A big “PLUS” for engineering components:

Superior aging resistance for easy to process specialty nylons

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DuPont™ Zytel® PLUS is a new family of nylons from DuPont which combines the ease of processing of conventional nylon resins with groundbreaking levels of resistance to chemicals, hot air, oil and coolant. Comprehensive research shows that, in comparison to traditionally stabilized nylons, the lifetime of components can be significantly extended. This, along with other benefits, such as low warpage and an excellent surface aspect, make the new polyamides ideal for a range of applications which to date have been reserved for metals or considerably more expensive high-performance thermoplastics. The initial emphasis for application developments will be on automotive engine and exterior components, although the encapsulation of sensors as well as applications for the electric and electronic, household equipment and general industry also offer great potential.

For more than 25 years, glass fiber or mineral reinforced, heat- and hydrolysis-stabilized nylon 6 and 66 grades have been the material of choice for under-the-hood applications in the automotive sector. This is due in principle to their high levels of cost-efficiency and because, in contrast to many more expensive alternatives such as the specialty nylons 46, 6T and PPA or the high performance thermoplastics such as PEEK and PSU, they are easy to process, ductile and impact resistant. The first applications in these materials were simple cover caps, fan guards and coolant tanks. Today they are used for air duct components around the turbocharger, for cylinder head covers, resonators, water pump housings, oil pans and exhaust pipe brackets (Image 1).

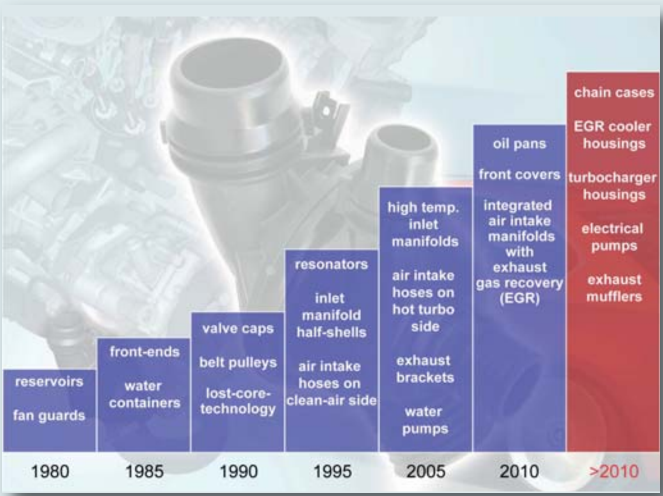

Image 1. *Nylons have 25 years of use in the engine compartment behind them, with many more to come*

Higher performance engines and a reduction in the amount of air passing through the engine compartment due to the increasingly limited available space, combined with the encasing of engines and the end-to-end cladding of the undercarriage, will all lead to an increase in temperatures under-the-hood from 150 °C to 180 °C and more, with peaks of 230 °C possible in some cases. This, along with the simultaneous effects of humidity, lubricants and fuels and aggressive road salts will pose a challenge beyond the performance capabilities of many of the polymers available to date.

It is for this reason that there is a growing requirement within the automotive industry for cost-efficient, easily-processable thermoplastics that are able to reliably withstand the rigorous demands of the engine compartment or automotive exterior for the entire lifetime of the vehicle. Leading OEMs currently demand of these materials that they retain at least half of their original properties, such as tensile strength or strain at break, after 1,000 hours of hot oven aging at 210 °C, whereas in the past it was 170 °C or 180 °C. Similarly high demands are made with regard to aging resistance in hot oil and hot coolant.

New additive technology enables cost-efficient resistance

One direct response to these requirements is provided by the new Zytel® PLUS nylon grades from DuPont. Their development marks a successful increase in the thermal and chemical resistance of nylons to new levels. Their major benefits, in terms of their low specific weight, high-flow and therefore ease of processing at moderate temperatures way below their decomposition temperature, are fully retained.

New Zytel® PLUS nylon receives its endurance boost from SHIELD Technology, exclusively from DuPont. DuPont™ SHIELD Technology combines several innovations, including a new polymer backbone, polymer modifications and a special set of additives, to enhance many performance characteristics. Using an exact combination of base material and additives, multifaceted benefits are delivered which, depending on the targeted application, meet resistance requirements far better than nylons commonly available today (Image 2). The efficiency of this technology is best illustrated by the microscopic images of two heat-stabilized, glass fiber reinforced PA66 grades (Image 2). They show microtomed sections through samples with an initial thickness of 4 mm, which have been exposed to a temperature of 210 °C for 1,000 hours. The resulting damage to the

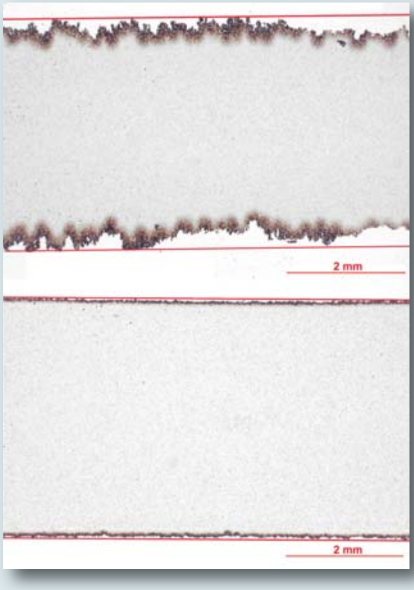

Image 2. *In comparison to traditionally-stabilized PA66 grades (above), the long-term exposure to high temperatures (in this case: 1000 h at 210 °C) causes considerably less damage to the new Zytel® PLUS grades (below)*

traditionally-stabilized PA66 is shown above, the lower image shows a grade of Zytel® PLUS nylon, which has been stabilized with the new technology. Whereas surface carbonization of the standard grade is considerable, the Zytel® PLUS nylon sample is almost unscathed, and the damaged layer is only a few hundredths of a millimeter deep.

The excellent long-term temperature and chemical resistance of the new, high-flow Zytel® PLUS nylons means that they can cost-effectively fill the wide gap between standard nylons and many typical high performance thermoplastics such as PPA and PPS (Image 3). It

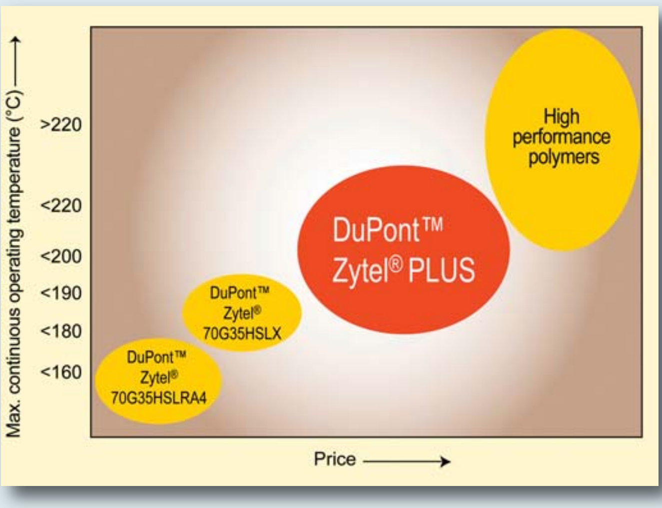

Image 3. *The new Zytel® PLUS nylon grades are positioned between conventional nylon grades and high performance thermoplastics*

is therefore likely that the lifetime of certain components in the engine compartment can be doubled compared to those made of standard, heat-stabilized nylon. As a result, there are a multitude of opportunities to replace metal components in the engine compartment or to replace existing polymer applications with more lightweight constructions. In turn, this will help vehicle manufacturers to not only reduce their costs but also weight, thereby helping to reduce both fuel consumption and emissions. The new, highly-resistant nylons, which demonstrate mechanical properties over a wide temperature range and are as ideally suited to long flow distances as they are to low wall thicknesses, also offer new perspectives in the design of applications such as electric and electronic components, sanitary equipment or parts for industrial facilities.

Four grades at launch

Initially the Zytel® PLUS nylon family will comprise four chemical-, heat- and oil-resistant grades, which are optimized based on the targeted application:

- Zytel® PLUS 95G35 is a high flow core product that displays outstanding properties even after long-term exposure to high air temperatures of up to 210˚C (short-term peaks of up to 230˚C) with very good surface quality and high resistance to hot motor oil and calcium chloride solutions. Principal applications will be in the area of air ducting components.
- Zytel® PLUS 95G50 is a further high-flow nylon with an increased glass fiber content of 50 percent. It combines very good resistance to the long-term effects of high temperatures up to 210 °C (short-term peaks of up to 230˚C) with increased stiffness and creep resistance at high temperatures, thus making it ideal for applications under-the-hood.
- Zytel® PLUS 93G35 offers a low melt temperature of 224 °C (all other grades: approx. 265 °C) and combines good long-term retention of properties when exposed to heat, oil and chemicals with very good weld line and burst pressure strength. Typical applications are components exposed to hot air.
- Zytel® PLUS 90G30 is notable for its outstanding resistance to hot engine coolant and hot water, and is ideal for the production of radiator end tanks, thermostat housings and other components that come into direct contact with coolants.

All grades have a high surface quality and high dimensional stability in common. For instance, the new universal grade Zytel® PLUS 95G35 exhibits a 30 percent higher degree of gloss and 20 percent less warpage than a corresponding standard PA grade. Image 4 compares the flow properties of the new grades with those currently available. An overview of the basic physical attributes of the five grades can be found in Image 5.

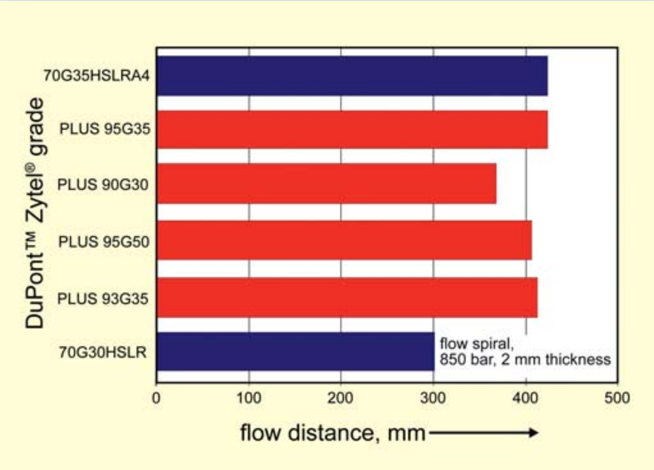

Image 4. *The flow properties of the new Zytel® PLUS nylon grades are comparable to those of traditionally-stabilized nylons*

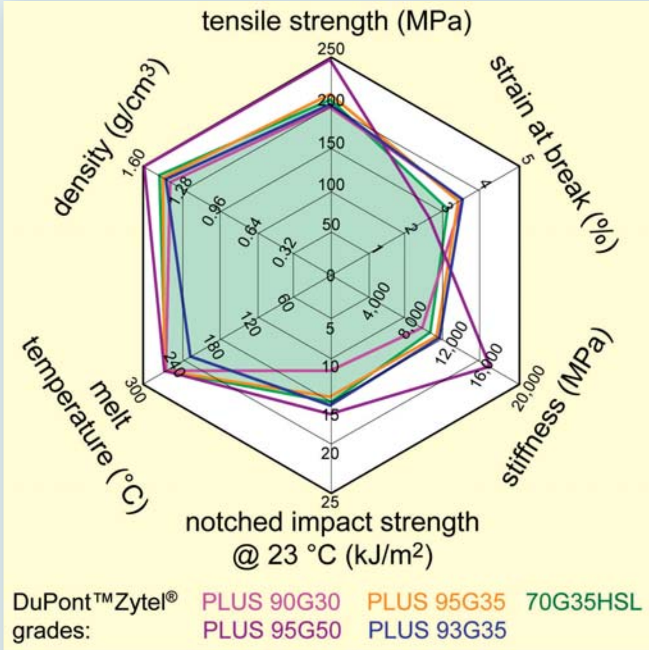

Image 5*. The physical short-term properties of new Zytel® PLUS nylon grades are comparable to those of traditionally-stabilized nylons such as Zytel®70G35HSL, while Zytel® PLUS 95G50, through its high stiffness and strength, stands out*

Hot air aging: 1,000 hours at 210 °C easily managed

How significant the improvements are in terms of aging behavior is illustrated by the comparison of mechanical properties after aging for the universal grade – Zytel® PLUS 95G35 nylon. At an aging temperature of 180 °C, a traditionally stabilized grade would lose approximately one half of its tensile strength (a decrease from 210 MPa to 105 MPa) after 3,000 hours (the equivalent of around 150,000 km for vehicle applications), whereas the PLUS grade shows almost no sign of deterioration at the same temperature (Image 6). A comparison at an aging temperature of 210 °C, which is becoming more and more the decisive factor in the automotive industry, makes the difference even more clear. In this case, the standard grade has lost half of its tensile strength after approximately 800 hours, whereas the PLUS grade withstands this temperature for more than 1,800 hours before its tensile strength is less than half of its initial value. At this stage, the standard grade is almost entirely carbonized.

An equivalent trend can be found in terms of strain at break (Image 7). Whereas this property is already at almost half of its original value after 2,000 hours at 180 °C for traditionally-stabilized grades, the new Zytel® PLUS 95G35 nylon shows little change in terms of its strain at break even after 3,000 hours. During air oven aging at 210 °C, the halfway point for the traditionally-stabilized grade lies at just under 700 h, whereas the Zytel® PLUS grade does not reach this point until after 1,500 hours, and even after 2,500 hours still retains a strain at break of 1 percent (approximately 1/3 of its original value).

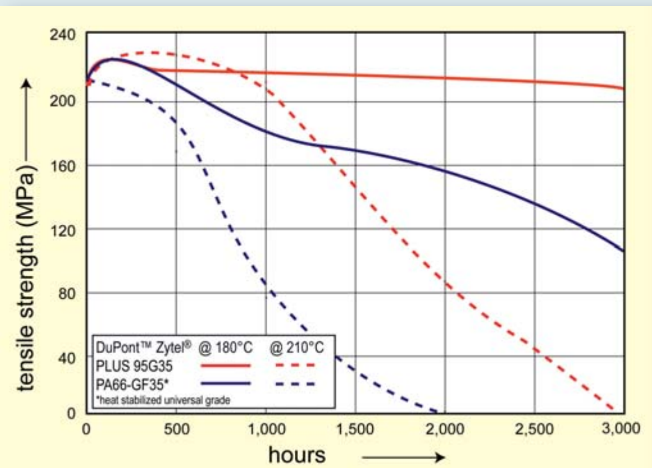

Image 6. *Effect of air oven aging on the tensile strength of traditionally-stabilized PA66 and the universal grade Zytel® PLUS 95G35*

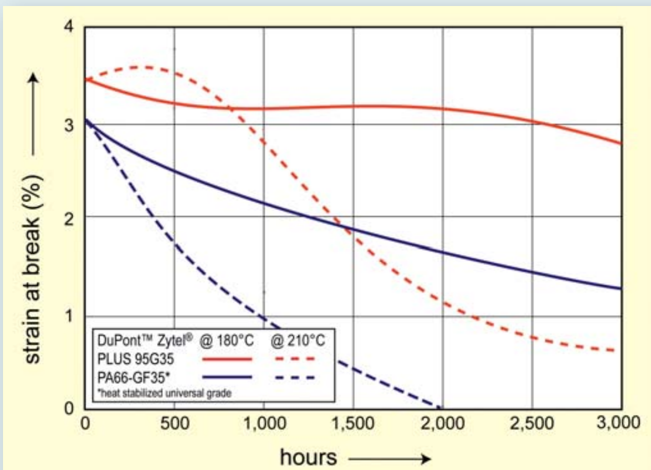

Image 7. *Effect of air oven aging on the strain at break of traditionally-stabilized PA66 and Zytel® PLUS nylon universal grade PLUS 95G35*

With an increased glass fiber content of 50 percent, Zytel® PLUS 95G50 nylon provides the highest levels of strength and stiffness within the new Zytel® PLUS family (see Image 5). Aging in air at a temperature of 180 °C causes no significant reduction in its high initial value of 250 MPa, and even after 2,500 hours at 210 °C the very good mechanical properties are retained at a very high level (see Image 8).

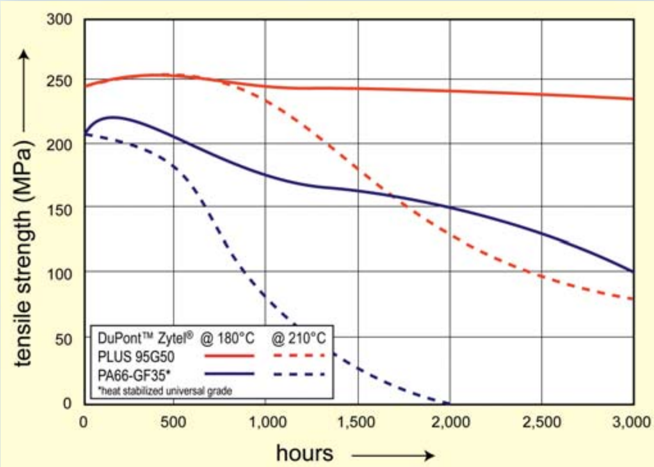

Image 8. *Effect of air oven aging on the tensile strength of a traditionally-stabilized PA66 standard grade and the high stiffness Zytel® PLUS 95G50 nylon grade*

Hot motor oil aging at 150 °C: Impact resistance retained

In light of the applications intended for Zytel® PLUS 95G35, such as cylinder head covers, oil pans and oil modules, the material's aging resistance in hot oil is a decisive criterion. At the same time, its impact resistance is of particular significance in terms of its practical usage. Image 9 depicts its behavior during hot motor oil aging, both for a traditionally-stabilized grade as well as for Zytel® PLUS 95G35. The continuous operating temperature of 150 °C is typical for modern engines with higher power densities.

The impact performance of the PA-GF traditional standard grade drops by 50% after 3,000 hours. Accordingly, high safety coefficients had to be used during the design. Thus the potential weight benefits of polymers when compared to metal could no be fully exploited.

The universal Zytel® PLUS 95G35 grade tested in this case retains its impact resistance under the same conditions – a result which also applies to all other new Zytel® PLUS grades. Indeed, at the start of the test, the hot oil aging improves ductility by around 10 percent, an effect which is neutralized after approximately 1,500 hours. Samples subjected to pendulum impact testing after this period of time demonstrated the same impact resistance as the unaged material, whereas the impact resistance of the traditionally-stabilized material had already fallen from 80 kJ/m² to under 55 kJ/m² by this time.

What is particularly impressive is the behavior of impact resistance levels over time: whereas the performance of the standard PA grade continues to fall towards half of its original value, the impact resistance of the new Zytel® PLUS 95G35 nylon grade remains unaltered and at its original level, even after 3,000 hours. In other words: hot motor oil aging at 150 °C, over a period of time which is of practical relevance, has no effect on the material. The consequence of this finding is the potential to use lower safety coefficients for the design of components exposed to hot oil, and thereby use less material for lower weight without compromising the component's safety.

Salt mist: Double the resistance

A decisive factor for components that are exposed on the underside of the vehicle is their resistance against calcium chloride ($CaCl_2$, which is used, for instance, in Asia, Russia and Canada as a road salt), dissolved in water. In order to test this, double-gated tensile bars were used to provide a centrally-running weld line. These were then exposed to a $CaCl_2$ solution spray for two hours at 100 °C, while under a tension of 20 MPa, before removal and visual evaluation. The number of cycles the samples are able to withstand before appearance of the first visible cracks and failures (along the weld line) is recorded.

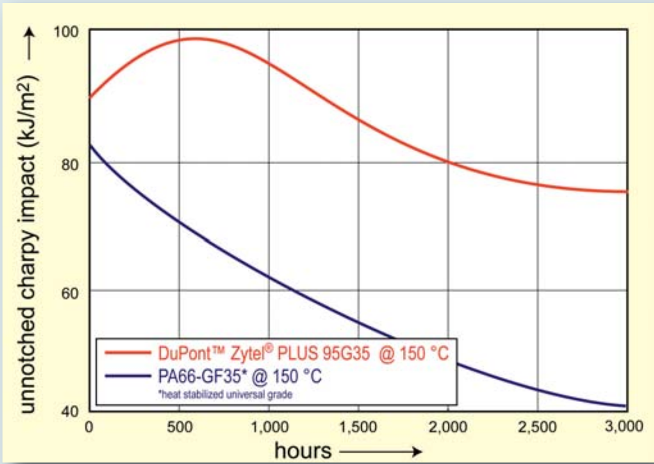

Image 9. *Effect of hot motor oil aging on the impact resistance of traditionally-stabilized PA66 and the core Zytel® PLUS 95G35 grade*

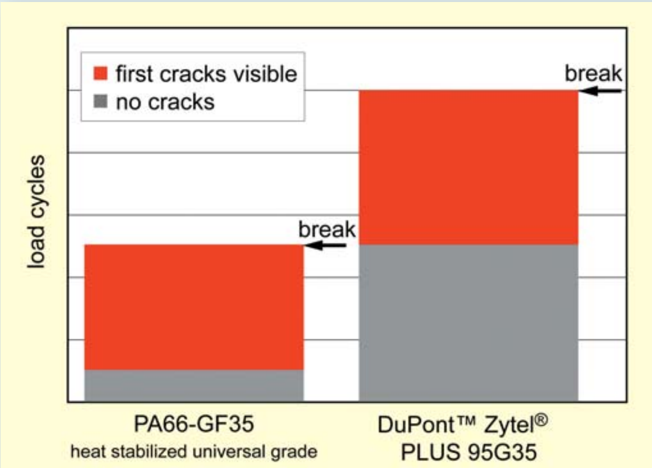

Image 10. *Crack formation in dual-gated samples made of traditionally-stabilized PA66 and the Zytel® PLUS universal grade PLUS 95G35 when placed under tension and exposed to salt mist ($CaCl_2$-water solution at 100 °C)*

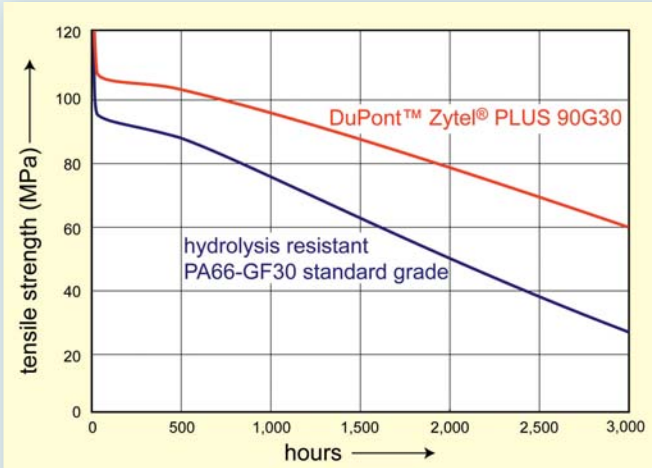

Image 11. *Effect of exposure to hot coolant (50% water, 50% Glysantin, 120 °C) on the tensile strength of coolant-resistant Zytel® PLUS 90G30 and a corresponding PA 66 standard grade*

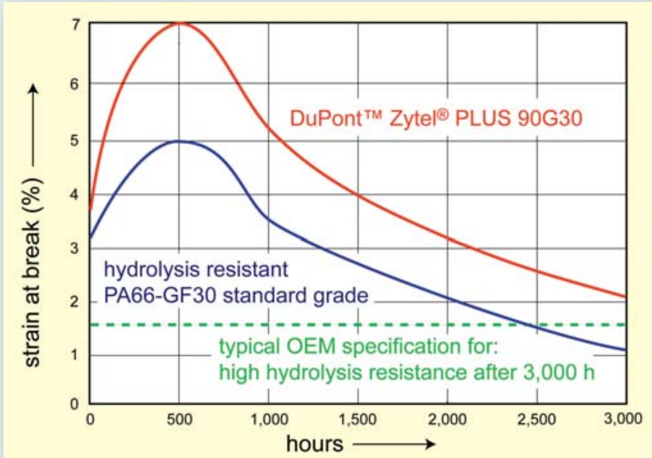

Image 12. *Effect of exposure to hot coolant (50% water, 50% Glysantin, 120 °C) on stress at break of coolant-resistant Zytel® PLUS 90G30 and a corresponding PA 66 standard grade*

Image 10 shows the summarized result of the test, which indicates that, under these conditions, the overall lifetime of the sample made of Zytel® PLUS nylon is twice as long as that of the sample made of traditionally-stabilized PA. Whereas the latter shows the first signs of damage at a very early stage, damage is only visible on the Zytel® PLUS part at a point in time when the standard material has already failed.

Top resistance to hot coolant

Where the resistance of nylons to hot coolant has been a limiting factor on their use in the cooling circuit – thermostat housings are one example – Zytel® PLUS 90G30 now opens new doors. Images 11 and 12 show the results of aging tests on tensile bars exposed to a 50/50 mixture of water and ethylene glycol (Glysantin G48) at 120˚C. A glass fiber reinforced, traditionally-stabilized PA66 serves as a comparison.

Once again, Zytel® PLUS demonstrates clear superiority: Initially both materials very quickly store a certain amount of the coolant mixture. This causes a rapid reduction in mechanical properties which is, however, more pronounced in the PA66 standard grade (at around 20 percent) than in the Zytel® PLUS grade (minus 10 percent). Thereafter a relative balance is quickly reached, which is reflected by the slow but consistent reduction in properties. The tensile strength of Zytel® PLUS 90G30 falls to 50 percent of its original value only after a full test cycle of 3,000 hours. This corresponds to the requirements of leading OEMs for highly hydrolysis resistant materials. The time required for the comparison material to reach its halfway point was significantly shorter. Similar results have been recorded with relation to stress at break and Charpy impact resistance.

Temperature resistant weld lines

A number of components in the intake system and air ducts consist of individually molded parts, which are subsequently welded together. In addition, more and more designs incorporate the welding of additional components on to a basic injection molded part, such as an oil pan or intake manifold, in order to increase functionality. Typical examples of this include the latest oil pans, where oil ducts have been integrated in the design and where, in the mid-term, the integration of the oil filter is also possible. In such cases, the weld line quality is of great significance, and can be tested in terms of its burst pressure resistance using a hollow container exposed to internal pressure.

Image 13 shows the burst pressures for a traditionally heat-stabilized PA66-GF35 as well as for three of the new Zytel® PLUS grades, recorded at room temperature and after storage at 210 °C for different periods of time. Initially all grades reach high values of around 15 bar and more, whereby the value for Zytel® PLUS 93G35, which has been optimized for welding application, is particularly impressive at 24 bar. Five hundred hours at 210 °C has no effect on the performance of the new grades, whereas the traditionally heat-stabilized grade has already lost around one third of its initial value. There is an even more notable difference following 1,000 hours at 210 °C: The traditionally-stabilized PA66 grade has completely lost its performance. In contrast, the burst pressure strengths of all three Zytel® PLUS grades remain outstandingly high, close to their initial performance levels.

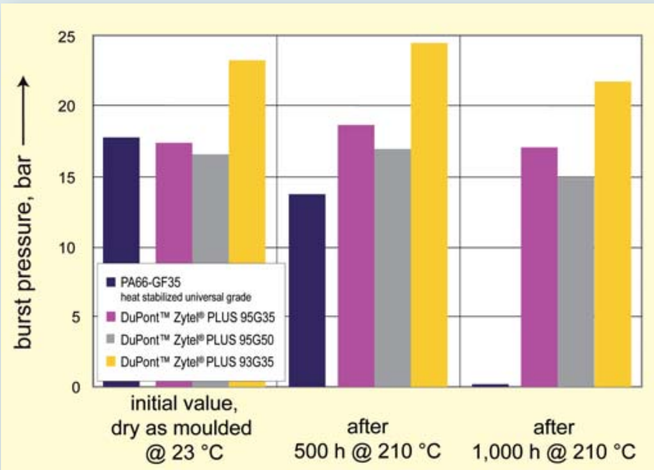

Image 13. *Results of burst pressure testing at various temperatures in comparison*

Limitless potential

With their high thermal and chemical resistance, the new Zytel® PLUS nylon family from DuPont Performance Polymers is a direct response to the consistently growing requirements of the automotive industry. Image 14 summarizes the properties of the Zytel® PLUS family. These new PA grades combine many of the positive attributes of the currently available heat- and hydrolysis-stabilized PA grades with those of the considerably more expensive specialty polymers, with none of the associated disadvantages of these material groups.

The principal benefits of the Zytel® PLUS family relate to their – in some cases remarkably – superior resistance to aging in hot oil and hot air. Moreover, their surface properties are of a high level, while the ease-of-processing and impact performance associated with conventional nylon products remain unchanged. Such a list of positive attributes creates new material-based opportunities for the design of a range of highly demanding components, which to date were not within the capabilities of conventional nylons. These include charge air coolers, exhaust mufflers, turbo air ducts, engine mounts, resonators, cylinder head covers, throttle housing, oil pans, EGR coolers, oil modules, thermostats, transmission, front covers and radiator end tanks.

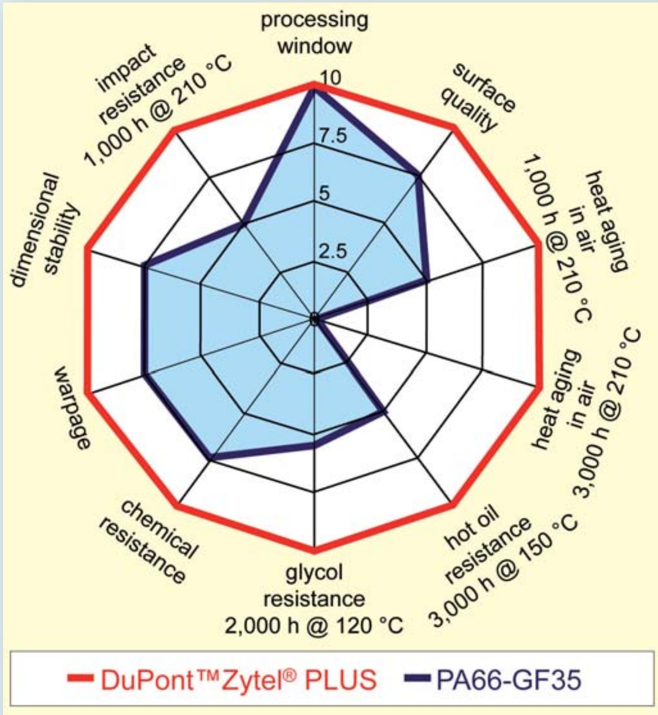

***Image 14**. Zytel® PLUS nylons from DuPont combine the positive attributes of conventional nylon resins with superior long-term resistance to challenging environments*

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L-14492-0 (02/2010)

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