

Trey: Hello, everyone and thank you all for joining us. Today's webinar, "New Concepts and the Use of Silanes for the Modification of Polyurethane Coatings" is presented by Momentive. Your presenter today is Dr. Dmitry Chernyshov. Dmitry holds a Ph.D. in polymer chemistry. After finishing his Ph.D. and postdoctoral studies at Bayer, he started his professional career within the Coating Division of DuPont as a formulation chemist for automotive and refinished paints. In 2011, he joined Momentive Performance Materials as an application development specialist with a focus on growing new market opportunities for organic functional silanes, and silicones and coatings. Dr. Chernyshov is an author of several academic papers and patent application inventions.

My name is Trey McDonald with UL and I'll be moderating today's event. You can send us questions by typing them in the question box located on your screen, and our panelists will answer them at the end of the presentation. We are recording today's event and we'll send you a link by email when the slides and video have been posted to the UL Prospector Knowledge Center. With that, I'd like to turn the presentation over to Dmitry. Dmitry?

Dmitry: Thanks a lot for the introduction. So dear ladies and gentlemen, it's my pleasure to present a short webinar course which will be dedicated to the application of Momentive's new silane technologies for modification of the various polyurethane coating systems. So I would like to start the webinar with a short introduction of the silane chemistry, and how this chemistry can be used and is actually used in coatings. So actually, silanes are organofunctional molecules which contain different functionalities and, in our company, we manufacture silanes with amino functionalities, epoxies, vinyl, isocyanato, mercaptan functionalities.

This is functionality on the one side of the molecule, and on the other side of the molecule there's an organosilicon part, which is typically an epoxy or a methoxy. The organosilicon and organic parts are linked with an organic spacer. Normally, silanes are used in coatings in three different application areas. The first and very big application area is the surface medication. Actually, a lot of pigments and fillers, and extenders that are used in the formulating coating systems, they already contain silanes in the form of modified inorganic particles.

The second application, which is very broad, this is silane as an adhesion promoter. Silanes are known to adhere to inorganic surfaces or to work as a binding agent between organic polymer and inorganic particles, or inorganic surfaces. The third very big application of silanes as coatings is the cross-linking agents, because silanes can react with themselves, making very dense cross-linking networks. In today's presentation, we'll demonstrate how silanes can be used to enhance cross-linking and also to enhance adhesion.

So in general, we would like to present two different silane technologies, and I would like to start with a new primary aminosilane, which is called "Silquest A-Link 600" silane. This is a new proprietary technology and we'll talk a little bit about the value proposition of that product, how it can be used in coatings, which applications, and how it can be introduced into the polyurethane. We'll demonstrate a couple of high-bake clearcoat systems using A-Link 600 concept, and I'll also demonstrate how the introduction of A-Link 600 can change the different properties. Especially, we will focus on scratch and mar resistance of coatings. I also will touch base shortly, examples of alternative use of this molecule clearcoat system.

So let's start with the value proposition for the Silquest A-Link 600 silane. So this is a new product, and it's a differentiated cell from standard primary aminosilanes, that this aminosilane is a non-yellowing product. So normally, aminosilanes, they demonstrate very strong yellowness, and this is not the case for Silquest A-Link 600. Here, on the slide, we have exposed several test silanes and several test liquids to QUV-B, and actually what you can see is that under QUV-B radiation, silanes, they start to yellow.

Some of them yellow very strong, and some of them less, but still they yellow. If we look at the vial with Silquest A-Link 600, it stays transparent, which is a unique property of this silane. So it means that this silane can be used in the polyurethane applications, especially for finishing applications. You can get benefits of using silanes without the disadvantage of getting a bad colorfastness of your system.

So another interesting feature of Silquest A-Link 600 silane is on the next slide. So normally, when we are talking about primary aminosilanes, formulators cannot introduce them as polyisocyanate activators, simply because primary aminosilanes are extremely reactive towards polyisocyanates. Normally, they react vigorously and with evolution of a lot of heat, and the resulting product is a precipitated gel.

However, the unique chemical structure of Silquest A-Link 600 allows a very gentle reaction of polyisocyanate with this primary aminosilane, yielding a very stable product. This is a very big difference to the standard primary aminosilanes. Here on the slide, you see the gelled product after introducing Silquest 1110, which is a primary standard primary aminosilane into the polyisocyanate. On the next picture below, it's a clear, transparent liquid, which one gets after introducing Silquest A-Link 600 into the same polyisocyanate.

Interestingly, so what we also did, we titrated the -NCO content of the product after introducing A-Link 600. What we found is that the first [inaudible 00:06:39] of amino groups to react very fast with isocyanate, yielding the mono-substituted urea products. The second [inaudible 00:06:46] reacts very slow, which allows

some window of opportunity to [inaudible 00:06:53] product, which is stable. In this case, it's very important for the formulators not to take too much of A-Link 600. Otherwise, the shelf life stability will be then strongly compromised.

On the next slide, we just propose then the mechanism of the reaction. So there's a general mechanism of the reaction. So first, as I just already mentioned, the first [inaudible 00:07:17] of aminosilane reacts very fast, forming the mono-substituted urea. But at the same time, the reaction is pretty gentle. There's not much heat evolution here in the reaction, and the product is stable. What happens then, there's a certain chain extension which happens with time. So each one will go to very high loadings of A-Link 600. What will happen, the viscosity will increase and the stability of the product will go down. So I wouldn't recommend going to very high loadings of A-Link 600.

So what we did next, we tried several high-bake clearcoat formulations, and formulated and introduced Silquest A-Link 600 as a part of the polyisocyanate activator, which is we prepare this polyisocyanate activator in advance, separately from the polyol part of the formulation. This is a standard formulation, which is based on acrylic polyol solvents, some flow and leveling additives, some UV-absorbers and catalysts. As catalysts, we used tin catalysts, and we tested two different loadings of A-Link 600 in the polyisocyanate activator, and looked at different properties of the resulting clearcoat systems, such as scratch resistance, and also weatherability and chemical resistance. So in a minute here, I will present the results. We tested the clearcoats on the basecoats. We used white and black basecoat for the formulation.

So the first slide demonstrates the Crockmeter, the scratch resistance of various clearcoats containing various amounts of silanes. What one sees on the slide is that introduction of silane improves the gloss retention of the system after the Crockmeter test. So if you look at the control system, we see very strong degradation of gloss after the polishing. Then, in the case of silane-modified systems, degradation is much less. So this is the effect of silane, and silane improves scratch resistance by providing additional crosslinking of a clearcoat system through the siloxane cure. We also extended this study to the AMTEC test.

So the AMTEC test simulates, I would say, the field exposure of a clearcoat finish when the car, for example is washed. Here, we've also seen the same phenomena compared to the standard 2K clearcoat. The system which was formulated with the silane demonstrated improved scratch and mar resistance after exposure to the AMTEC test. So then, on the next slide, we also checked scratch resistance with the Taber Abrasion test. This is a very severe test for this type of coatings, and we've seen some minor improvement which also supports the hypothesis of the silane effect on the crosslinking density and the scratch resistance of the clearcoat finish.

On the next slide, we present results of acid etch resistance. So what we've seen is that introduction of aminosilane on this is a very critical property. Because normally, silanes, they have a very negative effect on acid etch resistance, because the aminosilanes introduce functionality into the clearcoat. So we have seen some degrees of acid etch resistance upon introduction of aminosilane, but that wasn't that critical for the system. So I would say that still clearcoat systems demonstrated very good stability towards acid etch effect.

Then, we also exposed the clearcoat systems to weatherability investigation, the QUV-B and xenon test. Here, we haven't seen any negative effect of aminosilane on the weatherability, so accelerated weatherability of the test systems. So I would say all tested clearcoat systems [inaudible 00:12:04] as far as weatherability, as far as UV stability is concerned in both tests. So showing that, in general introduction, there is no negative effect of the primary aminosilane when it's introduced into the clearcoat system.

On the next slide, I would like just to shortly touch base on the standard products, standard technologies which are used to modify the 2K polyurethane clearcoats. Normally, if one goes into this technology, the secondary aminosilanes are a preferred option, because the secondary aminosilanes are cappers. So they cap the isocyanate groups of polyisocyanate, and are providing additional cure through the silane crosslinking. The difference between the standard approach and the Silquest A-Link 600 is that the reaction of A-Link 600 with polyisocyanate is more gentle. So the heat evolution is much less compared to Silquest, for example, standard secondary aminosilanes, such as Silquest 1170.

Important is that there are some disadvantages when one goes into the modification of polyisocyanate activators. The first disadvantage, a very big one is that if one goes to high degrees of silanization, viscosity increases. The higher the silanization, the higher will be the viscosity. The second one is the exothermic reaction, which I already mentioned and that causes a certain threat, or not every coating formulator wants to work with this type of technology. The third one, which is of course clear. By doing additional work with the polyisocyanate activator, we just incur additional costs to the final formulation.

Actually, unlike standard secondary aminosilane technology, with A-Link 600, formulators can go to directly adding the Silquest A-Link 600 silane directly into the polyol part, and the resulting product is unstable. So what we did, we repeated the same set of experiments with Silquest A-Link 600, where we put the silane into the polyisocyanate activator, but this time we just introduced the same amount of silane, but in the polyol part of the formulation. Actually, we [sprayed] coatings and tested their Crockmeter performance, and what we've seen was very close to the results that were produced when A-Link 600 was introduced into the polyisocyanate activator of the clearcoat.

We haven't seen any exothermic effects. So there was no negative effect of aminosilane in the polyol part of the application. We applied this by pneumatic spraying. We haven't seen any deteriorating effect during the application process. So this allows a very easy way of introducing aminosilane into the clearcoat formulation, not using special manufacturing process or additional process to modify the polyisocyanate activator.

So that was the first product and the first technology for polyurethane. The second technology is CoatOSil*T-cure silane. This is a new thiol-based, proprietary silane, which we also propose as an additive for polyurethane coating systems. But unlike A-Link 600, the aim of this silane is to improve [inaudible 00:16:08] UV adhesion performance of the coating system, and not crosslinking density. So I will show the product. I will also demonstrate formulations using the T-cure, and how this product can be introduced into the polyurethane and polyurea product, and show some mechanical properties and chemical resistance, and anticorrosion performances of the resulting direct-to-metal coating systems.

So on the next slide, there's a generalized structure of the CoatOSil*T-cure. CoatOSil*T-cure is an oligomeric glycoxysilane. It really implies some variations to standard silane structures. So because of the oligomeric nature, it's already a polymer-like structure. So there's very little VOC or no VOC [inaudible 00:17:07]. It's a glycolic silane, which means its hydrolysis is very fast. It's faster than the standard methoxy silane, because glycolic silanes are faster in hydrolysis because of several reasons. Also, what is very important is that because of the oligomeric structure, this product doesn't have a very unpleasant smell, which is typical to low-molecular weight sulfur silanes.

Actually, the unpleasant smell is one of the reasons why formulators do not really like to use this product in their formulations. So CoatOSil*T-cure doesn't have this problem. Actually, if you also look at the structure, next to thiol groups, there are also [00:17:47] groups, which makes it very complementary to polyurethane technology. Here, after the hydrolysis of this molecule, what you will get, you will get the glycol, which will be released into the coating. If you use excessive polyisocyanate, for example, you can completely consume the glycol, so there will be no VOC at all.

This can bring some additional hardness, or maybe some additional flexibility to your formulations. This will not happen if you will be using the low-molecular weight silane, because they [inaudible 00:18:15] emits a low-molecular methanol that leaves the coating much faster than it reacts with the polyisocyanate. So these are the major differences. [I show] on the next slide typical reactions that occur between the polyisocyanate activator and thiols. Normally, we have a thiol reacting with isocyanate, with the formation of thiourea products. Thiourea

products are very well-known for their hardness, toughness, and very good UV stability. The formulator will get all these benefits using CoatOSil*T-cure, of course.

So on the next slide, this is a standard direct-to-metal formulation that we tested. We introduced cure into the polyol part of the formulation, and tested different loadings from 0.7 to 3 weight percent. As a control sample, we used standard polyurethane, direct-to-metal coating, and the system, this is the last row, containing 3% of the monomeric thiol silane. We sprayed these coatings over different substrates mostly. In this case, sand-blasted steel is a 2.5 with a [inaudible 00:19:33] thickness of about 80 to 90 microns, and that dried under room temperature conditions, and then exposed it to the corrosion test and neutral salt spray test, 480 hours.

So what we've seen and the results are on the next slide, is that control sample which doesn't contain actually any functional pigments, it's just two components, topcoat, it doesn't have any good corrosion resistance, so we see full delamination of the system. But as long as we start increasing the CoatOSil*T-cure concentration in the direct-to-metal system, we see that [inaudible 00:20:11] of the coating improves. That's how CoatOSil*T-cure helps the coating to demonstrate better performances.

So actually, 3% loading, we see very good results. So this is a polyurethane topcoat without any functional pigments, which already have the performances of functionalized direct-to-metal. Interestingly, if we will switch to monomeric sulfur silane, we will not see this result. So probably, there are some synergies with the glycol and the thiol silane, which is introduced into the system. The next two direct-to-metal polyurethane, we tested effect of CoatOSil*T-cure in the polyamine, or aspartic-type systems. Aspartic-type systems are also very interesting, but they do not really have very good corrosion resistance. In many cases, they're very tough and they have a problem, sometimes, with flexibility.

In general, what we did, we just compared the standard polyaspartic type of direct-to-metal system with one modified with CoatOSil*T-cure. Also, in this case, CoatOSil*T-cure was added into the polyol part of the formulation. In general, just a short remark, it is possible to introduce CoatOSil*T-cure into the polyisocyanate part. But that will be limited by several, probably 1% to 3%. Otherwise, because of the polymeric nature of the CoatOSil*T-cure, it will modify and will compromise the stability [inaudible 00:21:56] the polyisocyanate.

So we did this to coating systems and looked at the mechanical properties and the corrosion resistance. What we've seen is that, interestingly, as I already mentioned many cases where these product systems are very tough and they have problems with the flexibility. So what CoatOSil*T-cure does, it really improves flexibility of the system. So after introduction of 5% of silane into the

system, we improved the bending resistance and the reverse impact dramatically. So in cases of a standard system, we failed with these tests.

But with T-cure, we really got systems that showed very good flexibility. The same as chemical resistance was much better in the case of T-cure, which is probably a result of thiourethane. Additional thiourethane crosslinks, that improves chemical resistance on the system. We also did corrosion resistance on aluminum, and here after 1,000 hours, we've seen very good stability of the CoatOSil*T-cure formulated product. At the same time, the standard one failed already after 500 hours and we didn't even get a good dry adhesion on the product, on aluminum, whereas CoatOSil*T-cure allows also to increase the adhesion to the aluminum dramatically.

So closing my presentation, I would like to summarize and just go through some most important bullet points. So the first product that we introduced today was the Silquest A-Link 600 silane, and this is a new non-yellowing, primary aminosilane. Unlike most of the primary aminosilanes, this one can be used for direct modification of the polyisocyanate activator. Introduction of A-Link 600 into the clearcoat improves scratch resistance of the clearcoat and can be used for that, or can be used to formulate highly scratch and mar-resistant coating systems.

Silquest A-Link 600 doesn't have any negative effect typical for aminosilanes on the discoloration of the system or on the QUV-B, or weatherability, weather stability. The chemical resistance of the clearcoat systems modified with A-Link 600 were less than standard products, but was at the acceptable level. We haven't seen big failures upon introduction of this product. The second product that we introduced today was CoatOSil*T-cure silane, which is used to modify polyurethane direct-to-metal topcoat systems.

Introduction of this product helps to improve anticorrosion resistance of the systems, of the polyurethanes, so that at 3% CoatOSil*T-cure loadings, one could get very good direct-to-metal coating systems, free from any functional pigments. So in general, one can convert standard polyurethane into direct-to-metal by adding CoatOSil*T-cure. Also, CoatOSil*T-cure demonstrated a very good set of mechanical properties in terms of modification of polyurea coating systems. So I'm through with my presentation. Thank you very much for your attention, and I would like to give the word back to the moderator.

Trey: Dmitry, thank you so much. At this time, we are going to move into our Question and Answer session, so we do encourage you to submit questions using the question box that's located on the right-hand side of your screen. We do have a great technical expert and Dmitry on the line here. So he's going to start reviewing those questions. Just a reminder to everybody that we do have on the line today, we will be sending a copy of the recorded presentation to your

email, along with the slides. So do be checking your email for that in the coming days.

We have had a lot of great questions already come in so far. So I will go ahead and pass it back over to Dmitry, and we can go ahead and start with our Question and Answer session. Whenever you're ready, Dmitry.

Dmitry: Okay. So the first question. "When blended silane with polyol part, what about the shelf life?" Yeah. So this is a good question. In many cases, what happens with silanes when they're introduced into the polyol part is that there's a re-esterification reaction. So you re-esterify your silane with the OH hydroxyls from the polyol. This reaction depends on the amount of silane used. In the case of Silquest A-Link 600 that we have used, we haven't seen this problem so far. It was pretty stable, the same as when CoatOSil*T-cure was introduced into the polyol part.

So we haven't seen any problems with the shelf life. Normally, you see that by increasing the viscosity. It goes up with time. You should be very careful with that, of course. But I suggest using silane at pretty low concentrations. So I would say 3%, this is the maximum concentration that you should use. If you go to very high concentrations, yes, that can be a problem and this is something that needs to be addressed before going to the final formulation.

So the next one is going to back to gloss and yellowing [inaudible 00:27:47] of silane, 600 is high. Well, the higher the yellowness index, the higher the yellowness of the system. It means that systems should remain the yellowness of the YI index. On the chart, it should remain as low as possible. So the next question, "Can the silane A-Link 600 be used in modern [inaudible 00:28:15] PU systems?" Yes, it can be used. But in this case, only as a part of a polyisocyanate activator. So if you will start introducing A-Link 600 into the polyol, it will [inaudible 00:28:30] your polyacrylate latex or emulsion systems.

Or you can introduce something [inaudible 00:28:39] Silquest A-Link 600 into water-based. Plus, in water, there's another problem. What will happen, Silquest will immediately hydrolyze and will be immediately consumed by pigments or extenders that you have in your formulation. What you will see, this effect of silane will just disappear. So it's like a perishable additive. You shouldn't use it in the polyol part in water-based.

Actually, this is true for all silane systems. For water-based, what I actually suggest, just take A-Link 600 and go with polyisocyanate modification. You can use whatever HDI or IPI-type isocyanates that are suggested for water-based systems. In my formulations, I'm normally using [inaudible 00:29:31] 3900, which is a pretty good one for water-based. Then, introduce, do the 5% silanization, and then this hybrid polyisocyanate activator can be used together with a water-

based polyol part. That should work.

The next question, "Does the CoatOSil*T-cure effect the cure rate of polyurea coating?" Yeah. It has a certain... Well, it's a very interesting question. Normally, polyurea coatings are very fast. Interesting, in fact, of CoatOSil*T-cure, this is a thiol silane. So if you have a DBTDL-type catalyst, the same as I did in my formulations, what will happen, CoatOSil*T-cure will normally deactivate tin very strongly, because it's a very strong, complexing [inaudible 00:30:25] for tin. What you will see then, the catalytic effect of tin will be less. However, in my aspartic systems, I never use tin as a catalyst, because the systems are very fast. So yes, I haven't seen any slowdown of the reaction. The reaction was a little faster. But that was very little.

So I haven't seen any big effect on curing kinetics, but it can happen. But I'm using the slowest polyaspartic resin that I have for pigmented systems. Because if you start using faster systems, then [inaudible 00:31:12] life will go down very sharply. So no strong effect on curing kinetics. There is a small acceleration. That's my answer. For CoatOSil*T-cure, as I already mentioned, in DTM systems, it slows down the curing kinetics. "Any patent restrictions on the use of this material?" Well, as far as the composition [inaudible 00:31:50] is concerned, we own the patents of products. As far as application is concerned, [inaudible 00:31:56] of our products, you should look into the patent literature. [inaudible 00:32:03]

The next question, I assume, regarding the CoatOSil*T-cure, "Can it be used with epoxy silicon technology from [inaudible 00:32:17]? What are your recommendations?" Well, I don't know very well epoxy silicon technology from [inaudible 00:32:23]. But I think, yes, both products can be used with epoxies. So Silquest A-Link 600 can be easily introduced into epoxy formulations and what you will get with this product is a non-yellowing silane formulation. So I would say that if you have a topcoat or topcoat finish, then Silquest A-Link 600 will be probably a good choice for that application.

As far as CoatOSil*T-cure is concerned, it also can be used in combination with epoxy systems. Actually, I also do have some formulation recommendations of how to use it in epoxy systems. But today's topic is polyurethane, so I don't want to spend too much on that. So the next question, "Can you please share contact information?" Yes, of course. I will provide the organizers with all our contacts so that you can always contact me directly if there are any technical questions. "Can T-cure affect metal oxidation?" It's possible. But I do not have any data on that. I don't have any data. I haven't seen any data, or I don't have any experimental data on that.

What I can tell you is that I haven't seen any problems with [inaudible 00:34:05] formation when using CoatOSil*T-cure in my polyurethane formulations. Okay.

So we don't have any other questions. I think that I... Okay. So then, I think, if there are no other questions, I can revert back to the moderator.

Trey: Great. Dmitry, thank you so much. A big thank you to everybody for attending, and also a big thank you to Momentive for this really great, informative presentation. Just a reminder again, one more time, we will have a copy of the slides and the recorded presentation. So you can watch that again. Share that at your leisure with others at your company. Again, a big thank you to everybody for attending and have a great rest of your day.