RESISTING AUTOMOTIVE TPE FOGGING with gas-to-liquids base oils

Shell gas-to-liquids (GTL) oils have been used in thermoplastic elastomer (TPE) compounding applications for many years. They provide low volatility and viscosity, excellent purity and thermal colour stability, which make Shell GTL oils optimal ingredients for producing TPEs. Recent legislation such as the German Association of the Automotive Industry standard VDA 278 and strict requirements from equipment manufacturers require that Shell Lubricants closely controls the fogging properties of the process oils used in TPEs. Therefore, a Shell technical team set out to determine how to ensure that every batch of product meets the fogging criteria. This required considering the entire supply chain, including Shell GTL oils and paraffinic Group II base oils.

Climate-related condensation is common in humid environments. TPE fogging is a very different issue that Shell researchers are helping to understand and eliminate.

Fogging: The issue

When TPEs are used in automotive interior applications, certain substances from the manufacturing process can evaporate at elevated temperatures and may cause the phenomenon of fogging on glass or other surfaces in the vehicle. This is distinct from climate-related problems such as humidity leading to condensation on cold surfaces. The fogging effect is due to the condensation of semivolatile organic components, termed FOG, released from materials, including TPE compounds, used in vehicles. These include the mineral or process oils that are typically used as plasticisers or extender oils in polymer compounding (see boxed text, TPE compounding oils).

In recent years, in a move to improve passenger comfort, health and safety, regulations have been introduced relating to odour, fogging and FOG emissions. Automotive interior materials are now tested according to standards such as VDA 270, VDA 278, ISO 6452 and DIN 75201-B. As major car manufacturers such as Daimler and the Volkswagen group have tightened their specifications, it is now necessary for producers to test process oils or commercially produced TPEs for use in automobile interior compounds for the same properties. Fogging is one of the most important of these. German standard VDA 278 defines FOG components as condensable substances in the boiling range of C_{14}–C_{32} n-alkanes.

Some attempts have been made to reduce fogging by using high-viscosity process oils and/or solid resins to produce TPE polymers. However, the use of high-viscosity oils causes undesirable increases in the viscosity of the TPE compounds leading to difficulties and increased energy costs when handling such high-viscosity substances at manufacturing plants.

GTL oils for TPE compounding

The Shell Lubricants business-to-business (B2B) team offers a wide range of technical-grade GTL process oils, including medicinal grade white oils, for TPE customers to enable better processability and finishing of their products (see boxed text, B2B or B2C?). These oils are cleaner, highly refined paraffinic oils that are suitable as plasticisers for the compounding of TPEs.

The portfolio of oils manufactured consequently has a uniform molecular structure: mainly highly saturated linear paraffins with few side chains. In comparison, conventional oils found on the market contain higher levels of polar components. This feature contributes to good compatibility, particularly with styrene-ethylene-butylene-styrene and styrene-ethylene-propylene-styrene type TPEs, thermoplastic vulcanisates and ethylene propylene diene monomer rubbers, as the molecular structure is similar.

Some of the key advantages of using Shell GTL oils

- They are colourless and virtually odourless, and have significant advantages for compound and rubber blend processing. Compared with conventional process oils, Shell GTL oils demonstrate up to three-times lower viscosities.
- Shell Risella X 430 GTL oil has up to a four-times lower Noack evaporation loss compared with conventional group I and II oils available on the market (tested according to ASTM D5800, 1 h at 250°C). This improves the production environment and reduces FOG emissions.
- They exhibit excellent ultraviolet (UV) stability properties and resist discoloration, which is of primary importance to TPE customers.
- They have excellent temperature stability at given test temperatures compared with group I and II conventional oils.
- Shell Risella X oils and Shell Ondina X have very low levels, comparable with medical white oils, of polycyclic aromatic hydrocarbons. Their purity is in line with the requirements for formulations that meet more stringent legislation, which makes them appropriate for applications requiring higher levels of purity.
- Shell GTL white oils meet the purity requirements of the US and EU pharmacopoeias. Additionally, Shell technical grades conform to US FDA 21 CFR 178.3620(b) requirements with respect to UV absorbance limits.
- Shell Risella X and Shell Ondina X oils have lower viscosity and more linear molecular structures than conventional mineral oils. When used in TPE applications, they can contribute to better flow of the melt and aid in providing better extrusion and injection-moulding characteristics, key elements in the production process.

Shell GTL oils are used as extender oils for producing various parts for automobile interiors; these include mats, instrument panels, dashboards, buttons, encapsulation seals, cup holders, gaskets, bushings, cables, car locks and comfort items.

TPE compounding oils

Most process oils are derived from a crude oil distillation stream by a refining process. This may involve dewaxing to reduce the pour point, solvent extraction to remove aromatic compounds and hydrotreating to chemically modify aromatic structures. The degree of reduction in the concentrations of aromatics and impurities such as sulphur- and nitrogen-containing compounds depends on the type and severity of the refining process and the nature of the crude oil processed.

The volatility of process oils increases from paraffins/isoparaffins to naphthene to aromatics. Group II paraffinic oils typically have more saturated rings and long paraffinic side chains. Paraffinic/isoparaffinic oils are generally the least volatile ones available on the market. They are characterised by good colour, stability and solubility of saturated compounds.

Highly refined paraffinic oils also have the lowest content of polar and unsaturated molecules. These unsaturates contain impurities such as nitrogen, sulphur and oxygen that are highly susceptible to oxidation and colour degradation when exposed to UV light and/or heat.

In contrast, Shell GTL oils are based on GTL synthesis technology that converts a very clean feedstock, natural gas, into high-quality liquid products that would otherwise be made from crude oil. The resultant base oil is very pure, contains almost no sulphur or nitrogen compounds, and is significantly more stable than conventional base oils.

Modelling development: Predicting fogging for process oils

Some key TPE customers may not have the appropriate laboratory equipment at their production sites for testing every batch of process oil delivered. If the customer subsequently produces a TPE compound and it does not meet the fogging performance criteria, they immediately see that a potential root cause could be the process oil they have used.

In consequence, there is the potential risk of Shell Lubricants losing their business. More immediately, the customer may submit a claim for the loss of the product for not meeting the fogging specification because of the process oil used.

Therefore, in a customer-centric approach and as part of the quality assurance for Shell process oil offerings to TPE customers, a Shell Lubricants technology team initiated a study that set out ▸▸▸

B2B or B2C?

B2B can be defined as any instance in which one commercial entity sells a product or service to another for use in its business. Selling to an end-user consumer, as an individual, for their own consumption or use would be a pure business-to-consumer (B2C) transaction.

When the Shell Lubricants business developed its accelerated growth definitions, it defined B2C lubricants as those relating to branded passenger car motor oils and lubricants for maintenance and construction, whereas B2B lubricants were those concerned with transport, industrial and process oil applications.

to understand the correlation between the initial boiling point (IBP) of the process oil used and the fogging performance of the TPE compound from the commercial production process. The reason for developing this correlation was to qualify each batch of product by setting a minimum IBP requirement for Shell process oils that would enable them to comply with the fogging criteria of TPE customers.

The oil samples used in this study included Shell GTL oils such as Shell Risella X 430 and Shell Ondina X 432, medicinal white oils such as Shell Ondina 941 and other types of oil. Fogging testing was done according to the DIN 75201:2011 gravimetric method. A series of oil samples was tested for fogging over a period of 6–8 mo. The initial phases of the process oil sample testing were mainly carried out at the laboratories at Shell Technology Centre Hamburg (STCHa), Germany, and Shell (Shanghai) Technology Ltd (SST), China (see boxed text, Measuring fogging).

The process oil samples were also tested by simulated distillation according to the ASTM D2887 test method at the Shell Grasbrook Lubricants Centre, Germany, to measure the IBP of each of the process oils used. The results were correlated with the fogging results (Figure 1).

Correlating IBP and fogging

The Shell team observed that the IBPs for different bulk deliveries of a high-viscosity, grade 600N base oil could range between 360 and 380°C. Figure 1 presents the correlation that the team developed and shows examples of Shell process oils.

To read the graph:

1. Identify the IBP of the oil on the left axis.
2. Read horizontally to the IBP correlation (green line).
3. Read vertically to the red line.
4. Read off the fogging value on the right axis.

The Shell team determined that a higher IBP correlates with less fogging and better colour. Lower volatility in the production environment will also contribute to improving employee health and

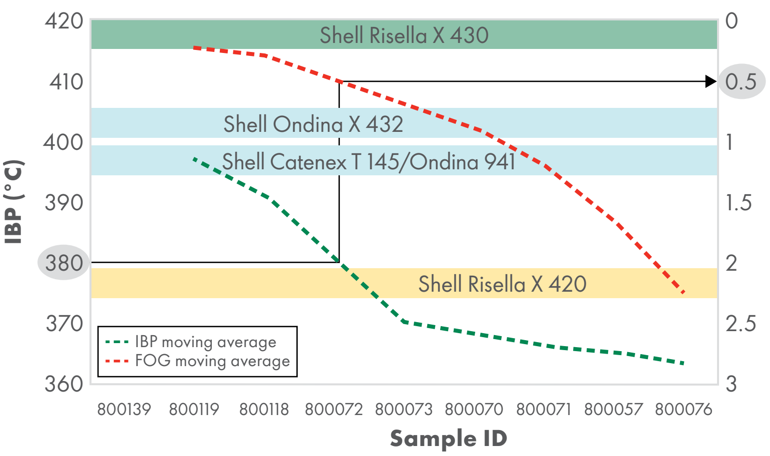


FIGURE 1
Correlation between the IBP of process oils and the expected fogging.

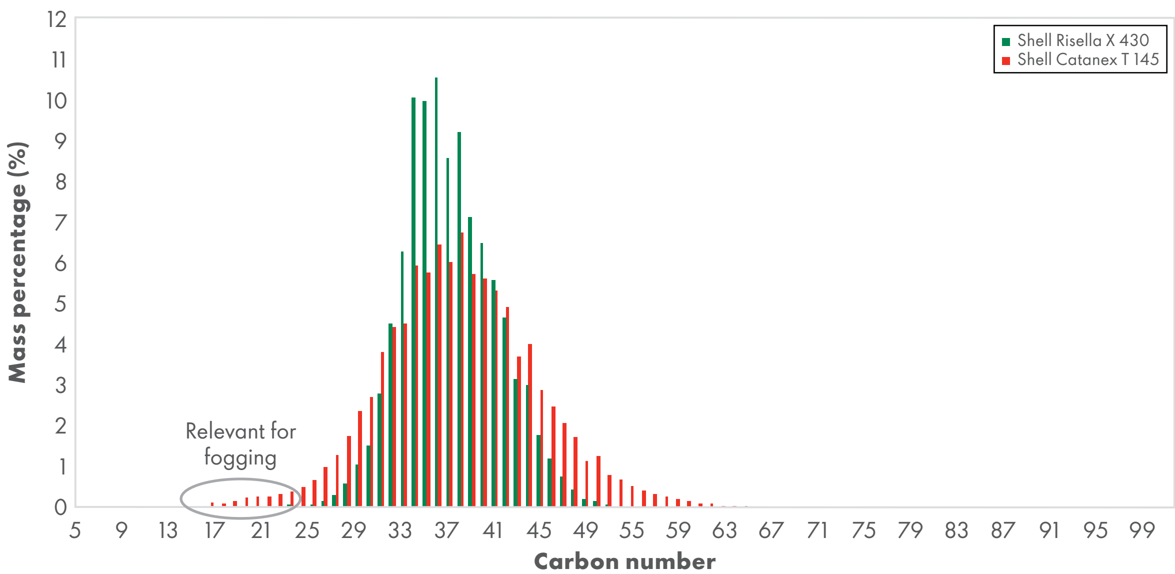


FIGURE 2
Carbon chain length distribution for process oils.

Sample ID	1900204	1900208	1900209	1500022	1900207	1900077
Product	Shell Ondina 941	Shell Catenex T 145	Shell Catenex T 144	Shell Risella X 420	Shell Risella X 430	Shell Ondina X 432
Fraction distilled (wt%)	Temperature (°C)					
IBP	390.5	352.1	391.2	378	421.1	400.1
1	404.4	361.3	402.8	384	434.1	413.3
2	419.0	393.2	419.4	390	445.4	427.2
3	428.0	410.7	430.8	393	452.1	435.7
4	434.6	421.1	438.4	395	456.9	442.0
5	440.0	428.5	444.0	397	460.8	447.1
10	457.5	450.6	461.2	404	472.4	463.6
20	477.4	473.3	479.6	412	483.3	479.8
30	491.0	488.0	492.2	420	490.9	489.7
40	502.3	499.8	502.7	427	497.8	498.4
50	512.6	510.4	512.5	435	504.6	507.0
60	522.9	520.9	522.5	443	511.8	515.9
70	533.6	531.8	533.1	452	519.8	525.7
80	546.1	544.3	545.8	461	529.1	537.0
90	563.4	561.4	563.3	470	541.3	552.7
95	578.1	575.9	577.9	476	550.4	566.1
96	582.3	580.0	582.1		552.9	570.3
97	587.5	585.0	587.4		555.9	575.6
98	594.6	591.8	594.8		559.9	582.8
99	606.3	602.7	608.1		566.1	594.4
Final boiling point	617.6	612.9	622.3	485	572.1	605.2

TABLE 1
Simulated distillation results.

safety. Current analytical results show that Group II oils generate product fogging results of up to 10 mg, 20-times higher than those exhibited by Shell Risella X 430.

On the basis of the data compiled, the team determined that a minimum IBP of 380°C is required to meet the gravimetric method minimum fogging criterion of <0.5 mg. The correlation developed is most useful for quality control of the certified product in customers' storage tanks and would avoid future claims from oils not meeting fogging criteria.

Figure 2 provides confirmation of the graphical correlation. The figure shows the carbon chain length distribution results for samples of two Shell oils and indicates the components relevant to high fogging values in the TPE compound. These are lower molecular weight carbon structures (C_{18} to C_{23}) with lower IBPs.

Table 1 shows the IBP results for various grades of process oils tested according to ASTM D2887. These were used in the correlation to estimate the fogging behaviour of process oil batches before supplying customers.

Measuring fogging

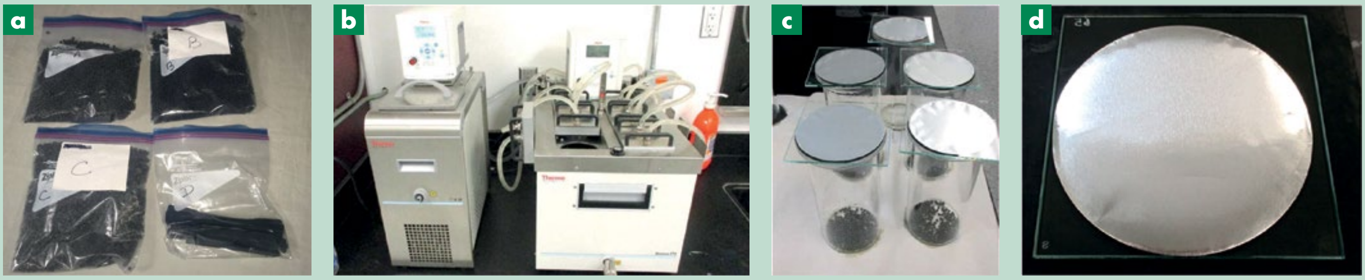
Fogging tests are carried out to measure the tendency of plastic or elastomeric materials to release volatile substances that can, in use, condense and collect on other surfaces. The test method typically used in the TPE industry is DIN 75201:2011.

There are two test methods, photometric and gravimetric. The gravimetric test used in this study involves the deposition of foreign material or residue on an aluminium foil surface.

Figure 3 shows the test material and apparatus. A TPE sample is placed in a beaker and covered with aluminium foil. After a conditioning, heating and cooling cycle, the weights of the TPE sample and the aluminium foil before and immediately after the test are compared. The differences in weights provide a measure of the process oil's volatility and its condensable constituents.

FIGURE 3

(a) TPE samples, **(b)** fogging apparatus, **(c)** material samples after exposure and **(d)** fogging foil after exposure.



Testing TPE compounds containing GTL oils

For this study, commercially produced TPE samples were collected from Shell Lubricants customers in North America. DIN 75201:2011 gravimetric fogging tests were carried out at the Intertek laboratory in Michigan, USA (see boxed text, Measuring fogging). This external laboratory was selected because it is approved by several car manufacturers for carrying out fogging testing for automobile interiors in North America.

Figure 3(a) shows solid and pellet TPE samples prepared by a customer for the fogging tests. These materials are typically used for floor- and trunk-mat applications by automotive manufacturers in North America. The samples for the fogging study were made using Shell Risella X 430 and commercially available competitors' oils composed of mid- and high-viscosity process oils. The formulations for producing the TPE samples included SEBS polymers, resins, filler, stabilisers and process oils. The only differences in the raw materials used to make the samples were in the process oils used.

The test results demonstrated that commercially produced TPE granulate samples using Shell Risella X 430 exhibited fogging of less than 2 mg, and less than 1 mg for some samples (Table 2). These TPE materials easily comply with manufacturers' criteria for use in automobile interiors. This study helped in achieving new technical approvals for the use of Shell Risella X 430 GTL oil in automotive interiors by TPE customers.

Conclusions

Through this study, the Shell Lubricants team has put in place a very precise benchmarking methodology for evaluating base oils and a relatively quick test method for understanding the expected fogging performance of the products. This method can also be used for quality control at storage facilities. In addition, Shell Lubricants now has a robust method for handling customer complaints and carrying out root-cause analysis.

From the supply chain perspective, the correlations are useful for qualifying Shell process oils. This is

TABLE 2

Fogging test results for TPE granulate samples using the DIN 75201 gravimetric method.

	TPE samples								
	Oil 1 100-006A	Oil 2 100-004D	Risella X 430 100-006C	Sample A Risella X 430	Sample B Risella X 430	Sample C	Sample D	Typical manufacturer requirement	TPE currently used for automotive interiors
Mean fogging (mg)	1.1	2.17	0.66	0.24	0.18	0.30	0.18	≤2.0	1.0–2.0
Control* (mg)	0.68	0.56	0.67	0.45	0.45	0.66	0.66		

**Control: Diisodecyl phthalate 0.65±0.25 mg (used for test equipment calibration)* relevant to those using GTL base oils and, more importantly, Group II paraffinic base oils to determine whether their products will meet the fogging criteria before they are supplied to TPE customers in various markets.

One of the first tests performed on commercially available, innovative TPE samples that used GTL base oil clearly demonstrated fogging characteristics 60% better than TPE materials using conventional paraffinic oils, thereby confirming the high potential of these GTL oils for such applications.

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Review:
Jason Brown, global technology manager, heavy-duty diesel engine oils

AUTHORS

Punith Veeralinga Shivaprasad is a product application specialist in the Shell Global Commercial Technology process oils team based in Houston, USA. He joined the Shell Global Commercial Technology team in 2007 and provides technology support to process oils customers including for data centres in North America. Punith has a PhD in civil engineering from University Visvesvaraya College of Engineering, India, and did postdoctoral research at Clemson University, USA.

Eduardo de Azevedo is a product application specialist in the Shell Global Commercial Technology process oils team based in Hamburg. He currently leads the Shell immersion cooling fluid research and development efforts for computer data centers and provides technology support to process oils customers for multiple applications. Eduardo has a degree in mechanical engineering, automation and systems from the Universidade São Francisco, Brazil.

Andree Hilker is a project leader and team leader for grease and industrial lubricants based at STCHa. He joined Shell in 2001 and works on the development of industrial lubricants such as transformer fluids, e-mobile fluids and process oils. Andree has a diploma in chemical engineering from the Hamburg University of Applied Sciences, Germany.

Andres Brosell is a product application specialist in the Shell Global Commercial Technology process oils team based in Germany. He has more than 20 years' experience in Shell Lubricants supply chain and retail. Currently, Andres provides technical support to the main polymer and rubber customers in Europe and other process oils customers. Andres is a mechanical engineer with a degree from Technische Universität Berlin, Germany.