The Particulars of Diesel Particle Emissions

New research looks at particle numbers and size as well as mass

By Imad A. Khalek, Ph.D.

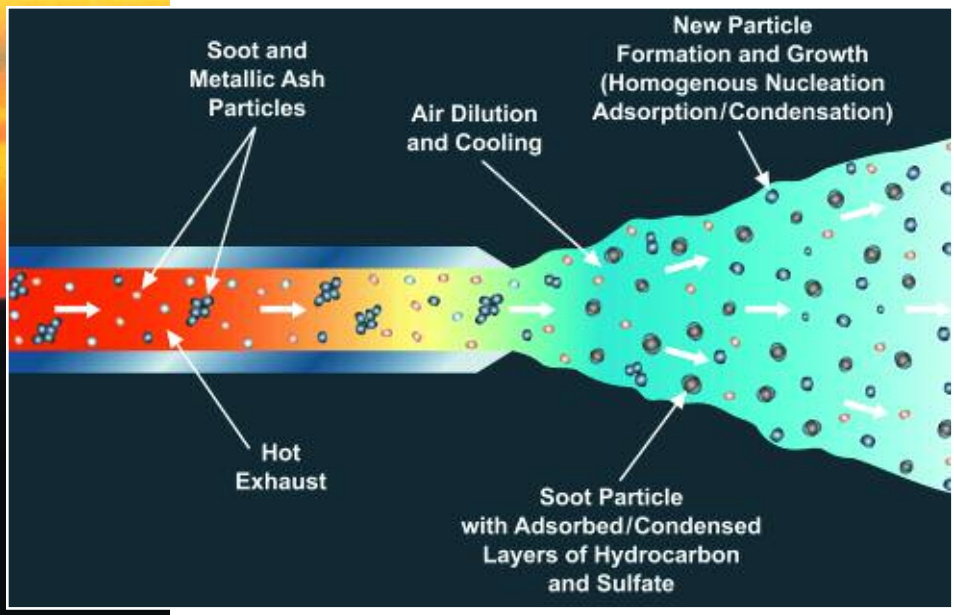
Diesel engines have long been the powerplant of choice for heavy-duty applications requiring high horsepower and torque, coupled with durability and fuel efficiency. While most attention usually concerns emissions regulations for gasoline-powered automobiles and light trucks that account for the great majority of the nation's vehicle fleet, on-highway diesel engine emisssions have also been significantly regulated, and additional regulations are required by the Environmental Protection Agency (EPA) beginning in 2007. The new standards require not only a 95-percent reduction in gaseous emissions such as the oxides of nitrogen by 2010, but also require a 90-percent reduction in particulate matter (PM) by 2007.

Diesel engines are a significant source of PM emissions. PM contributes to aesthetic and environmental concerns when particles are emitted as smoke or soot in high concentrations, but it has also been associated with potential health issues related to particle inhalation.

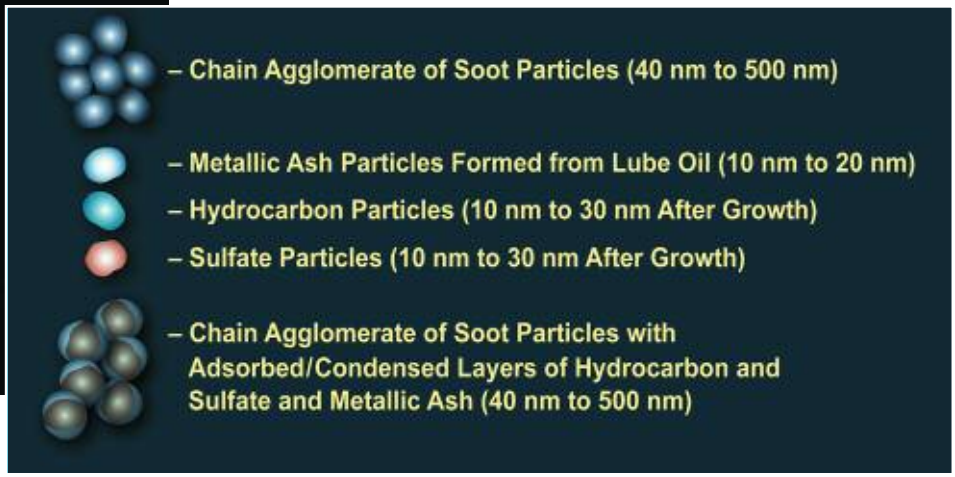
U.S. on-highway diesel engine particle emission regulations have grown progressively more stringent since 1988. Amounts are expressed as grams of particulate matter per horsepower-hour.

PM emission regulations are currently based on the mass collected from a dilute exhaust stream on a pre-weighed filter kept below 52 degrees Celsius. For 2007-level engines, the EPA has limited the filter face temperature range to 42–52 °C, among other changes, but the focus is still on PM mass. For more than 70 years scientists have been investigating the challenging task of providing better understanding of airborne particles, and their progress now allows more complete measurements of diesel particle emissions than collection of mass on a filter. In recent years, there is a growing interest in particle number and size emission characterization worldwide.

Engineers at Southwest Research Institute (SwRI) have conducted research activities to better understand and reduce PM emissions from diesel engines.



Atmospheric dilution and cooling of hot diesel exhaust may trigger the nucleation of new particles such as semi-volatile hydrocarbons and sulfuric acid.

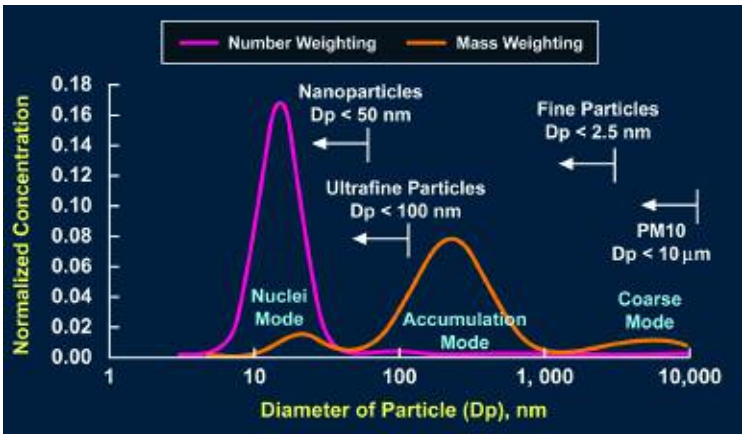


A general characterization of diesel exhaust particle size and composition is shown here. Actual particle composition is a complex mixture of hundreds of different species.

Particle Emission Regulations

In 2007, on-highway, heavy-duty diesel engines must meet a new stringent PM emission level of 0.01 gram per horsepower-hour (g/hp-hr), a 90-percent reduction from the current level, as measured in an engine laboratory on a specified transient cycle, where engine speeds and loads vary to simulate the changing speeds and grades typical of on-road driving. Furthermore, for 2007 and beyond, on-highway diesel engines are also required to meet the new PM standard on the road, under a range of operating conditions. This new PM emission regulation poses many challenges to engine manufacturers to better understand particle emissions to meet the standard while maintaining the durability and fuel efficiency of the diesel engine.

In addition to regulating PM mass emissions, health-driven concerns have increased the attention given to ultrafine particles, defined as smaller than 100 nanometers (nm) in diameter (a nanometer is a billionth of a meter); and nanoparticles, which are smaller than 50 nm in diameter. A debate has started about what metric and physical characteristics of PM emissions are more important for minimizing human health problems.



The size distribution of typical diesel exhaust particles ranges from nanoscale particles up to coarse soot particles.

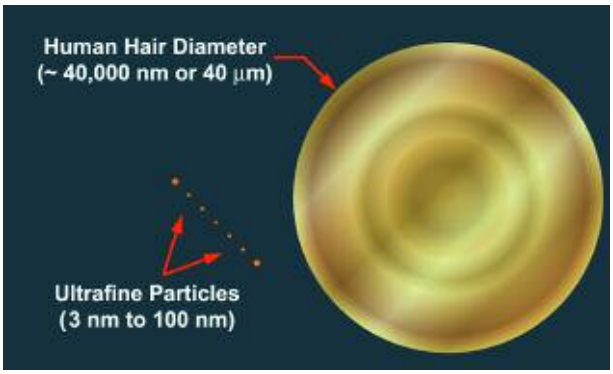
Composition and Physical Characteristics of Particulate Matter

Diesel PM is mainly composed of elemental carbon (soot), ash and volatile compounds derived from unburned and partially burned fuel and lubricating oil and sulfate. Soot particles are formed in the combustion chamber, while the

volatile compounds transform from gas phase to particle phase as the exhaust cools and dilutes with ambient air after exiting the engine exhaust pipe into the atmosphere.

Soot particles emitted from diesel engines are chain agglomerates in the size range of 40–500 nm in diameter. These chain agglomerates consist of small particles in the size range between 10–30 nm in diameter that are generated and coagulated inside the combustion chamber of a diesel engine to form larger particles. Other particles can be either a stand-alone metallic ash, derived from the lubricating oil, fuel containing additives, or metallic ash that has joined the soot particles. As the combustion gases are expelled, the dilution process may also produce sulfuric acid particles, hydrocarbon particles or a combination of sulfuric acid nuclei coated with adsorbed layers of hydrocarbons. Sulfuric acid and hydrocarbon species may also adsorb or condense onto the soot chain agglomerates instead of forming new, stand-alone particles.

All particles emitted from diesel engines are in the respirable size range. The greatest numbers of particles tend to concentrate in the "ultrafine" range of 3–100 nm in diameter, which is 1,000 to 10,000 times smaller than the average human hair. The ultrafine range usually contains soot particles larger than 30 nm in diameter, and volatile nuclei mode particles smaller than 30 nm that form as a result of dilution and cooling of hot exhaust.



Ultrafine particles (shown here in comparison to the diameter of a human hair) account for the greatest numbers of particles emitted from diesel exhaust.

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The greatest mass of particles, on the other hand, reside in the accumulation mode with a diameter from 100–300 nm. These particles are soot chain agglomerates that are generated by the combustion process. The coarse mode particles are larger than 2,500 nm in diameter, and are generated by the break-up of soot from the internal walls of the combustion chamber and the exhaust system. These coarse particles also contribute slightly to the mass.

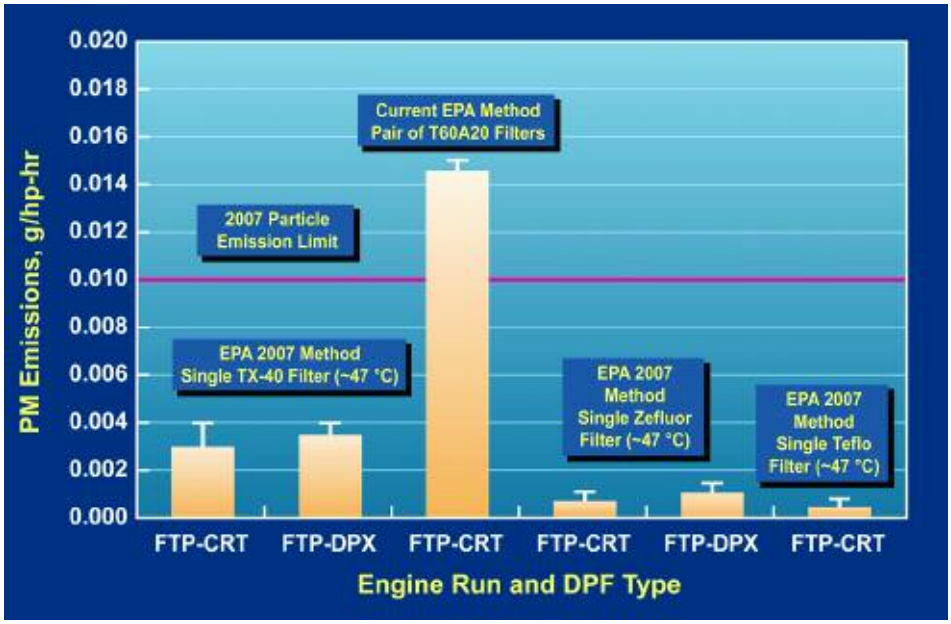
2007 Level Diesel Particulate Measurement Research

To meet the EPA PM emissions limits for 2007 and beyond, diesel engine manufacturers recognize the need to use a catalyzed diesel particle filter (DPF) in the exhaust. The DPF is mainly made of ceramic cordierite or silicon carbide material with a catalyst coating such as platinum. The use of a catalyzed DPF to meet the 2007 standard changes PM emissions, not only in mass but also in composition.

SwRI is conducting a diesel particulate measurement research project for the Coordinating Research Council, Department of Energy (DOE), National Renewable Energy Laboratory, Engine Manufacturers Association, EPA and California Air Resources Board. The objectives are to improve particle mass emission measurement methodology that uses filter media for particle collection, and to determine whether using the catalyzed DPF technology causes composition changes to the low levels of diesel exhaust that remain.

SwRI has shown that soot, or elemental carbon particles, are virtually absent from the exhaust of a diesel engine equipped with a wall-flow CRT-DPF. SwRI also showed that by using thin Teflon® membrane filter media to collect the remaining PM, the PM emissions were at 90 to 95 percent below the 2007 standard. The Teflon membrane filter mainly collects particles or aerosol droplets during filter collection, while other filter media used in the past may collect, or adsorb, gas-phase material that gives an erroneous increase in PM emissions.

While the DPF significantly reduces particle mass emission, a high number of nanoparticles (3 nm to 30 nm) still are emitted downstream of the CRT-DPF, particularly at exhaust temperatures greater than 400 °C. This is mainly related to the nucleation of sulfuric acid droplets originating from sulfur in fuel and oil. Sulfuric acid formation occurs due to the reaction between SO_3 and H_2O. While H_2O is a typical product of combustion, the platinum catalyst at the surface of the DPF promotes the oxidation of SO_2 to SO_3 that otherwise exists at much lower concentration than



The choice of filter media used for particle collection can have a large influence on measured particle emissions downstream of a diesel particle filter.

SO_2. The nanoparticle number count characteristics are complex and depend on catalyst formulation, exhaust temperature, engine load, dilution temperature, dilution ratio, dilution rate, and perhaps other parameters not yet investigated, thus more research is needed to fully understand exhaust nanoparticles. In the real world, people are typically exposed to a variety of dilution parameters and to different concentrations of particle number, mass and size distributions. It depends on whether one is driving behind a vehicle in an urban low-speed zone or cruising on the highway, living near a roadway or in an urban area, or whether one resides in cold Minnesota or hot Texas. Understanding the influence of dilution conditions on particle emissions will help in quantifying the effects of particle emissions on human health.

SwRI recently showed that the dynamic of nanoparticle formation and growth can be changed by varying the dilution parameters, such as the amount of air dilution and its mixing time with engine exhaust. One can report high number-emission and low mass-emission, or vice versa, by selecting different combinations of dilution parameters for the PM measurement process. Such ground-breaking information is important to health studies,
PM emission research and discussions related to developing more refined PM regulations that may require more research to better understand the link betweeen laboratory and real-world particle measurement.

Conclusion

With the implementation of the DPF in the exhaust stream of a diesel engine, a significant reduction of PM mass emission occurs, particularly relative to carbon particles or soot. The measurement method used to quantify particle emissions from engines equipped with diesel particle filters requires additional investigation to ensure accuracy at the low measurement levels of trap-equipped exhaust. In addition, as particle measurement techniques are developed, more thorough measurements are possible, thus opening the door for more complete understanding of emissions and ambient aerosol levels. SwRI is developing world-class capabilities to investigate all of these areas.v

Comments about this article? Contact Khalek at (210) 522-2536 or imad.khalek@swri.org. To discuss this article see www.swri.org/forums.

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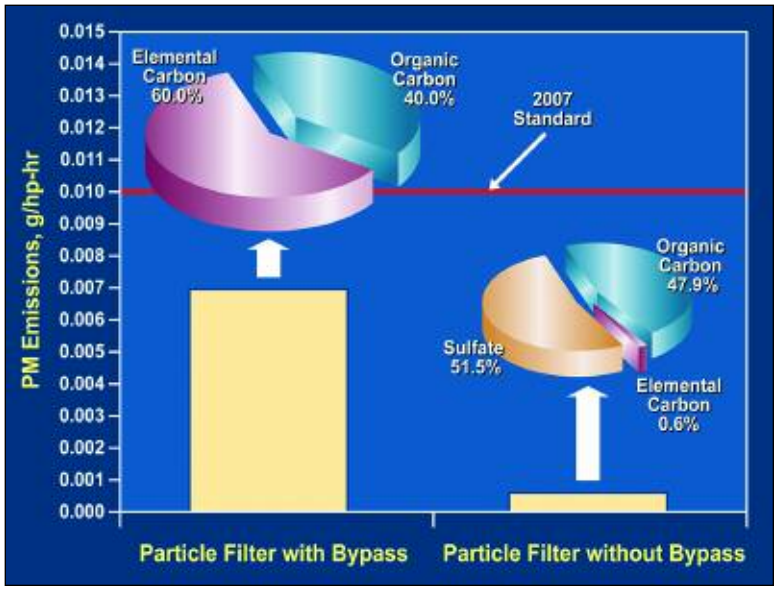

Under 2007 regulations elemental carbon, or soot, accounts for a very small fraction of particulate matter compared to organic carbon particles and sulfates derived from lube oil and sulfur in fuel. Particle composition, under current diesel engine technology or similar, is dominated by elemental carbon.
Note: "Particle Filter with Bypass" means that a small portion of the exhaust remained unfiltered. "Particle Filter without Bypass" means that the whole exhaust is filtered.