mix was prepared by blending the polyols, flame retardant, emulsifier, surfactant, catalysts, blowing agent and water together in a five-gallon bucket and mixing for several minutes with an air-powered mixer. For accelerated aging studies, the premix was poured into a metal 5-gallon container, crimped shut, and placed in a 50°C oven for 2 weeks. For room temperature aged studies, the premix was stored in a tightly closed pail in the laboratory at ambient temperature for 2 months. Spray evaluations were conducted at Air Products spray booth facilities using Graco-HVR equipment at 23 °C and 40% relative humidity conditions. All formulations were sprayed using a Graco gun equipped with an AR4242 mixing chamber. Machine chamber and hose temperatures were set to 125 °F and the dynamic pressure was kept constant between 1200-1500 psig. Formulations were sprayed in 3 passes approximately 1 inch thick each onto a 2 x 2 ft<sup>2</sup> cardboard square bolted on a wood pallet structure horizontal on the floor. Reactivity measurements were conducted by spraying a small amount into a bucket and using a wooden tongue depressor to measure cream time, string-gel time, and tack-free time. Reactivity measurements were conducted in triplicate and the average for each sample recorded. A representative picture of the machine spray application is shown in Figure 4.

### Instrumentation for Physical Measurements

The k-factor is reported in BTU·in/hr·ft<sup>2</sup>·°F (W/m·°C) and was measured on 20 x 20 x 2.54 cm samples in a Lasercomp Fox 200 heat flow meter. Dimensional stability and density were measured by a volume station which contains three Ames pneumatic gauges for (height, length and width). Sample to gauge contact pressure is fully adjustable to achieve accurate measurement of very low density rigid polyurethane foam without cell/surface crushing.

*Table 1. Formulations Used in the Study*

Chemicals	Parts
Terate® 4020 Polyester Polyol	50.2
Jeffol® R-470X Mannich Polyether Polyol	21.5
T CPP Flame Retardant	15.3
Dabco® PM300 Emulsifier	2.2
Dabco® DC193 Surfactant	0.5
Amine Catalyst	varied (1.0 Polycat 30 in control)
Metal Catalyst	varied (0.3 Dabco T120 in control)
Water	1.8
Blowing Agent	7.2
Rubinate® M Isocyanate	Polymeric MDI

*Table 2. Catalysts Used in Stability Studies*

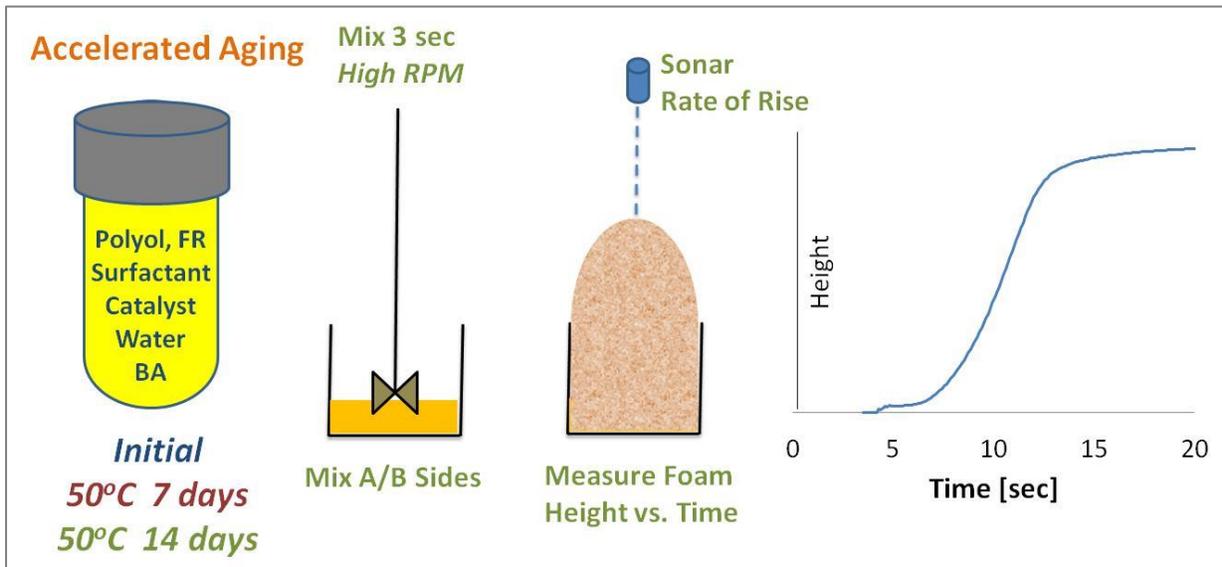
Commercial Catalyst	Description
Polycat 30	Balanced amine catalyst, low odor and improved stability for HFC-245fa
Polycat 9	Trisdimethylaminopropylamine, gel biased amine catalyst
Polycat 5	Pentamethyldiethyltriamine, blow biased amine catalyst
Polycat 8	Dimethylcyclohexylamine, gel biased amine catalyst
Polycat 12	Dicyclohexylmethylamine, gel biased amine catalyst
Dabco 2040	Amine gel catalyst that promotes adhesion in spray foam
Dabco T120	Moisture stable tin gel catalyst



**Figure 1.** Handmix foam preparation procedure.



**Figure 2.** Handmix foam.



**Figure 3.** Handmix stability study methodology.



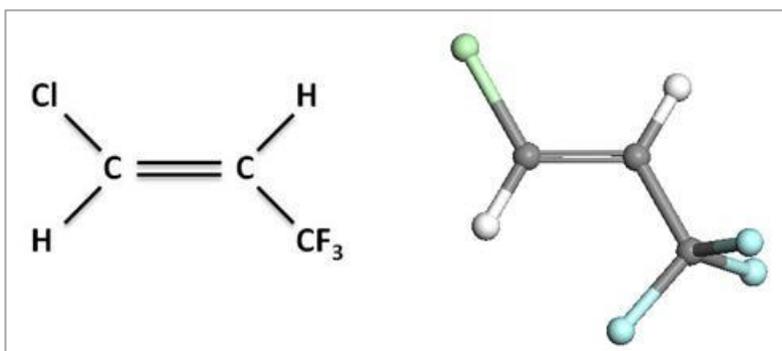
**Figure 4.** Machine foam preparation procedure.

## LOW GLOBAL WARMING POTENTIAL (GWP) BLOWING AGENTS

The Global Warming Potential, or GWP, of a substance is a relative measure of how much heat that substance has the potential to trap in the atmosphere, relative to carbon dioxide over a specific amount of time. For example, HFC-245fa has a 100 year GWP of 1020, which means it has the potential to trap over a thousand times the amount of heat as the same mass of carbon dioxide in the atmosphere over 100 years time [5,6]. The GWP of a substance is dependent on both the amount of radiation the molecule can absorb, and the lifetime of the molecule in the atmosphere.

Polyurethane foam used in applications such as appliances (refrigerators) or construction panels can be prepared using hydrocarbon blowing agents and meet low GWP guidelines (the GWP of cyclopentane is only 11). However, these applications process the foam where it is possible to utilize engineering controls in a plant environment to manage the flammability hazards of hydrocarbons. Spray foam is typically applied on a construction site, in a residential home, or at a commercial structure, and the hazards of flammable blowing agents would be difficult to mitigate. For this reason, there are a number of options currently being developed by blowing agent manufacturers for polyurethane foam applications that are low GWP, non-flammable, and have good insulation properties. Examples of several such blowing agents include Honeywell's Solstice LBA (trans-1-chloro-3,3,3-trifluoropropene), DuPont's Formacel® 1100 (cis-1,1,1,4,4,4-hexafluoro-2-butene), and Arkema's AFA-L1 (structure not released), and descriptions of the use of these blowing agents are found in the Reference section of this paper (this list is not all-inclusive) [7-15].

The focus of this paper will be Air Products' catalyst developments designed to provide both excellent system stability and reactivity for closed-cell spray foam systems incorporating the hydrofluoroolefin molecule trans-1-chloro-3,3,3-trifluoropropene, which will be referred to using the halocarbon nomenclature HFCO-1233zd(E), as shown in Figure 5.



**Figure 5.** *trans*-1-chloro-3,3,3-trifluoropropene, also known as HFCO-1233zd(E).

## CHALLENGES IN CHANGING THE BLOWING AGENT IN SPRAY FOAM FORMULATIONS

Foam formulators face a number of challenges when making a change in the blowing agent in the formulation. One of these challenges is in maintaining system reactivity over a period of time. Spray foam formulations are typically supplied in 55-gallon drums as an A-side consisting of MDI isocyanate, and a B-side, consisting of polyol, water, blowing agent, flame retardant, surfactant, catalysts and other additives. The B-side drums are filled with the formulation at a blending facility, and stored in a warehouse until being shipped to a job-site. This means that the fully formulated B-side must have a usable shelf life of several months to a year.

It is important that the reactivity of the system does not drift considerably over this time period. The chemical reaction of the water and the polyol with the isocyanate is typically catalyzed by both amine and metal catalysts. There are a number of decomposition pathways that can occur in the fully-formulated B-side that can lead to a potential change in system reactivity over time. For example, it has been shown previously that amine catalysts can catalyze the decomposition of HCFC's in polyurethane foam formulations, leading to the production of hydrofluoric or hydrochloric acid which can further decompose the polyester polyols, flame retardants silicone surfactants, the amine or metal catalysts, and lead to loss of efficiency of the blowing agent [16]. Hydrofluoroolefins such as HFCO-1233zd(E) can be additionally challenging due to the electrophilic nature of the  $sp^2$  carbon of the olefin, making it more susceptible to coordination of the amine catalyst, leading to various possible decomposition pathways.

Another challenge formulators may face when changing the blowing agent in the formulation is maintaining good foam processing and physical properties of the resulting polyurethane foam. It is important that the blowing agent has a vapor pressure that is matched to the kinetics of urethane polymerization catalyzed by the amine and metal catalysts, as well as the heat generated by the chemical reactions, allowing the blowing agent to volatilize at the right point in the chemical reaction. If the blowing agent converts to a gas too soon, it may escape to the atmosphere and not be captured in the foam matrix. This could then lead to poor insulation values and high density of the final foam. Conversely, if the blowing agent converts to a gas too late in the foaming reaction, the polymer matrix will be cured to the point where the gas is not sufficiently able to expand the foam, potentially leading to dimensional stability issues and foam cracking. Therefore, the catalyst package usually requires some adjustments to balance the reactivity of the system with the vapor pressure of the blowing agent.

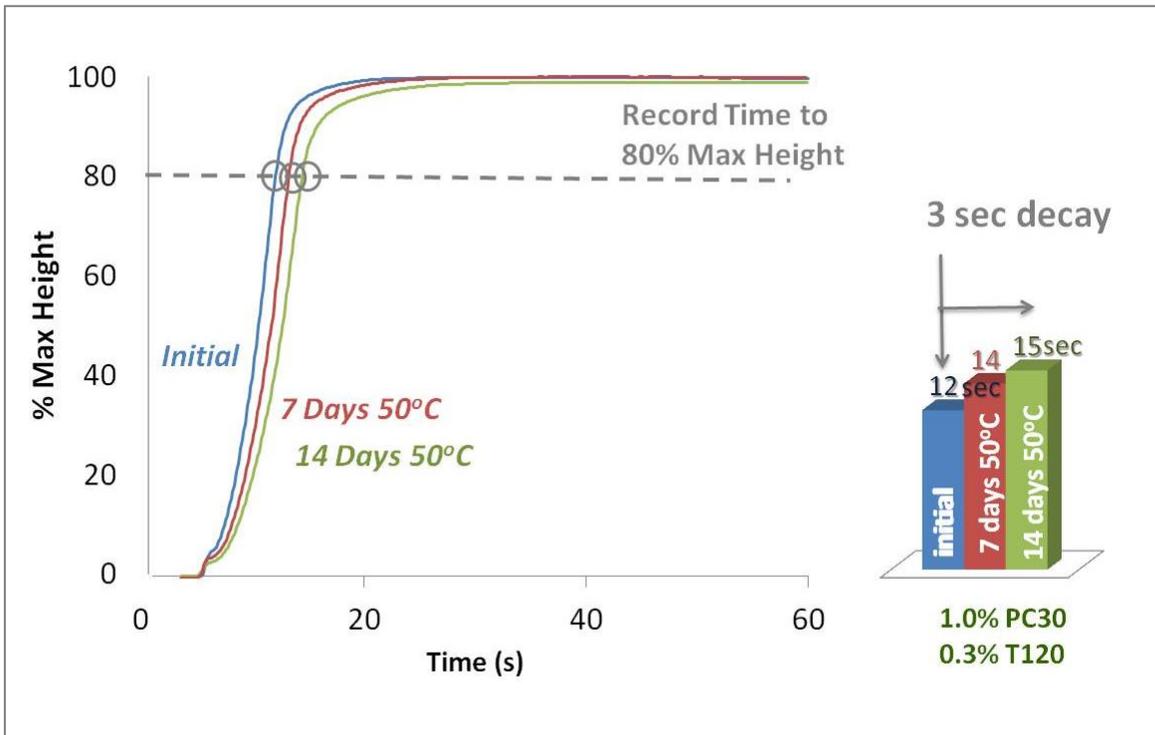
Finally, another aspect related to B-side stability is the phase stability of the fully formulated system. The new blowing agent must remain solubilized in the polyol and compatible with the other components in the B-side over the entire shelf life of the system. In addition to the polyol choice, this compatibility can be influenced by the silicone surfactant, emulsifiers, and even the catalysts.

## COMMERCIAL CATALYSTS AND HFCO-1233zd(E) FOAM FORMULATION STABILITY

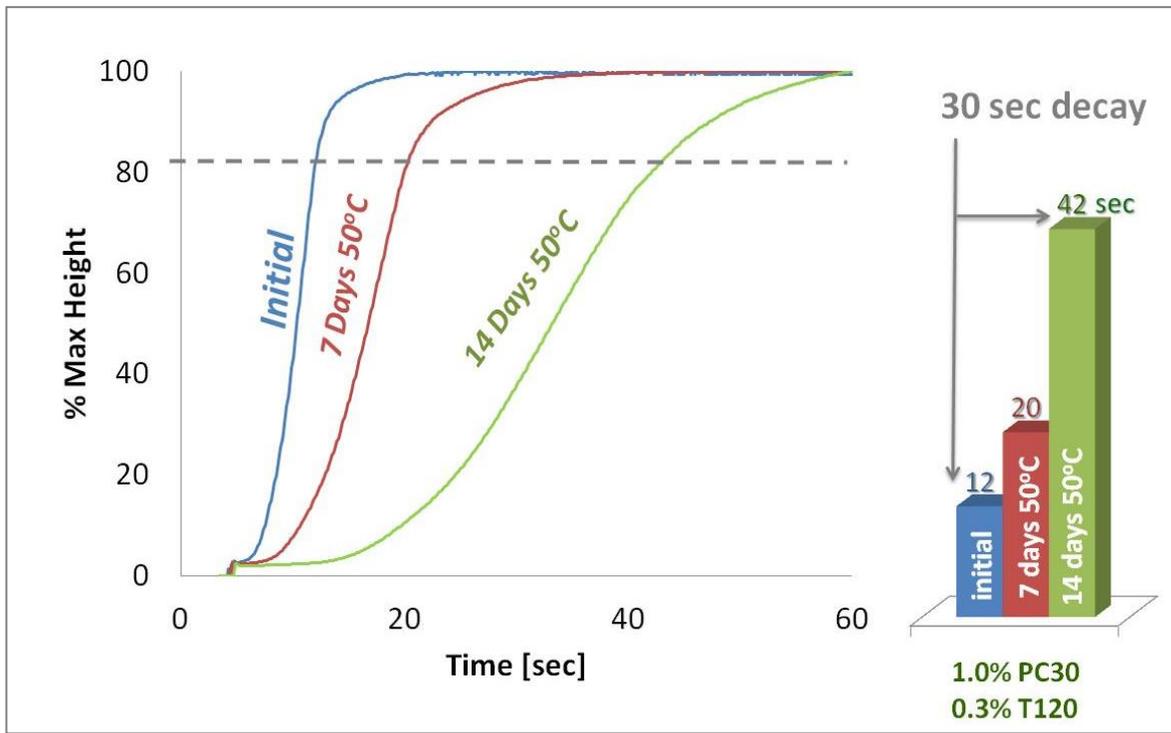
The system reactivity stability of a typical medium-density spray polyurethane foam formulation utilizing a number of commercially available catalysts was evaluated as described in the Experimental Methods section of this paper. Air Products has previously developed Polycat 30 as a balanced amine catalyst that provides good system stability for HFC-245fa systems, and therefore Polycat 30 was chosen as the control catalyst in combination with the tin catalyst Dabco T120 for our initial reactivity studies, as shown in Table 1. Both products are currently used in HFC-245fa spray foam formulations. Although the industry typically requests a 6 month shelf life of a B-side formulation at room temperature, our initial studies were completed at an elevated temperature of 50°C of the fully formulated B-side to accelerate the testing. The aged B-side formulations were allowed to cool to room temperature before mixing at high RPM with isocyanate, and quickly placing under a Fomat sensor for reactivity measurements. The schematic in Figure 3 shows the methodology of these reactivity studies. The Fomat instrument and software is a convenient tool to quantify the reactivity of a system by plotting the "rate-of-rise" curve, which is a plot of the foam height versus time.

As shown in Figure 6, a foam rate-of-rise curve generated using a B-side formulation containing HFC-245fa blowing agent in our standard formulation with 1.0% Polycat 30 and 0.3% Dabco T120 as the catalyst package begins to react within the first few seconds, and reaches full rise-height by about 20 seconds. For the purposes of this paper, comparisons will be made for the time at which the foam reaches 80% of its final height. For the control with HFC-245fa, this time is 12 seconds for the freshly prepared system. This time drifts slightly to 14 and 15 seconds after aging the formulation at 50°C for 7 days and 14 days, respectively, representing an overall delay of 3 seconds over the course of the aging study. This type of drift is not unusual, and represents a system with acceptable stability.

A similar experiment conducted on the same formulation, with the same catalyst package of 1.0% Polycat 30 and 0.3% Dabco T120, using the HFCO-1233zd(E) as the blowing agent gave very different results. Although the initial reactivity was similar and gave acceptable quality foam, the reactivity drift after B-side storage at 50°C was as high as 30 seconds longer after 2 weeks, as shown in Figure 7. We believe this represents a dramatic shift in reactivity, and would certainly cause problems for the foam applicator in a commercial installation.



**Figure 6.** Rate of Rise for Control Formulation, 1.0% PC30 and 0.3% T120 with HFC-245fa blowing agent, illustrating acceptable reactivity drift.



**Figure 7.** Rate of Rise for Control Formulation, 1.0% PC30 and 0.3% T120 with HFCO-1233zd(E) blowing agent, illustrating unacceptable reactivity drift.

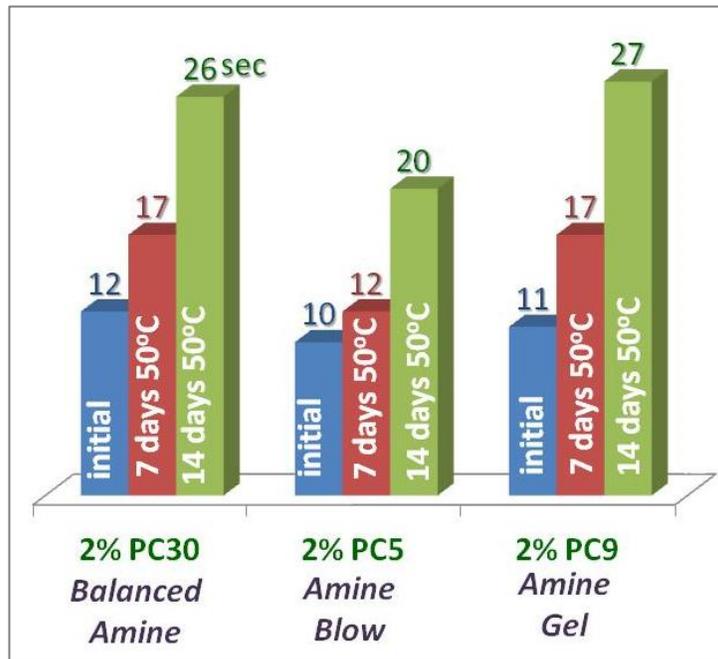
A variety of other known catalysts used in the spray polyurethane foam industry were also evaluated, including the gel-biased (urethane-forming reaction) amine catalysts Polycat 8, Polycat 9 and Polycat 12, the blow-biased (urea-forming reaction) amine catalyst Polycat 5, the adhesion-promoting amine catalyst Dabco 2040, and the tin gel catalyst Dabco T120, as described in Table 2. All amine catalysts were evaluated at approximately an equal use level of 2%, and were not used in combination to simplify the results. Dabco T120 was used at 0.5%. Figure 8 illustrates a significant delay of 10 seconds or more each for Polycat 30, Polycat 9 and Polycat 5 when aged at 50°C in combination with the HFCO-1233zd(E). However, fairly good stability was obtained when using the Polycat 8, Polycat 12, Dabco 2040, or Dabco T120 individually, as shown in Figure 9. These results indicate that the catalyst in the spray foam B-side of the formulation plays a large role in the stability of the system when using the HFCO-1233zd(E). The results of all of the handmix stability studies are tabulated in Table 3.

It is interesting to note that the reactivity drift in the control formulation utilizing a combination of 1.0% Polycat 30 and 0.3% Dabco T120 is worse than the reactivity drift of either Polycat 30 or Dabco T120 when used individually. One explanation for this difference may be the significant difference in levels of Polycat 30. If the decomposition of the HFCO-1233zd(E) generates by-products that deactivate amine catalyst, then the formulation with only 1% Polycat 30 may be too deficient in remaining active amine catalyst to be effective. There may also be a negative synergistic effect of having an amine catalyst that promotes the decomposition reactions with HFCO-1233zd(E) in combination with the tin metal catalyst. Although the tin catalyst seems fairly stable in the absence of the amine, it may further promote decomposition once the amine has generated byproducts.

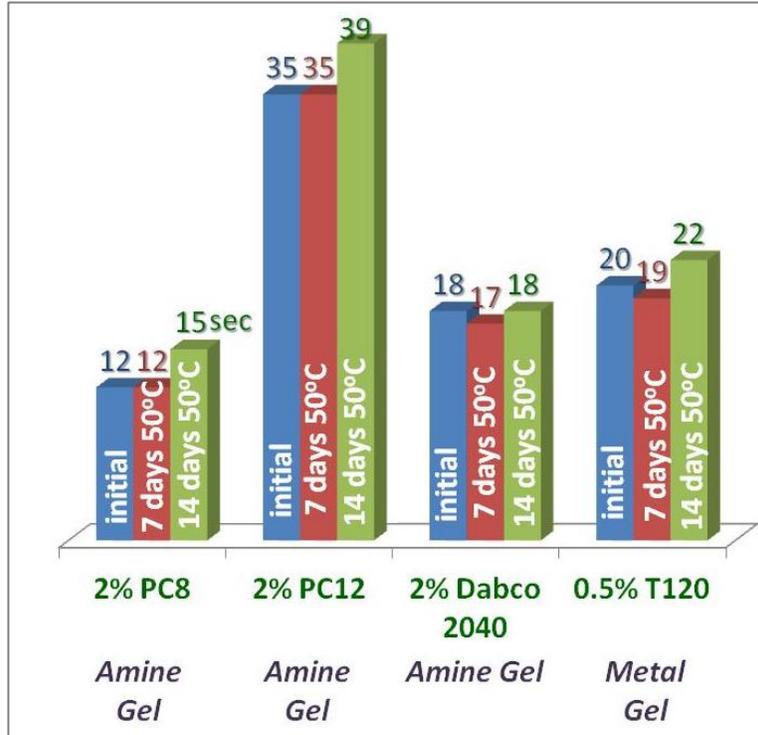
The use of the stable commercial catalysts is also problematic, as all of these catalysts are gel-biased, and a polyurethane spray foam formulation usually requires the addition of a blow-biased catalyst as well to balance the urethane and urea forming reactions. Furthermore, the Polycat 8 has a strong odor and is an emissive catalyst from the resulting finished foam. For this reason, the use of Polycat 8 is typically not recommended for indoor spray foam applications. The efficiency level of Polycat 12 is also quite low due to the high molecular weight, and this product will also have an odor and be emissive. Dabco 2040 has a lower odor than Polycat 8, but is still emissive and biased towards the gel-reaction. Dabco T120 is purely a gel catalyst, and although a foam can be produced using only a metal catalyst, the cell structure is extremely closed, and the foam shrinks and cracks as the foam cools. For these reasons, we focused our efforts on developing new catalysts that are low or non-emissive, have good stability with the HFCO-1233zd(E) blowing agent, and have a good balance of blow and gel reactivity.

*Table 3. Time in Seconds to 80% Maximum Height in Handmix Experiments with HFCO-1233zd(E) Blowing Agent with Commercial Catalysts*

Commercial Catalyst	Initial	1 week @ 50°C	2 weeks @ 50°C	Total Delay
1% Polycat 30 + 0.3% Dabco T120	12	20	42	30
2% Polycat 30	12	17	26	14
2% Polycat 9	11	17	27	16
2% Polycat 5	10	13	18	8
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2% Polycat 8	12	12	15	3
2% Polycat 12	35	35	39	4
2% Dabco 2040 (based on actives)	18	17	18	0
0.5% Dabco T120	20	19	22	2



**Figure 8.** Time to 80% of the maximum foam height in stability studies with common spray foam catalysts using the HFCO-1233zd(E) blowing agent in a medium density formulation.



**Figure 9.** Time to 80% of the maximum foam height in stability studies with alternate polyurethane catalysts using the HFCO-1233zd(E) blowing agent in a medium density formulation.

## EXPERIMENTAL CATALYSTS AND HFCO-1233zd(E) FOAM FORMULATION STABILITY

Air Products remains committed to providing foam formulators catalyst options that not only provide excellent performance with respect to reactivity balance and system stability, but also options that have reduced environmental impact by being low odor and low- or non-emissive. To this goal, three new experimental catalysts are currently under development, referred to in this paper as Cat2, Cat3 and Cat4, as summarized in Table 4. The reactivity and system stability of these new catalysts were explored by the method described in the Experimental Methods section of this paper for a fully formulated B-side with the HFCO-1233zd(E) blowing agent over 2 weeks time at 50°C. The amount of experimental catalysts used in these experiments was chosen to optimize the front-end reactivity of the reaction, as these formulations were also used for the machine spray studies described in the next section of this paper.

Cat2 is an amine catalyst balanced for both the blow and gel reaction, similar in reactivity to Polycat 30. Although emission studies have not yet been completed, Cat2 is expected to have reduced emissions and significantly reduced odor compared to Polycat 8 and Polycat 12. As shown in Figure 10 and summarized in Table 5, the stability of Cat2 as the sole catalyst in a fully formulated B-side with the HFCO-1233zd(E) is very good, with only a 2 second delay in the time for the foam to reach 80% of the maximum foam height after 2 weeks at 50°C.

Cat4 is a new reactive amine-based catalyst that has strong front-end reactivity and exhibits a balanced overall foam-forming reaction. Preliminary testing has been completed on the emissions of a foam produced with Cat4 according to the procedures described in a previous paper in a HFC-245fa formulation, and there were no emissions detected that were due to the Cat4 component [17]. As shown in Figure 10 and Table 5, the stability of Cat4 as the sole catalyst in a fully formulated B-side with the HFCO-1233zd(E) is very good, with only a 3 second delay in the time for the foam to reach 80% of the maximum foam height after 2 weeks at 50°C.

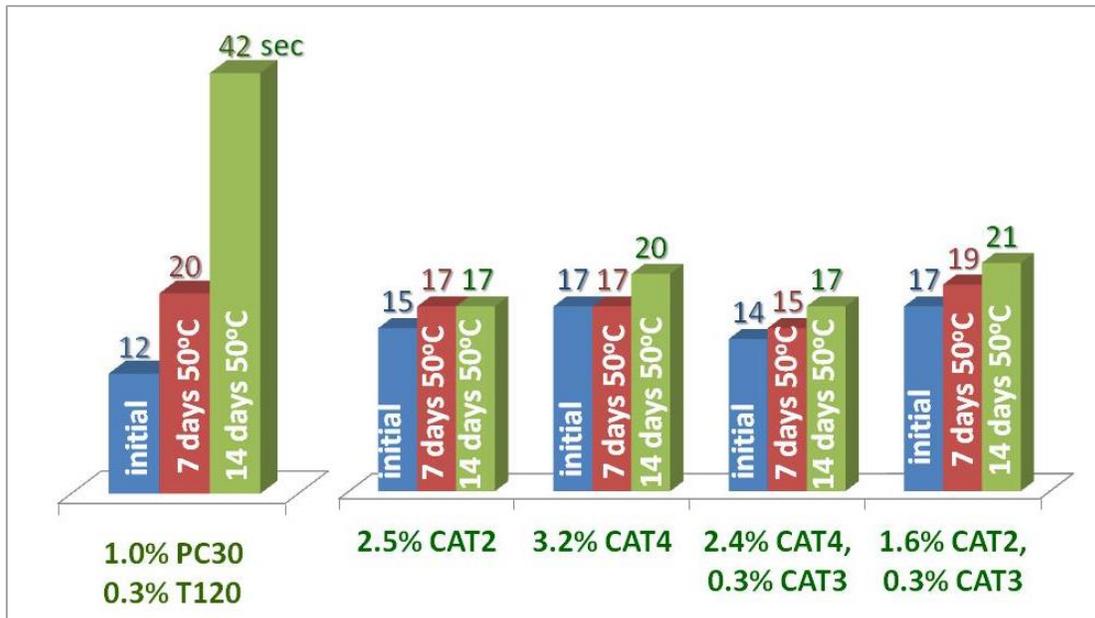
Cat3 is a new metal-based composition that can be used to provide a stronger finishing reaction to the foam, and allows the formulator to reduce the level of amine catalyst required to achieve a sufficiently fast reaction. As shown in Table 5 and Figure 10, Cat3 pairs well with both Cat2 and Cat4 at levels similar to those typically used for tin-based catalysts such as Dabco T120. The stability of the Cat2/Cat3 and Cat4/Cat3 combinations in a fully formulated B-side with the HFCO-1233zd(E) is very good, with only a 3-4 second delay in the time for the foam to reach 80% of the maximum foam height after 2 weeks at 50°C. A direct comparison of the rate of rise curves for the control catalyst package of 1.0% Polycat 30 with 0.3% Dabco T120 versus the experimental catalyst package of 2.4% Cat4 with 0.3% Cat 2 for the initial, 1 week, and 2 week stability tests is shown in Figure 11.

*Table 4. Experimental Catalysts Used in Stability Studies*

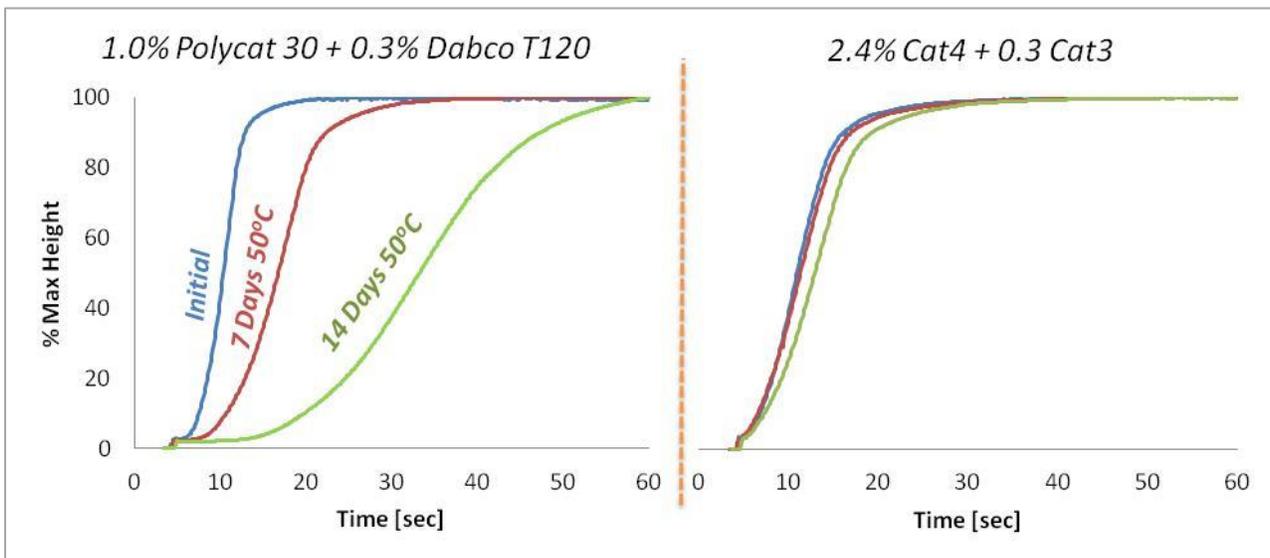
Experimental Catalyst	Description
Cat2	Balanced amine catalyst, low odor, reduced emissions compared to Polycat 8 and Polycat 12
Cat3	Metal-based gel catalyst, low odor, non-emissive, pairs well with Cat2 and Cat4
Cat4	Balanced amine-based catalyst, low odor, non-emissive

*Table 5. Time in Seconds to 80% Maximum Height in Handmix Experiments with HFCO-1233zd(E) Blowing Agent with Experimental Catalysts*

Experimental Catalyst	Initial	1 week @ 50°C	2 weeks @ 50°C	Total Delay
2.5% Cat2	15	17	17	2
3.2% Cat4	17	17	20	3
2.4% Cat4 + 0.3% Cat3	14	15	17	3
1.6% Cat2 + 0.3% Cat3	17	19	21	4



**Figure 10.** Time to 80% of the maximum foam height in stability studies with Experimental Catalysts using the HFCO-1233zd(E) blowing agent.



**Figure 11.** Rate-of-Rise Profiles for stability studies with Control versus Experimental Catalysts using the HFCO-1233zd(E) Blowing Agent

## MACHINE SPRAY RESULTS WITH HFCO-1233zd(E)

Handmix foam-making and rate-of-rise data collected using the Fomat instrument are useful techniques in screening foam formulations and studying kinetics and reactivity stability over time. However, machine spray foam trials are necessary to evaluate the ease of processing and physical properties of the polyurethane foam formulation. For this study, 5-gallon pails of fully formulated B-side were prepared and aged at either laboratory room temperature or at 50°C in an oven and sprayed using a Graco-HVR machine according to the procedure described in the Experimental Methods section of this paper. The formulations chosen for spray evaluation were the same as those used in the handmix experiments comparing Polycat 30/Dabco T120 to the experimental Cat2/Cat3 and Cat4/Cat3 catalyst packages. The cream, string gel and tack free times are shown in Tables 6, 7, and 8, respectively. Spray data was not collected on the Cat2/Cat3 sample at the 2 month room temperature aging condition, but it was collected after 2 weeks at 50°C. It should be noted that the density increase observed in all of the samples aged at 50°C for 2 weeks was attributed to blowing agent loss to the atmosphere due to pails that did not retain their hermetic seal during heating in the oven. This was verified by a slight weight loss measured in the pails before and after heating. The density increase is not related to catalyst stability.

Property	Initial	2 Months 22°C	2 Weeks 50°C
<i>Cream Time (seconds)</i>	1.2	1.6	3.6
<i>String Gel (seconds)</i>	4.9	11.7	20.4
<i>Tack Free (seconds)</i>	7.5	19.7	34.6
Density (lb/ft <sup>3</sup> )	2.4	2.4	3.1
k-factor (BTU in/ft <sup>2</sup> h°F) at 75°F	0.162	0.170	0.165
k-factor (BTU in/ft <sup>2</sup> h°F) at 35°F	0.139	0.139	0.145

Property	Initial	2 Weeks 50°C
<i>Cream Time (seconds)</i>	1.4	1.5
<i>String Gel (seconds)</i>	7.5	10.5
<i>Tack Free (seconds)</i>	11.7	17.1
Density (lb/ft <sup>3</sup> )	2.5	3.1
k-factor (BTU in/ft <sup>2</sup> h°F) at 75°F	0.160	0.164
k-factor (BTU in/ft <sup>2</sup> h°F) at 35°F	0.139	0.143

Property	Initial	2 Months 22°C	2 Weeks 50°C
<i>Cream Time (seconds)</i>	0.8	0.9	1.0
<i>String Gel (seconds)</i>	5.1	5.8	7.2
<i>Tack Free (seconds)</i>	9.3	9.1	12.3
Density (lb/ft <sup>3</sup> )	2.4	2.4	3.0
k-factor (BTU in/ft <sup>2</sup> h°F) at 75°F	0.160	0.156	0.162
k-factor (BTU in/ft <sup>2</sup> h°F) at 35°F	0.138	0.137	0.140

All three of the formulations containing the different catalyst packages gave good reactivity and foam with acceptable physical properties and cell structure when freshly prepared. Aging of the formulations at room temperature for 2 months resulted in a significant delay the time to string-gel in the formulation utilizing the Polycat 30/Dabco T120 catalyst package, which increased from 5 seconds in freshly made batch, to almost 12 seconds after 2 months. Aging at 50°C caused even a further delay in the system reactivity, with an increase in string gel time to 20 seconds. The experimental catalyst package of Cat2/Cat3 performed much better, which increased from a 7 second string gel time to 10 seconds after aging at 50°C for two weeks. The best performing system was that which utilized the Cat4/Cat3 formulation, with almost no increase in cream, string gel, or tack free times observed after aging either at room temperature or elevated temperature. A comparison of cream, string gel, and tack free times for the Polycat 30/Dabco T120 versus the Cat4/Cat3 system at the initial, 2 months aging at room temperature, and 2 weeks aging at 50°C is shown in Figure 11.

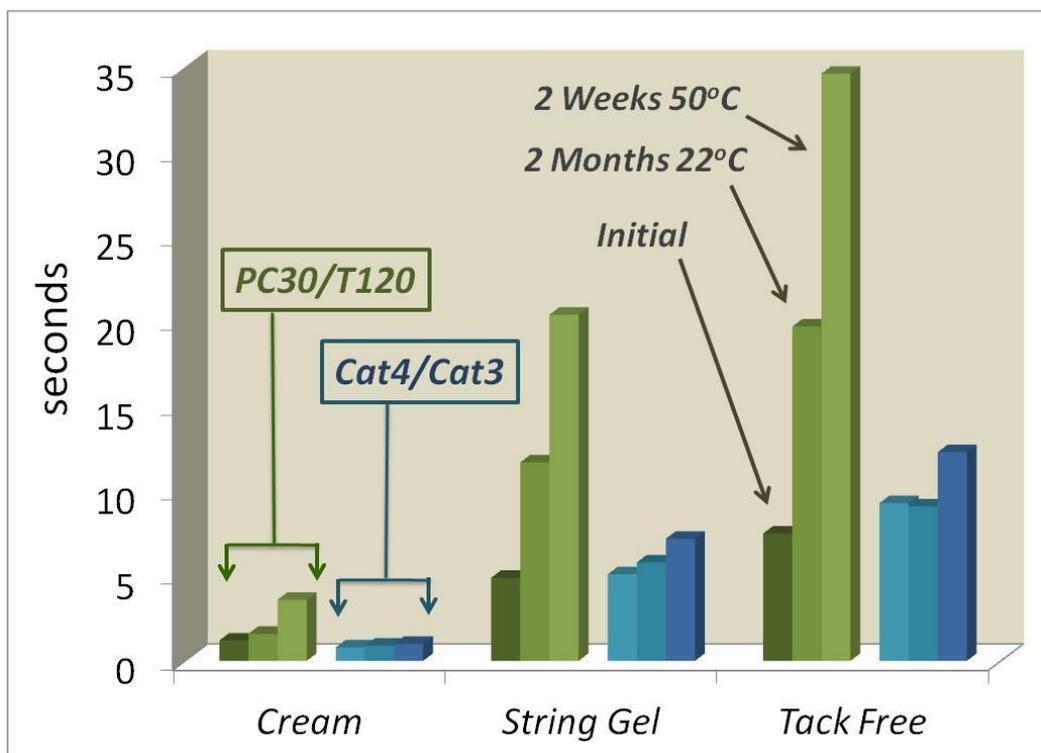


Figure 11. Machine sprayed reactivity measurements

The decay in reactivity for the Polycat 30/Dabco T120 system also corresponded to an increase in the k-factor, or a decrease in the insulating capability of the sprayed polyurethane foam. The reactivity shift for aged Polycat 30/Dabco T120 system is also clearly indicated by the presence of foam that ran or dripped over the side of the cardboard substrate. Figure 12 shows the difference in the edge of the cardboard substrate for the 50°C aged Polycat 30/Dabco T120 sample versus the Cat4/Cat3 sample. The reactivity was delayed enough in the aged Polycat 30/Dabco T120 formulation that the foam dripped over the side before it could cure, while the similarly aged Cat4/Cat3 formulation produced a foam with a clean edge that rose and cured rapidly.

As a side note, it has been an accepted practice in the industry to estimate the stability of a formulation by approximating of 1 week storage at 50°C to 1 month storage at room temperature. However, the results of the spray trials in this study suggest that aging at 50°C for 2 weeks is much more aggressive than aging for 2 months at 22°C based on our findings.



**Figure 12.** Machine sprayed samples, foam edge after three passes to show foam dripping and lack of cure.

## **CONCLUSIONS**

The system stability of a medium density polyurethane spray foam formulation utilizing the low GWP blowing agent HFCO-1233zd(E) was explored. Many of the commercially available amine catalysts used for HFC-245fa systems including Polycat 30, Polycat 9, and Polycat 5 resulted in significant reactivity decay after aging of the fully formulated B-side at 50°C for 2 weeks. Several commercially available amine catalysts such as Dabco 2040, Polycat 8 and Polycat 12 gave acceptable reactivity stability, but these catalysts present challenges with blow/gel reactivity balance, may have use level limitations, and present odor and emissions that would limit the use of these catalysts at high concentrations to outdoor applications. Air Products is currently developing several experimental amine and non-amine catalysts that are low odor, low- or non-emissive, and provide excellent system stability when used in combination with HFCO-1233zd(E).

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