

DIESEL EMISSIONS: A BREATH OF FRESH AIR Part 1 of 2

By Steven Lumley, Technical Manager

INTRODUCTION

As the world moves to adopt more planet-friendly strategies, air pollution is a key focus area for engine-manufacturers and operators. In this *Technical Bulletin* - the first of a two part series - global diesel engine emission standards are discussed, along with a range of techniques that reduce emissions, which ones are most effective, and why.



In a nutshell, global warming is not something that is going to happen in the future, it's happening right now, and it is threatening our health, our economy, our natural resources and the future of generations to come.

Barely a week goes by where climate change, global warming, and the quality of air and airborne pollutants are not in the news, and quite often vehicle emissions are the primary focus of the headline.

It is well known that one of the main causes of climate change is global warming, which in turn is caused by the greenhouse effect, and the greenhouse effect in turn is caused by the atmospheric accumulation of greenhouse gases like carbon dioxide, methane, nitrous oxide, ozone and water vapour.

The greenhouse effect is actually a natural process that plays a major role in shaping the earth's climate, but since the Industrial Revolution began in the latter half of the 18th century, human activities have contributed substantially to climate change by adding more heat-trapping greenhouse gases into the atmosphere. These greenhouse gas emissions have increased the greenhouse effect and caused the earth's surface temperature to rise.



So, what's all the fuss about? It's going to get a bit warmer, right? Is that really such a problem? Well, it's a bit more serious than just a couple of extra hot days in summer. Increased global temperatures result in glacier retreat, ocean levels rising, changes in weather patterns and the timing of seasonal events, like pollination and blooming of flowers and plants, which will result in species that depend on one another becoming out of sync. Whole ecosystems will change along with migration patterns as animals migrate to where the optimal food and temperature is. Other side effects are higher wildlife extinction rates, ocean acidification due to carbon dioxide dissolving in the sea and the resultant destruction of coral reefs and various marine food chains. There will also be an increase in the occurrence of extreme weather phenomena, changes in agricultural productivity as well as the socio-economic effects, which are numerous.



AIR POLLUTION AND DIESEL ENGINES

Greenhouse gases from human activities are believed to be the most significant drivers of observed climate change since the mid-20th century, and 80% of human-related greenhouse emissions come from industrial processes and, more relevantly, the burning of fossil fuels.

One of the main causes of environmental pollution and poor air quality is the release of unburned hydrocarbon molecules, nitrogen oxide, carbon monoxide and particulate matter during the combustion of petroleum products like diesel.

Every day, millions of diesel-powered vehicles busily move consumer goods and raw materials from ports, distribution centres and rail yards to stores and industrial facilities throughout the world. Diesel powered ships, trains and trucks play a pivotal role in local, regional and global commerce. Most freight trains and ocean-going ships are also powered by diesel, as are the overwhelming majority of on- and offroad trucks. Diesel engines are not only fundamental in mobile vehicles and machinery but are also widely employed in stationary applications such as pipeline pumps, electric and water plants, industrial machinery, mining tools, factories and oil fields. Unmatched in their reliability, durability and fuel efficiency, diesel engines play a fundamental role in allowing economic development of human societies. However, in spite of these undeniable benefits, diesel engines are also associated with a number of environmental and health-related issues.

DIESEL EMISSION REGULATIONS

Since the introduction of the first diesel emission standards in the 1970s by the Environmental Protection Agency (EPA) in the USA, many policies have been imposed worldwide to reduce the negative effects of diesel engine emissions on human health and the environment. The standards that followed were to become one of the main driving forces behind the development of the diesel engine in the years to come.



While these emission regulations are good for the environment, they present very real challenges to engine manufacturers, lubricant formulators and fuel suppliers as they work together to develop products that can deliver high performance while meeting strict emissions mandates.

To successfully navigate the road to zero harmful emissions, we must understand the emissions we are trying to limit, the standards that govern them, the technologies we employ to meet these laws and, finally, the effect they will have on the selection of the fuels and lubricants that will feed this new generation of cleaner engines.

In this first instalment of a two-part *Technical Bulletin*, we focus on the first three aspects: the emissions, the standards and finally the technologies that support the mitigation of these emissions.



I would like to apologies in advance for the eyewatering array of acronyms, abbreviations and chemical symbols used in these *Technical Bulletins*, all of which are entirely necessary and listed below:

Commonly-used abbreviations and symbols				
Abbreviation	Definition	Symbol	Name	
ASC	Ammonia slip catalyst	NH ₃	Ammonia	
DEF	Diesel exhaust fluid	CO2	Carbon dioxide	
DOC	Diesel oxidation catalyst	СО	Carbon monoxide	
DPF	Diesel particulate filter	CH ₄	Methane	
EGR	Exhaust gas recirculation	NO	Nitric oxide	
EPA	Environmental Protection Agency	NO ₂	Nitrogen dioxide	
EURO	European emissions standards	N ₂	Nitrogen gas	
НС	Hydrocarbons	NOx	Nitrogen oxides	
LNC	Lean NOx catalyst	SO ₂	Sulphur dioxide	
NAC	NOx adsorber catalysts	SO ³	Sulphur trioxide	
РАН	Polycyclic aromatic hydrocarbon			
PM	Particulate matter]		
SCR	Selective catalytic reduction]		
SOF	Soluble Organic Fraction]		
WHO	World Health Organisation			

THE EXHAUST GASES

Every breath you take, you inhale and exhale air. The volume of one breath, known as the tidal volume, can vary considerably from person to person depending on a number of factors such as age, activity level and health, but it is widely accepted that an average value for a healthy adult is around 0.5 litres of air. The average breathing frequency or respiratory rate in a healthy adult at rest is +/- 16 breaths per minute which equates to 8 409 600 breaths per year. At 0.5 litres per breath, that means that an average healthy adult breathes over four million litres of air a year. That's a lot of air to breathe in without knowing what your lungs are gulping down, so let's explore what is in every breath you take.

Air is a mixture of water vapour and some solid particles, but mainly different gases - namely nitrogen (78%), oxygen (21%) with trace amounts of other natural gases - as well as a cocktail of emissions from various sources, including diesel engines.

Diesel exhaust exposure is widespread in the modern world and, consequently, diesel engines are considered one of the largest contributors to environmental pollution caused by exhaust emissions, which have been classified as a potential carcinogen by various international environmental protection and health agencies like the World Health Organisation (WHO). Diesel fuel is a mixture of hydrocarbons which, during an ideal combustion process, would produce only carbon dioxide (CO_2) and water vapor. Unfortunately, exhaust from diesel engines brings a complex mixture of soot and gases to our roadways and cities. Health concerns about diesel exhaust relate not only to cancer, but also to other health problems such as lung and heart diseases.

The four main pollutant emissions generated by diesel engines are carbon monoxide (CO), hydrocarbons (HC), particulate matter (PM) and nitrogen oxides (NOx).

NOx is a general term referring mainly to nitric oxide (NO) and Nitrogen Dioxide (NO₂) gas - a family of poisonous and highly reactive compounds.

When broken down, diesel exhaust is made up of two main parts: gases and PM (otherwise known as soot). Each of these, in turn, is made up of many more different compounds.

The gas portion of diesel exhaust is mostly CO_2 , CO, NOx, sulphur dioxides (SO_2), and HCs, including polycyclic aromatic



hydrocarbons (PAHs). CO and HCs are generated in the exhaust as the result of incomplete combustion of fuel, but exhaust hydrocarbons can also come from the lubricant.



 SO_2 is generated from the sulphur present in diesel fuel so the concentration of SO_2 in the exhaust gas depends on the sulphur content of the fuel. Oxidation of SO_2 produces sulphur trioxide (SO_3) which is the precursor of sulphuric acid which, in turn, is responsible for the sulphate particulate emissions and acid rain.

Out of the various compounds produced, NOx gas and PM are typically portrayed as the two bad boys of diesel exhaust and have proven to be the most challenging of regulated pollutants when it comes to diesel engine design that is compliant with emission standards.

NOx gases are generated from nitrogen and oxygen under the high pressures and temperature conditions in the engine cylinders. Diesel engines run both hotter and at higher pressures than their petrol counterparts and subsequently produce more NOx gases.

Diesel emissions of NOx contribute to the formation of ground level ozone, which irritates the respiratory system, causing coughing, choking, and reduced lung capacity. Ground level ozone pollution, formed when nitrogen oxides and hydrocarbon emissions combine in the presence of sunlight, presents a hazard for both healthy adults and individuals suffering from respiratory problems.

SOOT

Perhaps the most controversial of all regulated emissions is the soot portion of diesel exhaust, which is made up of particles such as carbon, organic materials like PAHs, and traces of metallic compounds. PM or soot is created during the incomplete combustion of diesel fuel. Its composition often comprises hundreds of chemical elements, including sulphates, ammonium, nitrates, elemental carbon, condensed organic compounds and heavy metals such as arsenic, selenium, cadmium and zinc. Though just a fraction of the width of a human hair, particulate matter varies in size from coarse particulates (less than 10 microns in diameter) to fine particulates (less than 2.5 microns) to ultrafine particulates (less than 0.1 microns).



Ultrafine particulates, which are small enough to penetrate the cells of the lungs, make up 80-95% of diesel soot pollution. When one inhales these microscopic particulates, they can become embedded in your lungs and impair their function. As a result of this, diesel PM was officially classified as carcinogenic by the WHO in 2012.

THE EMISSION STANDARDS

Emission standards are legal requirements governing air pollutants released into the atmosphere.

Emission standards set quantitative limits on the permissible amount of specific air pollutants that may be released from specific sources over specific timeframes. They are generally designed to achieve air quality standards and to protect human life. Different regions and countries have different standards for engine emissions.

In order to conform to these emission standards, engines need to produce cleaner exhaust emissions by producing less harmful by-products.



There are largely four main sets of standards: United States (TIER), Japanese (CEC - Central Environment Council), India (BHARAT) and European (EURO) with various markets outside of these regions mostly using these as their base. The European standards are the most widely-followed vehicle emission guidelines in the world, and as such South Africa has elected to follow this standard- although in a somewhat lagged fashion.

Although emissions regulations date back to 1970, the first EU-wide standard – known as Euro I – wasn't introduced until 1992. Since then, there has been a series of Euro emissions standards, leading to the current Euro VI, introduced in September 2015.

The aim of Euro emissions standards is to reduce the levels of harmful exhaust emissions, primarily NOx, CO, HC, PM and additionally ammonia (NH_3) emissions in the case of Euro VI-compliant engines.

Every evolution of emissions standards leads to more advanced and efficient emission control technologies. Table 1 below summarises the progressions of technologies that meet increasingly stringent emissions standards for diesel engines in heavy duty vehicles.

THE TECHNOLOGIES

Now that we have an understanding of the legal requirements, let's look at the different technologies used to attain these

emission standards and air quality requirements.

Diesel emission control systems can be broadly broken down into two categories: (1) in-cylinder strategies and (2) aftertreatment systems, and the selection and configuration of technologies utilised is dependent on the engine manufacturer and machine application.

IN-CYLINDER

As emissions standards tightened, more advanced in-cylinder control strategies were applied, that included energy-efficient cylinder heads and valve train systems, closer piston-to-bore clearances and modified ring positioning to assist in lower emissions output.

In the last two decades, the design of diesel engines has progressed rapidly, most significantly in the areas of fuel injection systems, electronic controls and air handling through the use of variable-geometry turbochargers.

Many of the latest generation engines have common-rail or unit-injector designs, a common feature which produces far higher injection pressure than the old mechanical systems, coupled with precise electronic control of injection timing. Other in-cylinder techniques also included the adoption of the Miller cycle, diesel water injection and homogenous charge compression ignition (HCCI). These various techniques help achieve a more complete combustion and reduce particulate formation and fuel consumption.

Table 1			
Emission standards	Technology		
Euro II and Euro III	 Emissions are controlled via air and fuel mixing strategies No aftertreatment system 		
Euro IV	 NOx control through vanadium-based, open-loop selective catalytic reduction (SCR) system or exhaust gas recirculation (EGR) PM control through the use of a diesel oxidation catalyst (DOC) in some engines. Aftertreatment system comprising DOC and SCR 		
Euro V	 Same technology as Euro IV with combinations of EGR and SCR Small changes to NOx limits which are met with minimum hardware changes – mainly engine calibrations Aftertreatment system comprising DOC and SCR 		
Euro VI	 NOx control through zeolite-based, closed-loop SCR systems or a combination of SCR and EGR. Ammonia slip catalyst (ASC) for ammonia control as this is a by-product of SCR reactions. PM control through DOC and diesel particulate filters (DPF) Aftertreatment system is composed of DOC, DPF, SCR and ASC. 		



Air handling strategies have been focused on the use of variable geometry turbochargers to provide the right amount of air under specific engine operational conditions. Increasing the pressure of the air entering the chamber increases the air density and allows for better combustion in the brief time available. Tuning these parameters minimises production of both PM and NOx.

Another popular in-cylinder technology for NOx control is exhaust gas recirculation (EGR). An EGR system recirculates a portion of cooled exhaust gas back to the engine's cylinder, which reduces both peak combustion temperature and temperature-dependent NOx formation. EGR is the most effective and commonly-used technology for in-cylinder NOx reduction in diesel engines. The EGR fraction, the share of recirculated exhaust gas in the total intake charge, is tailored to each engine operating condition and can vary from 0% to 40% of the incoming air.



Since EGR reduces the available oxygen in the cylinder, the production of PM increases when EGR is applied. NOx and PM are traded against each other in many aspects of diesel engine design. Very high temperatures in the combustion chamber help reduce the emission of soot but produce higher levels of NOx gases. Lowering the peak temperature in the combustion chamber reduces the amount of NOx produced but increases the likelihood of soot formation.

AFTERTREATMENT SYSTEMS

An aftertreatment system treats postcombustion exhaust gases prior to tailpipe emission. In other words, it is a device that cleans exhaust gases to ensure the engines meet emission regulations.

Within the aftertreatment category there are a further two classes – filters and catalysts

CATALYSTS

In chemistry, a catalyst is a substance that causes or accelerates a chemical reaction without itself being affected. Catalysts participate in the reactions but are neither reactants nor products of the reaction they catalyse.

A humorous and simplified example of this process, as explained to me by a tenured chemistry professor, is as follows: when a woman asks you if she looks fat in a particular piece of clothing, irrespective of your answer you will become a catalyst in a reaction. You yourself will remain unchanged but the reaction, irrespective of your answer, will take place for better or for worse.

A catalytic convertor in the broad sense of the term is a device that uses a catalyst to reduce the toxicity of emissions from an internal combustion engine either through the process of oxidation or reduction.

The first diesel emission catalysts, introduced in the 1970s for underground mining applications, were simple oxidation catalysts designed for the conversion of CO and HC but as the years rolled on and requirements intensified, more specialised catalysts were developed as can be seen in the table below:

Diesel engine catalysts				
Catalyst technology	Reaction type	Target emissions		
Diesel oxidation catalyst	Oxidation	CO, HC, PM- (SOF)		
Urea-SCR catalyst	Selective catalytic reduction by ammonia	NOx		
Ammonia slip catalyst	Selective oxidation of the ammonia slip	NH₃		
Hydrocarbon-SCR or Lean NOx catalyst	Selective catalytic reduction by hydrocarbons (HC-SCR)	NOx, CO, HC		
NOx adsorber catalyst or Lean NOx Trap	Adsorption (trapping) of NOx from lean exhaust, followed by release and catalytic reduction under rich conditions	NOx, CO, HC		



FILTERS

A filter does exactly as its name implies - that is, it physically filters out something. To be more specific, a filter is a porous device for removing impurities or solid particles from a liquid or - more relevantly - gas, passed through it.

Ultimately, using a combination of physical mechanisms and chemical reactions these systems can, under the right conditions, achieve near complete removal of particulates and harmful gases. Let's take a closer look at how these devices work.

DIESEL PARTICULATE FILTER (DPF)

One of the major combustion by-products of burning diesel is soot. Soot comprises impure carbon particles resulting from the incomplete combustion of diesel. A DPF is a device designed to remove soot from diesel engine exhaust gases.

DPFs operate by trapping soot particles from the engine exhaust, preventing them from reaching the environment. Unlike catalytic converters which are designed to reduce gasphase emissions flowing through the catalyst, the particulate filter is designed to trap and retain the solid particles until the particles can be oxidised or burned in the DPF itself, through a process called regeneration.

The most common DPFs in widespread use are cellular ceramic honeycomb filters with channels that are plugged at alternating ends. The ends of the filter, plugged in a checkerboard pattern, force the soot-containing exhaust to flow through the porous filter walls. While the exhaust gas can flow through the walls, the soot particles are trapped within the filter pores and in a layer on top of the channel walls. Soot particles are captured and retained in the DPF through a combination of depth filtration inside the filter pores and surface filtration along the channel walls. Given the small pore size and design of the honeycomb filters, DPFs can achieve a particle trapping efficiency of 99% or greater.



The honeycomb design provides a large filtration area while minimising pressure losses, and has become the standard, so-called wall-flow filter for most diesel exhaust filtration applications. Ceramic materials are widely used for particulate filters, given their good thermal durability, with the most common ceramic materials being cordierite, silicon carbide, and aluminium titanate.

REGENERATION

However, over time the trapped soot accumulated in the filter, if not removed, increases backpressure. High backpressure caused by overloading the DPF can compromise engine performance, increase fuel consumption and eventually lead to DPF failure. To prevent this, the DPF must periodically be regenerated to remove soot through a process that burns off (oxidises) the soot.

There are two broad categories of the regeneration processes, (1) active and (2) passive, although most commercial applications use some combination of the two.

Active regeneration requires the addition of heat to the exhaust to increase the temperature of the soot to the point at which it will oxidise in the presence of excess oxygen in the exhaust. The combustion of soot in oxygen typically requires temperatures in excess of 550 °C. Since these high temperatures generally do not occur in the exhaust / DPF during normal engine operation, several strategies are used to actively increase the exhaust temperature. Active regeneration systems may include the use of a diesel burner to directly heat the exhaust entering the DPF or the use of a diesel oxidation catalyst (DOC) to oxidise diesel fuel over the catalyst as a means for increasing the DPF temperature. Use of the DOC also requires excess diesel fuel in the exhaust, which may be accomplished through a fuel injector (hydrocarbon doser) mounted in the exhaust upstream of the DOC, or through late in-cylinder post injection strategies. Other forms of active regeneration include the use of electrical heating elements, microwaves, or plasma burners. The use of a DOC in combination with some form of exhaust fuel dosing is, however, the most common active regeneration strategy currently used for on- and off-highway applications.

Passive regeneration, as the name implies, does not require additional energy to carry out the regeneration process. Instead, this strategy relies on the oxidation of soot in the presence of NO_2 , which can occur at much lower temperatures. In order to achieve this, a passive system uses a catalyst,



which contains precious metals like platinum, to covert NO in the exhaust to NO_2 , which reduces the ignition temperature of the soot below 550°C in order to start the regeneration process. In some cases, the catalyst coating is applied directly to the DPF, or an upstream oxidation catalyst may also be used. Many commercial systems utilise a combination of a DOC and Catalysed DPF (C-DPF).

CATALYTIC CONVERTERS

DIESEL OXIDATION CATALYST

CO, as well as gas and liquid-phase HC emissions, result from the incomplete combustion of diesel. Diesel oxidation catalysts (DOCs) - historically the first type of diesel catalyst - are highly effective devices that reduce these emissions by 80% or more from diesel.

In most applications, a DOC consists of a stainless-steel canister that contains a honeycomb structure called a substrate, which is made up of thousands of small channels. Each channel is coated with a highly porous layer containing precious metal catalysts such as platinum or palladium. As exhaust gas travels down the channel, CO and HCs react with oxygen within the porous catalyst layer to form CO_2 and water vapor.



The DOC also protects the DPF. Hydrocarbon liquids or vapor can interfere with the DPF's ability to trap and remove particulate matter, so engine manufacturers often route the exhaust through the DOC first, then into the DPF.

SELECTIVE CATALYTIC REDUCTION (SCR)

As mentioned, NOx is a general term referring to NO and NO_2 gases. These gases are generated from nitrogen and oxygen under the high pressures and temperature combustion conditions.

NOx gases can however be successfully converted to N2 and water using SCR – one of the most effective technologies available today. SCR systems are classified into two groups, Urea-SCR and Hydrocarbon-SCR - the latter is most commonly known as a lean NOx catalyst (LNC).

UREA-SCR

Urea-SCR uses a reductant known as a diesel exhaust fluid (DEF), which is injected into the exhaust gas to help reduce NOx emissions, over a catalyst. Aqueous urea has been the reductant of choice in SCR systems for mobile diesel engines, but this fluid will be covered in more detail later in the second part of this *Technical Bulletin*.



The urea-SCR system uses a metallic (e.g. vanadium-based) or ceramic (e.g. zeolite-based) wash-coated catalysed substrate and the chemical reductant - usually aqueous urea - to convert nitrogen oxides to molecular nitrogen and oxygen in oxygen-rich exhaust streams like those encountered with diesel engines. Upon thermal decomposition in the exhaust, urea decomposes to ammonia (NH_3) which serves as the reductant. As exhaust and reductant pass over the SCR catalyst, chemical reactions occur that reduce NOx emissions to nitrogen and water. Urea-SCR catalysts are often combined with a particulate filter for combined PM and NOx reduction.

AMMONIA SLIP CATALYST (ASC)

The reaction between NOx and NH_3 is never perfect and, even though SCR systems can achieve efficiency rates often higher than 95%, there is sometimes a waste stream of un-reacted NH_3 that goes into the atmosphere. This excess NH_3 is known as NH_3 slip.

For this reason, SCR systems may also include an oxidation catalyst downstream of the SCR catalyst to control ammonia slip. This catalyst is aptly referred to as the ammonia slip catalyst (ASC).



The task of the ASC is the selective oxidation of the ammonia slip to harmless N2 and water - usually over a platinum / aluminium oxide base. The ACS becomes increasingly important in SCR systems designed for high NOx conversion efficiency, especially in the higher-rated Euro engines.

LEAN NOX CATALYST (LNC)

Although the urea-SCR catalyst is widely recognised as a promising de-NOx technology, it has some drawbacks such as NH_3 slip, the additional process of urea injection, storage space limitations and the low freezing point of the aqueous urea-based reductant. In an attempt to overcome the inherent shortcomings of existing urea-SCR catalysts, hydrocarbons have been considered as alternative reducing agents for the SCR process.

Catalytic reduction of NOx with hydrocarbons is an attractive NOx abatement method under lean burn conditions, especially when the diesel exhaust is used as a reducing agent.

In this process the system injects a small amount of diesel fuel or other hydrocarbon reductant into the exhaust upstream of the catalyst. The fuel or hydrocarbon reductant serves as a reducing agent for the catalytic conversion of NOx to N2.

A lean NOx catalyst often includes a highly-ordered porous channel structure made of zeolite, along with either a

precious metal or base metal catalyst. The zeolites provide microscopic sites that are fuel/hydrocarbon rich where reduction reactions can take place.

NOX ADSORBER CATALYSTS (NAC)

NOx adsorber catalysts (NAC), also referred to as lean NOx traps (LNT), provide another catalytic pathway for reducing NOx in an oxygen-rich exhaust stream. They are known as adsorbers or traps because part of their function also includes trapping the NOx in the form of a metal nitrate during lean operation of the engine.

Typically, NACs consist of precious metals (e.g. platinum or palladium), a storage element (e.g. barium hydroxide or barium carbonate) and a high surface area support material.

Under lean air to fuel operation, NOx reacts to form NO₂ over the precious metal catalyst, followed by reaction with the barium compound to form barium nitrate. Following a defined amount of lean operation, the trapping function will become saturated and must be regenerated. This is commonly done by operating the engine in a fuel-rich mode for a brief period of time to facilitate the conversion of the barium compound back to its original state and giving up NOx in the form of N₂ or NH₃ gas – the latter being an unwanted emission from the process. However, NACs can be combined with SCR catalyst to trap NH₃ and further reduce NOx via a selective catalytic reduction reaction to N₂.



So, let's put this symphony of technologies together into something we can visualise. The below image is an example of a typical Euro VI / Tier 4 configuration.



Be sure to look out for the next instalment in this two-part Technical Bulletin, where we will explore how all these emission control strategies will affect the selection of fuels and lubricants that will have to feed the changing appetite of the diesel engine.

About the writer...



Steven Lara-Lee Lumley is in charge of technical development and training for WearCheck. She holds an N6 mechanical engineering diploma (HND N6) as well as Honeywell aerospace and ICML III accreditations.

Steven joined WearCheck in 2008 as a diagnostician and worked her way up to the position of senior diagnostician, during which time she diagnosed her millionth used oil sample in addition to running oil analysis training courses for customers in several countries. In 2015, Steven was promoted to the position of Technical Manager.

Planet-friendly option

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Head Office KwaZulu-Natal No. 4 The Terrace, Westway Office Park, Westville, KZN, 3629 PO Box 15108. Westmead, KZN, 3608 t +27 31 700 5460 e support@wearcheck.co.za w www.wearcheck.co.za

> **Gauteng Office** 30 Electron Avenue, Isando, Gauteng, 1600 t +27 11 392 6322 e support@wearcheck.co.za



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