Shelf life evaluation of PU rigid foams blown with Ecomate

Reactivity drift (typically a slowdown with time) of spray polyurethane foam (SPF) systems has been experienced since the use of CFC-11 systems. A slower reactivity can cause problems like running or sagging during the foaming process. Reactivity drift can be attributed to a number of reasons considering the many raw materials present in the polyol blend (polyol, surfactant, catalyst, blowing agents, flame retardants, etc.). The industry's need for optimization of all aspects of polyurethane foam systems, including shelf life, is therefore paramount to the performance of the system. In this paper, different catalysts will be evaluated in Ecomate spray foam formulations to determine which choice of catalysts promotes longer shelf life. The liquid polyol blends will undergo an accelerated shelf life aging at 50 °C (122 °F) for four weeks. Many different catalyst types will be evaluated including metal, amine, blowing, and gelling families. The intent is to meet or exceed a six month shelf life without compromising other physical properties of the finished product.
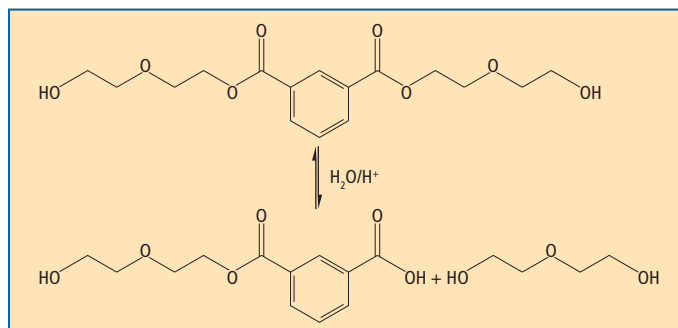
1. Introduction

SPF form a significant part of the growing polyurethane industry. They have the advantage of easy application and fast cure, thus allowing them to be sprayed directly on the surface to be foamed. SPF can be used at a construction site and applied even after most of the construction has been completed. Because of the application methods used with this product, polyurethane spray foams must have a very rapid reactivity profile, rising and gelling within a few seconds of being applied. This is accomplished by adding high amounts of catalysts, typically an amine catalyst and a metal catalyst. The two catalysts work in synergy to create a polyurethane foam that rises and gels quickly.

Unfortunately, spray foam systems have always had one major problem, a limited shelf life. This is usually the result of chemicals in the polyol blend that can decompose and/or react with other ingredients in the blend. Most commonly, polyester polyols, flame retardants, blowing agents, and other additives generate a small amount of acids. These acids then attach themselves to the catalysts and prevent the catalysts from doing their intended function during the foaming process. This is evident when the spray foam takes longer to react and cure. From an application standpoint, slower reacting spray foam can cause sagging or drooping, which diminishes foam performance and will generate solid foam waste.
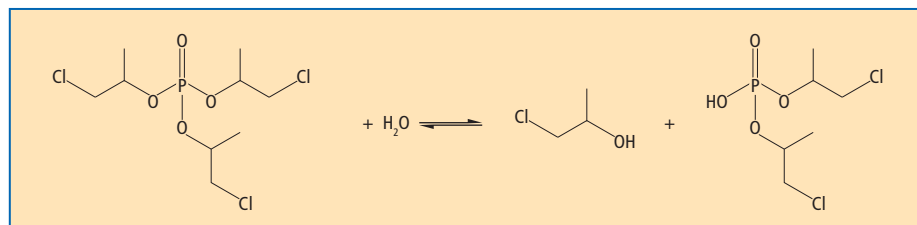
In order to understand how acid formation occurs in the polyol blend, the acid generating reactions will now be studied one at a time in greater detail. First, the hydrolysis of the polyester polyol will be examined. Polyester polyols terminate in hydroxyl groups, but have ester groups built within their chemical chain. The ester groups can combine with any water present and generate an alcohol and a carboxylic acid **(fig. 1).**

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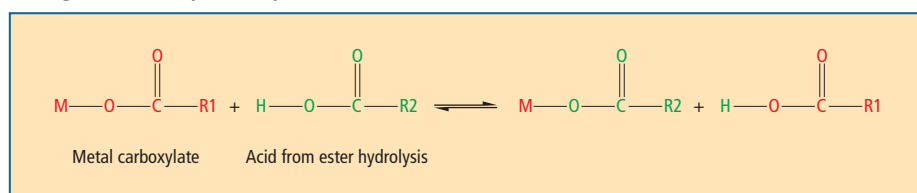*Fig. 1:*
Polyester polyol hydrolysis

▼ **Fig. 2:** *TCPP hydrolysis*

▼ **Fig. 3:** *Metal catalyst carboxylate substitution*

Metal carboxylate   Acid from ester hydrolysis

The acid produced can then block the amine catalysts present in the polyol blend and thus delay the reaction.

One of the most common chemicals used in polyurethane foams is the flame retardant tris(1-chloro-2-propyl)phosphate or TCPP, a halogenated organic phosphate. Like the polyester polyol, it can hydrolyze in the presence of water and form an acid and a halo-

hydrin, which in this case is, 1-chloro-2-propanol **(fig. 2)**. The acid produced can then block the amine catalysts.

In a similar manner, other ingredients in the polyol blend can combine with water and generate an acid. This includes other flame retardants, certain thinning agents, certain blowing agents, and even some surfactants.

Another less understood phenomenon is the interaction of metal polyurethane catalysts with these same acids. Since all metal catalysts are metal carboxylates, it is possible that the carboxylate on the metal can be substituted with a carboxylate from the acid of a hydrolyzed ester **(fig. 3)**.

The new metal carboxylate would have a different catalytic activity or even worse, it could precipitate out of the polyol blend

causing an even greater slowdown of the spray foam.

While spray polyurethane foams are initially made with a very rapid reactivity, often the reactivity slows down with time leading to application problems. A polyurethane foam formulator must keep in mind the possibility of hydrolysis when adding ingredients to the polyol blend, as hydrolysis can lead to a change in reactivity profile over time. In the following experiments, a method will be developed for optimizing spray polyurethane foam shelf life using several different catalyst combinations.

2. Experimental

In order to completely test the effect of acid generation in spray foam formulations, a formula was assembled that would provide several scenarios for acid generation over time so that the effect on certain catalysts can be studied. For this experiment, the formula Blend 12B56 **(tab. 1)** was assembled.

In this formula, there is the potential to generate acid from the polyester polyol and the TCPP flame retardant. Prior to conducting any accelerated aging tests, different catalyst packages were tested in the formula for their viability in making a spray foam. In other words, the foam formula must have a rapid reactivity profile that produces a good quality spray foam that does not droop or sag upon application. Foams were tested by using a high-speed pneumatic hand mixer. In each trial, specific amounts of catalysts were added to Blend 12B56 and then tested for their reactivity profile. Upon analyzing the results, the catalyst packages were rated based on reactivity to determine their viability to make spray foams. The different catalyst combinations are shown in **table 2.**

From the many different trial results given in **table 2,** it can be seen that the most active catalyst packages are those that contain an amine blowing catalyst and a metal gelling catalyst in the same formula. From these experiments, 15 different catalyst combinations were set up using three amine cata-

▼ **Tab. 1:** Blend 12B56

Chemical	%
Amine polyol	15.0
Polyester polyol	21.0
Sucrose-glycerin polyol	33.0
Tris(1-chloro-2-propyl)phosphate (TCPP)	20.0
Silicone surfactant	1.5
Water	2.0
Ecomate	5.0

▼ **Tab. 2:** Catalyst package trial runs

Try #	Catalyst package	Cream time	Tack-free time	Spray foam viability
1	2.0 % Amine blowing catalyst A 0.3 % Metal gelling catalyst 2	4	11	Viable
2	2.0 % Amine blowing catalyst A 0.3 % Metal gelling catalyst 1	3	11	Viable
3	2.0 % Amine blowing catalyst A 0.3 % Metal gelling catalyst 4	4	11	Viable
4	2.0 % Amine blowing catalyst A 1.0 % Amine gelling catalyst D	4	16	Too slow
5	2.5 % Amine balanced catalyst C	6	20	Too slow
6	2.0 % Amine blowing catalyst A	4	27	Too slow
7	2.0 % Amine balanced catalyst C 0.3 % Metal gelling catalyst 2	5	13	Viable
8	2.0 % Amine blowing catalyst B 0.3 % Metal gelling catalyst 2	3	11	Viable
9	2.0 % Amine blowing catalyst E 0.3 % Metal gelling catalyst 2	5	16	Too slow
10	0.5 % Amine blowing catalyst A 1.5 % Amine balanced catalyst C 0.2 % Metal gelling catalyst 2	5	14	Viable
11	0.5 % Amine blowing catalyst A 1.5 % Amine balanced catalyst F 0.2 % Metal gelling catalyst 2	5	16	Too slow
12	2.0 % Amine blowing catalyst A 0.3 % Metal gelling catalyst 3	4	12	Viable
13	2.0 % Amine blowing catalyst A 0.4 % Metal gelling catalyst 5	4	12	Viable
14	2.0 % Amine blowing catalyst A 1.0 % Amine gelling catalyst G	4	17	Too slow
15	2.0 % Amine blowing catalyst B 1.0 % Amine balanced catalyst C	3	17	Too slow
16	2.0 % Amine blowing catalyst H 0.4 % Metal gelling catalyst 2	5	18	Too slow
17	2.0 % Amine blowing catalyst I 0.4 % Metal gelling catalyst 2	7	20	Too slow
18	2.0 % Amine blowing catalyst J 0.4 % Metal gelling catalyst 2	5	16	Too slow

lysts and five metal catalysts. The amine catalysts used were amine blowing catalyst A, B, and C. The metal catalysts used were metal gelling catalysts 1 – 5. Each catalyst combination will have one amine catalyst and one metal catalyst. Each catalyst combination was added to Blend 12B56 using 2.0 % of the amine catalyst, and 0.4 % of the metal catalyst. Each formula (Blend 12B56 plus catalysts) was named according to the catalysts used. **Table 3** shows the name of each formula.
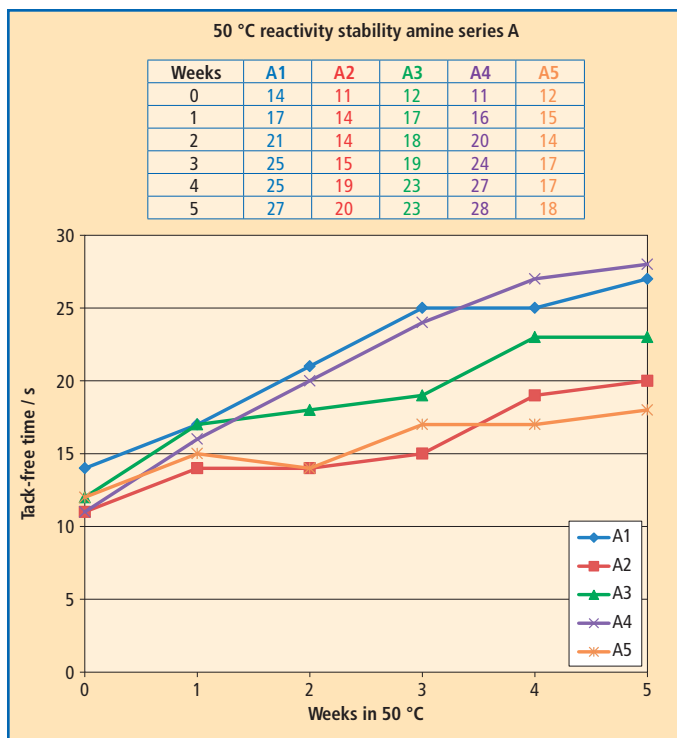
All formulas were tested using a high-speed pneumatic hand mixer. All chemicals were at 25 °C (77 °F) when reacted. The foams were tested for cream time and tack-free time.

An accelerated aging test was started on all 15 of these formulas. They were placed in metal cans in an oven at 50 °C (122 °F). This is a standard aging temperature used in the industry for shelf life stability testing. Our own test data show that one week in 50 °C stability oven is equivalent to about six to eight weeks at ambient temperature. After one week, the 15 samples were removed from the oven, brought back to 25 °C and tested once again. This process of aging for
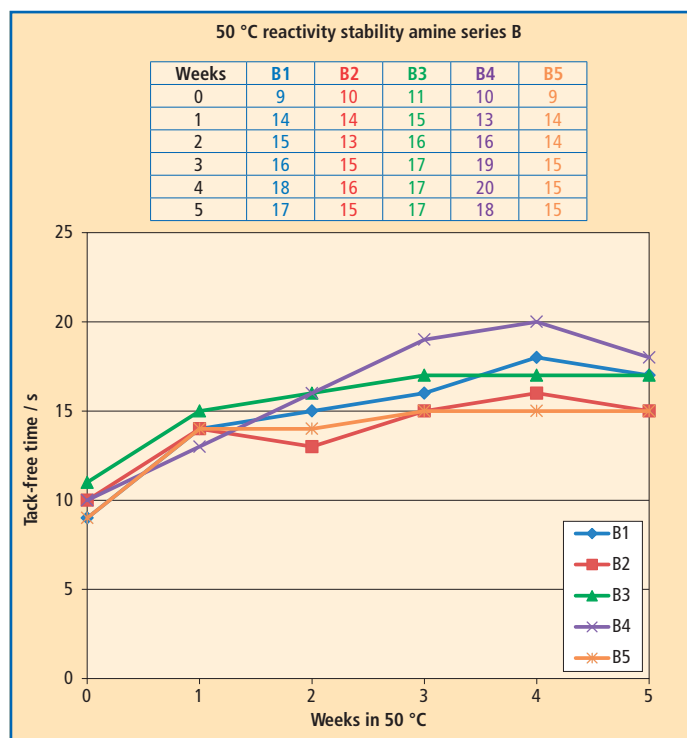
Tab. 3:
Chart of formula names

	Metal catalyst 1	*Metal catalyst 2*	*Metal catalyst 3*	*Metal catalyst 4*	*Metal catalyst 5*
Amine Catalyst A	A1	A2	A3	A4	A5
Amine Catalyst B	B1	B2	B3	B4	B5
Amine Catalyst C	C1	C2	C3	C4	C5

Fig. 4:
Graph of each formula with amine catalyst A

50 °C reactivity stability amine series A

Weeks	A1	A2	A3	A4	A5
0	14	11	12	11	12
1	17	14	17	16	15
2	21	14	18	20	14
3	25	15	19	24	17
4	25	19	23	27	17
5	27	20	23	28	18

Fig. 5: *Graph of each formula with amine catalyst B*

50 °C reactivity stability amine series B

Weeks	B1	B2	B3	B4	B5
0	9	10	11	10	9
1	14	14	15	13	14
2	15	13	16	16	14
3	16	15	17	19	15
4	18	16	17	20	15
5	17	15	17	18	15

Fig. 6: *Graph of each formula with amine catalyst C*

50 °C reactivity stability amine series C

Weeks	C1	C2	C3	C4	C5
0	5	12	13	9	12
1	12	14	17	15	13
2	12	12	16	15	14
3	16	15	20	17	17
4	17	17	20	20	17
5	17	15	20	19	18
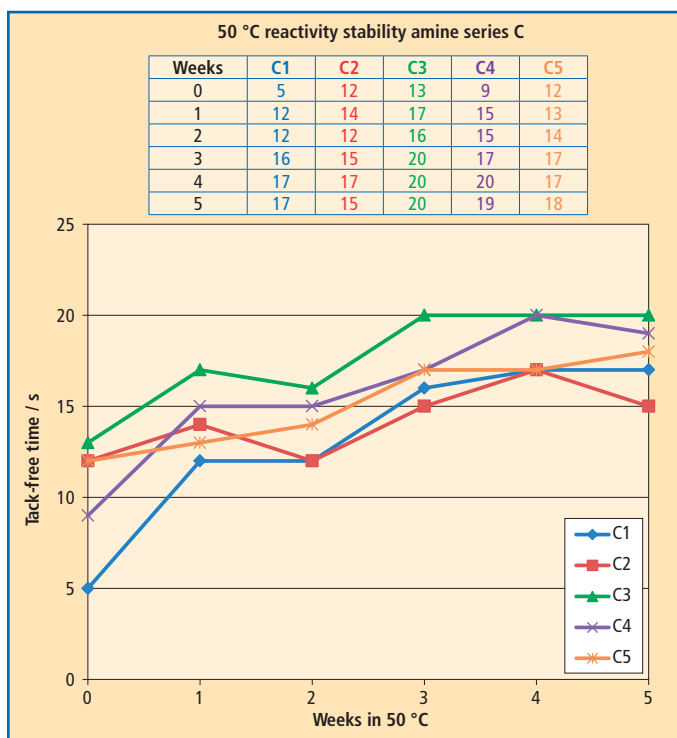
a week and testing was continued for a total of five weeks. The results are shown in **table 4.**

Analyzing the data, it is evident that the cream time did not shift on any formula more than 1 s or 2 s. Although some of the catalysts are acid blocked, there is still sufficient catalytic activity remaining to initiate foam rise at 5 s or less. On the other hand, the tack-free times varied greatly in each of the formulas. This was not only due to the different catalyst combinations, but also due to the loss in reactivity from the acid formation.
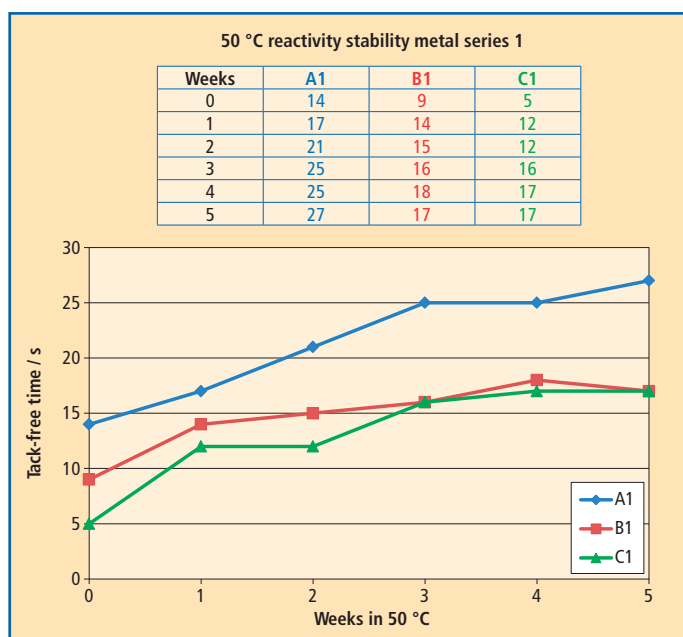
As each formula aged, the acid that was generated affected each formula differently producing a distinct reactivity aging curve. Each aging curve was compared to others in the same group to determine which catalyst worked best.

First, the formulas with amine catalyst A will be analyzed. The tack-free time data is organized by each metal catalyst and by weeks in stability oven.

By plotting the data on a graph **(fig. 4),** a trend for each formula can be seen. While each formula showed some slowdown, some metal catalysts performed better than others. By looking at the amount of reactivity change with time in **figure 4,** each of the metal catalysts can be ranked according to performance. In this case, metal catalyst 5 was the best followed by 2, 3, 1, and 4.

This same analysis was done for amine catalyst B. Again, graphing the tack-free times of each formula, we can see a trend for each formula **(fig. 5).** In this case, the resulting series curves are closer together. According to the plots in **figure 5,** metal catalyst 2 was the best followed by 5, 3, 1, and 4.

The analysis was done again on amine catalyst C. A trend again is shown for the tack-free times of each formula **(fig. 6).** This data is a little more difficult to interpret. Metal catalysts 1 and 4 actually perform poorly

50 °C reactivity stability metal series 1

Weeks	A1	B1	C1
0	14	9	5
1	17	14	12
2	21	15	12
3	25	16	16
4	25	18	17
5	27	17	17

◄ **Fig. 7:**
Graph of each formula with metal catalyst 1

Metal catalyst rank	Amine series A	Amine series B	Amine series C
First	5	2	2
Second	2	5	5
Third	3	3	3
Fourth	1	1	4
Fifth	4	4	1

◄ **Tab. 5:**
Ranking of each metal catalyst in spray foam

▼ **Tab. 4:** *Initial and aged test results*

Formula	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5	C1	C2	C3	C4	C5
Cream time / s															
Initial	2	3	3	3	4	2	3	3	3	3	2	5	5	4	5
After one week	3	3	3	3	4	3	3	4	3	3	2	5	5	4	4
After two weeks	3	3	3	3	3	3	3	3	3	3	3	4	4	4	4
After three weeks	3	3	3	3	3	3	3	3	3	3	3	3	3	4	4
After four weeks	3	3	3	3	3	3	3	4	3	3	4	4	5	4	4
After five weeks	3	3	3	3	3	3	3	3	3	3	4	4	5	5	4
Tack-free time / s															
Initial	14	11	12	11	12	9	10	11	10	9	5	12	13	9	12
After one week	17	14	17	16	15	14	14	15	13	14	12	14	17	15	13
After two weeks	21	14	18	20	14	15	13	16	16	14	12	12	16	15	14
After three weeks	25	15	19	24	17	16	15	17	19	15	16	15	20	17	17
After four weeks	25	19	23	27	17	18	16	17	20	15	17	17	20	20	17
After five weeks	27	20	23	28	18	17	15	17	18	15	17	15	20	19	18

since they started off much faster than the others. Looking at the graphs in **figure 6,** metal catalyst 2 was the best followed by 5, 3, 4, and 1.

If the rank of each metal catalyst's performance is organized in a chart, there is a clear consistent trend. Looking at **table 5,** when choosing a metal catalyst for spray foam, metal catalyst 2 or 5 seem to perform very well while metal catalyst 4 or 1 should
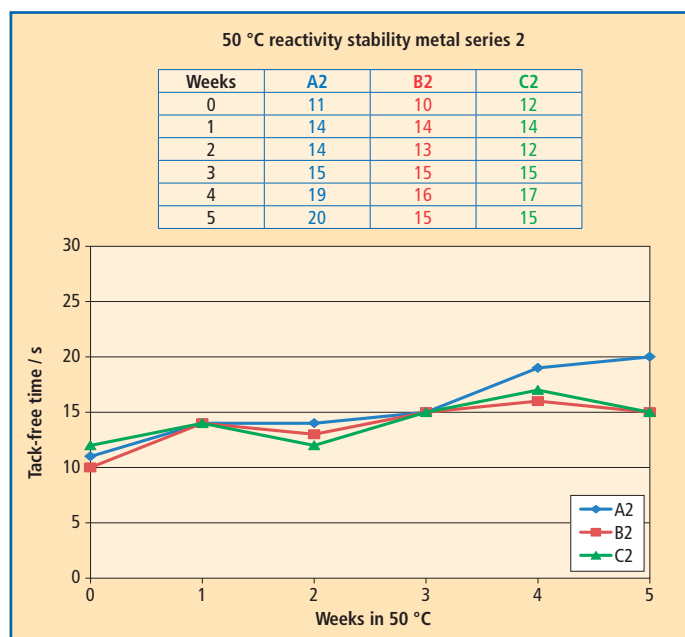
probably be avoided if shelf life stability is to be optimized.

In the following, the formulas with the same metal catalysts (but different amine catalysts) will be analyzed. First, the tack-free times of the formulas with metal catalyst 1 were organized by each amine catalyst and by weeks in stability oven. This data is in shown **figure 7.** Just like the amine series, when plotted, a clear trend
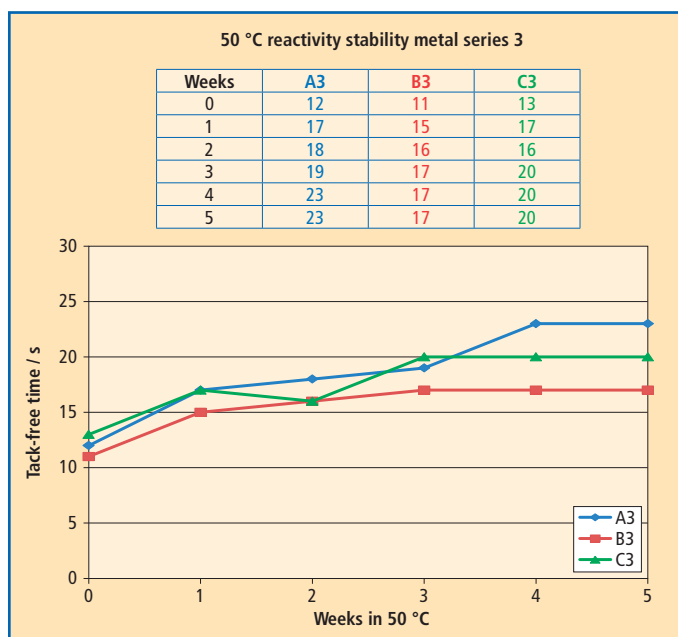
for each formula is shown. In the graphs in **figure 7,** amine catalyst B was the best followed by C, then A. This analysis was repeated for the other four metal catalysts.

In the graphs in **figure 8** of metal series 2, the results are much closer together, reflecting the improved stability of metal catalyst 2. In this series, amine catalyst C was slightly better than B, followed by A.
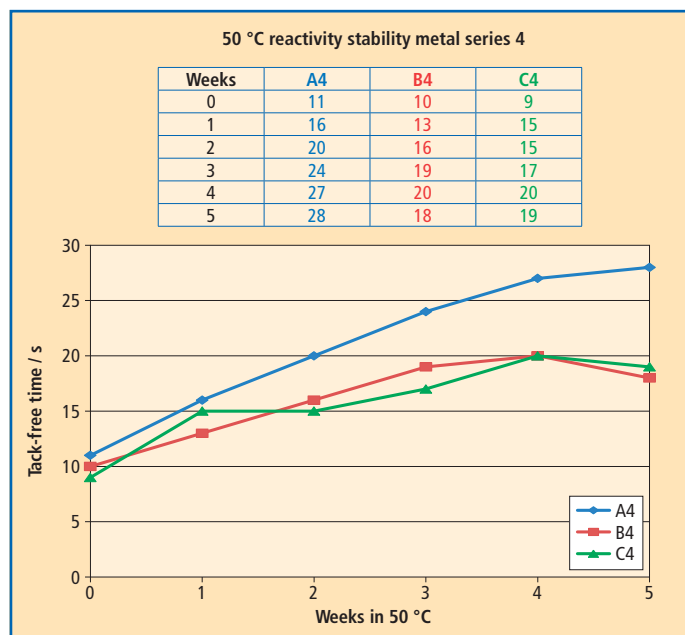
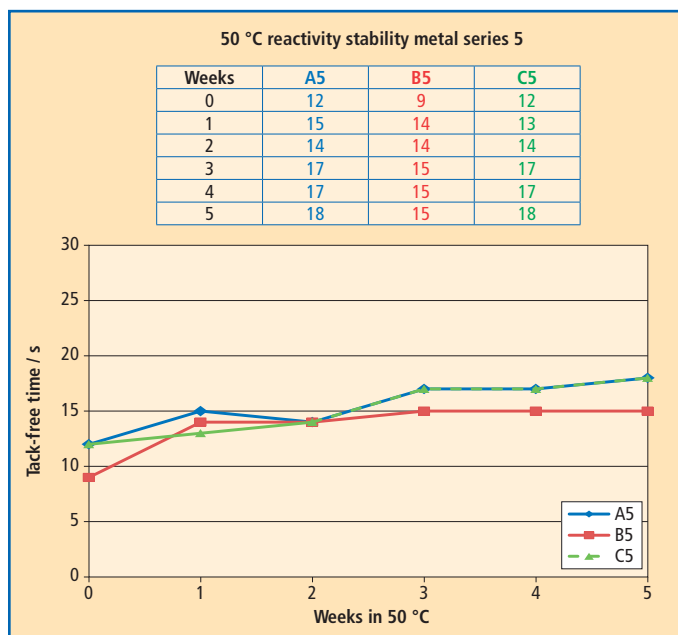▼ **Fig. 8:** Graph of each formula with metal catalyst 2

50 °C reactivity stability metal series 2

Weeks	A2	B2	C2
0	11	10	12
1	14	14	14
2	14	13	12
3	15	15	15
4	19	16	17
5	20	15	15

▼ **Fig. 9:** Graph of each formula with metal catalyst 3

50 °C reactivity stability metal series 3

Weeks	A3	B3	C3
0	12	11	13
1	17	15	17
2	18	16	16
3	19	17	20
4	23	17	20
5	23	17	20

▼ **Fig. 10:** Graph of each formula with metal catalyst 4

50 °C reactivity stability metal series 4

Weeks	A4	B4	C4
0	11	10	9
1	16	13	15
2	20	16	15
3	24	19	17
4	27	20	20
5	28	18	19

▼ **Fig. 11:** Graph of each formula with metal catalyst 5

50 °C reactivity stability metal series 5

Weeks	A5	B5	C5
0	12	9	12
1	15	14	13
2	14	14	14
3	17	15	17
4	17	15	17
5	18	15	18

In the graph in **figure 9,** amine catalyst B was the best followed by C then A.

The poor performance of metal catalyst 4 can be clearly seen in **figure 10** with each formula in this series undergoing a large reactivity drift with time. In this series, amine catalyst B was the best, followed by C, then A.

Figure 11 shows the superior performance of metal catalyst 5 with all three amines series showing only a little bit of drift, even after five weeks in the stability oven. In this series, amine catalyst B was the best, followed by C, then A.

If the rank of each amine catalyst's performance is organized in a chart, there is a clear consistent trend **(tab. 6).**

According to these rankings in **table 6,** the best amine catalyst to use for polyurethane spray foam stability is amine catalyst B, while amine catalyst A should probably be avoided if shelf life stability is to be optimized.

3. Conclusions

Optimization of any polyurethane formulation is important. All aspects of the foam including foam strength, burn characteristics, nominal density, etc. have to be considered. In the case of polyurethane spray foam, optimizing the catalyst package for shelf life is of utmost importance.

When developing a polyurethane spray foam formula, it is important to choose a catalyst package that will yield a viable spray foam. Through experimentation, it was found that using an amine blowing catalyst and a metal gelling catalyst together provided the best synergy for a rapid reactivity profile required for polyurethane spray foams. It was this combination of catalysts that was used as the model for the formulas made for the accelerated aging tests.

Proper catalyst selection was demonstrated to be highly significant to the performance of each formula in the shelf life testing. In the above experiments, it was shown that one of the amine catalysts, amine blowing catalyst B, showed the best shelf life in spray foams of the amine catalysts tested and metal catalyst 2 showed the best shelf life in spray foams of the metal catalysts tested. On the other hand, amine blowing catalyst A, and metal gelling catalysts 1 and 4 performed poorly in the experiments, showing large reactivity drifts especially in the formulas in which they were used together. Amine catalyst A, and metal catalysts 1 and 4 should be avoided if shelf life is to be optimized.

When formulating a polyurethane spray foam, amine blowing catalyst B and metal gelling catalyst 2 should be used together. Using these two catalysts together will result in a polyurethane spray foam with a rapid reactivity profile that will have a shelf life of at least six months.

Amine catalyst rank	Metal series 1	Metal series 2	Metal series 3	Metal series 4	Metal series 5
First	B	C	B	B	B
Second	C	B	C	C	C
Third	A	A	A	A	A

◄ **Tab. 6:**
Ranking of amine catalyst performance in spray foam

New market study: The Chinese market for thermal insulation products

IAL Consultants has recently published a new, fully updated edition of its report entitled "The Chinese Market for Thermal Insulation". With the enforcement of energy saving policies in China, a large market demand for thermal insulation materials has emerged. The consumption of thermal insulation materials amounted to over 173 million m^3 or nearly 6 million t and the turnover reached CNY 106.4 billion (~ EUR 12.7 billion) in 2012, compared to 130 million m^3 or 4.4 million t and a turnover of CNY 64 billion (~ EUR 7.6 billion) in 2010.

During China's 11th Five Year Plan period (2006 – 2010), building energy consump-tion was reduced by 30 % according to the Chinese State Development and Reform Committee. This project covered new building construction and old building reconstruction. According to the new 12th Five Year Plan (2011 – 2015), building energy consumption will be reduced by a further 50 % and by as much as 65 % in the major cities in China, which would provide great future opportunities for thermal insulation materials.

The government has implemented new policy to ensure the enforcement of energy saving standards in new buildings. Improvement in incomes and living standards will further boost demand for thermal insulation, as heating and air conditioning in homes become more popular.

The report includes both data for 2012 and forecasts to 2017 for the following product categories: glasswool and stonewool, expanded polystyrene (EPS), extruded polystyrene (XPS), polyurethane foam, and phenolic foam. Market data split by region and by end-use application is also provided.

"The Chinese Market for Thermal Insulation" is available to purchase in one volume (200 pages), priced EUR 3,500. **Contact:** Cathy Galbraith, e-mail cgalbraith@brg.co.uk