INVESTIGATION OF CARBON NANOTUBE AND ZINC OXIDE AS ADDITIVE FOR ENHANCED LUBRICANT PERFORMANCE

RAMEISH RAO S/O SUBARMANIYAN

Report submitted in partial fulfillment of the requirements
for the award of Bachelor of Mechanical Engineering with Automotive Engineering

Faculty of Mechanical Engineering
UNIVERSITI MALAYSIA PAHANG

JUNE 2012

ABSTRACT

This project reports on the use of carbon nanotubes and zinc oxide as additives in order to increase the operational characteristics of conventional lubricants. The objective of this project is to investigate the thermo-physical and tribological properties of conventional lubricants dispersed with nanoparticles in order to improve the operational characteristics of the nanolubricant thus reduce friction and wear of the system. In this study, the tested lubricants are prepared by dispersing nanoparticles into base lubricant at five different concentrations as 0.5 % vol, 1.0 % vol, 1.5 % vol, 2.0 % and 2.5 % vol, have their properties tested and be compared against the standard lubricants. Experimental results shown that the thermal conductivities and flash points of the base lubricants dispersed with both types of nanoparticles have increased with the higher percentage of nanoparticles concentrations. The pour points data have shown the decrement values when dispersed with both types of nanoparticles at higher concentrations. Adding the carbon nanotube has decreased the pH values of the samples whereas the zinc oxide shown a reverse pattern for pH values. As a conclusion, dispersion of carbon nanotubes and zinc oxide as additives have improved the operational characteristics of the conventional lubricants.

ABSTRAK

Projek ini melaporkan kesan penggunaan *carbon nanotube* dan *zinc oxide* sebagai bahan tambah untuk meningkatkan prestasi minyak pelincir konvensional. Objektif projek ini adalah untuk mengkaji ciri-ciri termo-fizikal dan tribologi minyak pelincir konvensional yang ditambah dengan nanopartikel untuk mencapai tahap operasi yang lebih baik bagi mengurangkan geseran dan kesan haus kepada sistem. Dalam kajian ini, pelincir yang diuji disediakan dengan menambahkan nanopartikel pada lima kepekatan isipadu yang berbeza pada 0.5 % , 1.0 % , 1.5 % , 2.0 % dan 2.5% dan sifat-sifat asasnya diuji dan seterusnya dibandingkan dengan minyak pelincir biasa di pasaran. Hasil uji kaji ini menunjukkan bahawa nilai konduksi terma dan titik kilat bagi minyak pelincir yang ditambah dengan jenis kedua-dua nanopartikel telah meningkat dengan peningkatan peratusan kepekatan nanopartikel. Data titik tuang menunjukkan corak penurunan apabila ditambah dengan kedua-dua jenis nanopartikel pada kepekatan yang lebih tinggi. Penambahan *carbon nanotube* pula menunjukkan penurunan nilai pH manakala penambahan *zinc oxide* pula meningkatkan nilai pH campuran. Sebagai kesimpulannya, campuran kedua-dua jenis nanopartikel telah meningkatkan ciri-ciri operasi minyak pelincir konvensional.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
cm	Centimeter
cP	Centipoise
F	Fahrenheit
G	Gram
g/kW.h	Gram per kilowatt hour
kg	Kilogram
km	Kilometer
ℓ	Liter
m	Meter
m/s	Meter per second
m^2.K/W	Square meter Kelvin per Watt
mm/s^2	Millimeter per Square second
N	Newton
Nm	Nanometer
P	Pressure
Pa	Pascal
rpm	Rotation per minute
vol %	Volume concentration
w %	Weight fraction
W/m-K	Thermal Conductivity
ρ	Density

LIST OF ABBREVIATIONS

API	American Petroleum Institute's
ASTM	American Standard of Testing Materials
AW	Anti-Wear
CCS	Cold Cranking Simulator Test
CNT	Carbon Nanotube
CuO	Copper Oxide
EDS	Energy Dispersion Spectrum
EP	Extreme Pressure
EPA	Environmental Protection Agency
FKM	Faculty of Mechanical Engineering
FTP	Federal Test Procedure
FYP	Final Year Project
h-BN	hexagonal Boron Nitride
HRTEM	High Resolution Transmission Electron Microscope
HTF	Heat Transfer Fluids
HTHS	High Temperature High Shear
MO	Mineral Oil
MoS_2	Molybdenum dithiocarbamate
MWNTs	Multi-Walled Nanotubes
Ni	Nickel
PAO	Polyalphaolefins
PI	Polyimide
SAE	Society of Automobile Engineers
SEM	Scan Electron Microscope
SSA	Specific Surface Area
SWCNTs	Single Walled Nanotubes
TFOUT	Thin-Film Oxygen Uptake Test
TiO_2	Titanium Oxide
UMP	Universiti Malaysia Pahang
ZrO_2	Zirconium Dioxide
ZnO	Zinc Oxide

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Project Background

Nanotechnology is a revolutionary concept introduced in the twenty first century that has the potential to improve the characteristics of materials in many fields. In recent years, nano sized materials have emerged as a new additive as it possess improved properties, such as a larger surface area which has applications in Tribology. Hence it has received considerable attention for use as an additive in lubricating oil. Many researchers have reported that nanolubricants are effective in decreasing wear and friction. They have applied various kinds of nanoparticles made of polymer, metal, organic, and inorganic materials for the preparation of nanolubricants which has been reported by Chang et al. (2009)

Lubricants represent one of the important areas for commercialization of nanotechnology. Ever since the invention of the internal combustion engine, lubricant oils had been as an essential component. An increasing range of additives had been incorporated into lubricating oils to confer chemical stability, improved performance and beneficial physiochemical properties. The decreasing wear and friction are dependent on the characteristics of lubricants

The main aim of this project is to determine the tribological properties of conventional lubricants to obtain better performance when used in an engine by decreasing friction and wear rates. One approach is to use additives in a conventional lubricant to enhance its properties. Recently, carbon nanotube has emerged as a new additive because of their size, shape and other thermal physical properties. A nanolubricant is a new kind of engineered lubricant dispersed with nanoparticles, in a base lubricant. In this study, to enhance the operational quality of conventional lubricants is to add carbon nanotube (CNT) and Zinc oxide (ZnO) as an additive to have its properties improved

1.2 Problem Statement

Numerous mechanical systems require various functional lubricants in order to decrease the friction and wear of contacting surfaces so that the total energy consumed as well as operational reliability of that system can be improved. However, the use of conventional lubricants is limited because the properties will change after a few hours of operation. One approach to enhance the operational quality of conventional lubricants is to add nanoparticles as an additive and have its properties improved. Dispersion of nanoparticles improves the key operational properties of a lubricant such as tribological characteristics and thermal performance.

1.3 Project Objectives

The objectives of this project are listed as follows;

i. To study the thermal-physical properties of standard lubricants added with various volume concentrations of CNT and ZnO.

ii. To develop a nanolubricant based on the results obtained from (i), and have a lubricant with improved performance characteristics for diesel engine applications.

1.4 Project Scope

In this study, CNT and ZnO particles are selected as an additive due to their high thermal conductivity. It is proposed to determine operational characteristics of lubricants in percent volume concentrations of 0 % vol, 0.5 % vol, 1.0 % vol, 1.5 % vol, 2.0 % vol and 2.5 % vol and at different temperatures. Testing of the lubricant characteristics will be evaluated as per the American Standard of Testing Materials (ASTM). The following tests are planned to be conducted.

i. Thermal conductivity of lubricant is to be measured under transient conditions. This method of measurement is undertaken by many researchers. The measurement of temperature change with time is used in the determination of thermal conductivity of the lubricant.

ii. The flash point temperature of a lubricant and is the lowest temperature at which an ignition source causes the vapors of the lubricant to ignite under specific conditions.

iii. The pour point is the lowest temperature at which no movement of the specimen is observed is to flow out of the container.

iv. pH is an important parameter for controlling the particle size of colloids because it influences the stability of surface charge and particle interactions. Further the state of the lubricant whether acidic, neutral or alkaline is an essential parameter useful in storage and transportation.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Various studies on lubricant properties have been carried out by many researchers in the past. This chapter reviews the previous published literatures, which lays the foundation and basis for further work in this project. This helps give a better understanding about the topic and also acts as a guideline for the whole report structure. The main focus of the study is on lubricant performance and the use of the CNT and ZnO as its additive. This section deals with literature reviews on lubricant, performance characterizations, as well as its thermo-physical properties.

2.2 Background of Study

In engine tribological studies, lubricant is required especially at the piston ring and cylinder liner interface to provide hydrodynamic or mixed lubrication in order to reduce friction and prevent seizure between the rubbing components. Furthermore, lubricant also operates as a medium that transports and removes heat from the engine to the surroundings as this has been investigated by Simon and Michael (2004). Lubricants can be circulated within the engine system either directly or indirectly and the mechanism for lubrication circulation normally depends on the size of the engine as well as the required amount of lubricant. Small and high-speed engines use the splash lubrication system as the amount of lubricant circulated using this mechanism is usually sufficient for thermal management of the engine.

Lubricants must be able to protect automotive components which it lubricates. Lubricants are typically used to separate moving parts in a system. This has the benefit of reducing friction and surface fatigue, together with reduced heat generation, operating noise and vibrations. Lubricants achieve this by several ways. The most common is by forming a physical barrier that is a thin layer of lubricant separates the moving parts. This is analogous to hydroplaning, the loss of friction observed when a car tire is separated from the road surface by moving through standing water. This is termed hydrodynamic lubrication. In cases of high surface pressures or temperatures, the fluid film is much thinner and some of the forces are transmitted between the surfaces through the lubricant.

In other cases, the lubrication provides wear protection by typically the lubricant-to-surface friction which is much less than surface-to-surface friction in a system without any lubrication. Thus, the use as a lubricant reduces the overall system friction. Reduced friction has the benefit of reducing heat generation and reduced formation of wear particles as well as improved efficiency. Lubricants may contain additives known as friction modifiers that chemically bind to metal surfaces to reduce surface friction even when there is insufficient bulk lubricant present for hydrodynamic lubrication and improved lubricant properties. This objective will be archived through increased in the viscosity and thermal conductivity for lubricant by adding some nanoparticle to it.

2.2.1. General Engine Lubrication

The requirement for enhanced the performance of engine is the use of high viscosity lubricants with friction modifier additives to protect engine cylinder surfaces against wear. The authors, Taylor et al. (2005) had performed tests in the USA and it showed pass–fail limits of SAE 0W20, SAE 5W20, SAE 0W30, SAE 5W30 and SAE 10W30. The authors stated that hydrodynamic lubrication friction varies with the square root of the lubricant viscosity. The performance of the engine improved by more than 2 % as expected, in comparison with a reference lubricant SAE 20W30.

According to Carvalho et al. (2010) kinematic viscosities of the lubricants were analysed at two extremity limits which are at 40 °C and 100 °C of temperature, according to the ASTM D445 Standard, as shown in Figure 2.1. Lubricant grade SAE 50 showed consistently higher viscosity values than any other lubricants tested. Synthetic lubricant grade SAE 0W20 showed the lowest viscosity values, and this is followed by synthetic lubricant grade SAE 5W30. Lubricant with various grades namely SAE 5W40, SAE 10W40 and SAE 15W40 showed close intermediate viscosity values. At temperature 40 °C, mono grade mineral oil SAE 40 showed higher viscosity than all Multigrade lubricants, but, at 100 °C, its kinematic viscosity was close to those of lubricants grade SAE 5W40, SAE 10W40 and SAE 15W40.

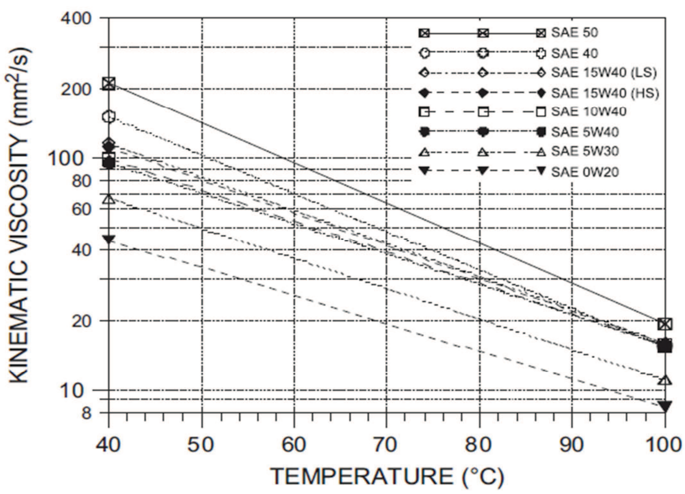

Figure 2.1: Variation of kinematic viscosity with temperature.

Source: Carvalho et al. (2010)

2.2.2 Spark Ignition Engines

The addition of Molybdenum dithiocarbamate (MoS_2) to a grade SAE 5W20 low viscosity lubricant increased the performance of the engine at high temperature operation and increased its energy efficiency by 2.7 % in comparison with a conventional lubricant grade SAE 10W30 which was investigated by Carvalho et al. (2010). The test was developed to evaluate the lubricant influence with used Federal Test Procedure (FTP) to measure the performance. The authors verified that the use of low viscosity lubricant is an efficient way to increase engine performance. Variations of up to 10 % in engine speed, lubricant temperature and coolant temperature did not significantly affect performance of the engine but 5 % torque variation of 4 % did.

Figure 2.2 shows the relationship between the lubricant's high temperature high shear (HTHS) viscosity and the specific fuel consumption. The specific fuel consumption is reduced linearly as the lubricant HTHS viscosity is decreased. This result according to Devlin et al. (2009), realized that simultaneous reduction of HTHS viscosity limit friction coefficient and pressure–viscosity coefficient resulted in decreased fuel consumption. A good correlation was obtained considering all lubricants, except grade SAE0W20 lubricant. Loud noise observed during the tests with this oil indicated that its HTHS viscosity could be below the minimum limit to guarantee safe engine operation.

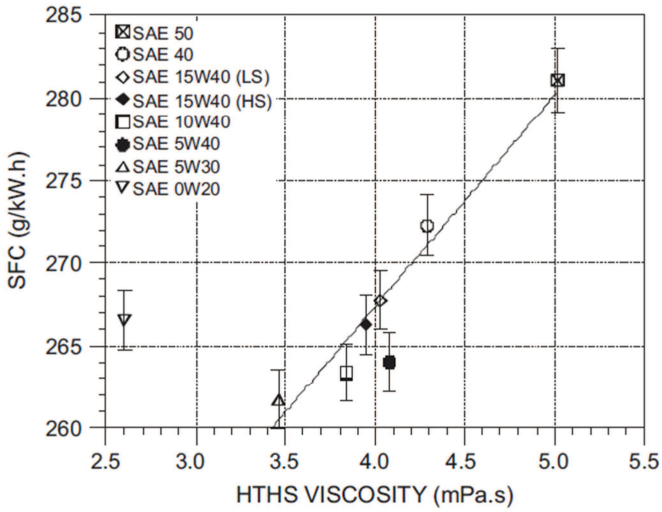

Figure 2.2: Variation of specific fuel consumption with HTHS viscosity

Source: Taylor et al. (2007)

Tseregounis et al. (2002). Tested different grade of lubricants was in four vehicles to quantify the effects of lubricant viscosity and friction modifier additive on engine performance of gasoline fueled engines. Tests were conducted according to U.S. 1975 Federal Test Procedure, which simulates a driving cycle. Performance was observed with reducing lubricant viscosity for the engines with the lowest displaced volumes, of 2.3, 3.1 and 3.8 litres, especially with the cold engine start .The larger-displacement engine, of 5.7 litre, was equipped with components sensible to limit lubrication. With regard to performance, all engines had a good response to the use of friction modifier additives, especially for extra-urban operation under high temperature.

The lubricants and the engines were aged along 13,000 km, simulating and fuel economy characteristics were evaluated at each 1600 km. Both lubricants showed low fuel economy deterioration rate with aging within the range investigated. The Environmental Protection Agency's (EPA) Federal Test Procedure to measure fuel economy deterioration rate of two vehicles equipped with 3.1 litre, 16-valve engines. An SAE 5W20 lubricant with molybdenum- based friction modifier additive and an SAE 5W30 lubricant with a detergent-dispersant additive pack and an organic friction modifier were tested by Tseregounis and McMillan. (2002).

2.2.3 Light Duty Diesel Engines

The effects of lubricants characteristic on diesel engine performance, fuel economy and lubricant consumption were investigated by Manni et al. (2002). A significant increase of engine performance was observed with the use of high viscosity lubricants. As a consequence, lubricant consumption was also reduced.

2.2.4 Heavy Duty Diesel Engines

Fotheringham et al. (2002) investigated exhaust emissions and performance by evaluating thirty diesel trucks operating according to the standard European Transient under cold start and warm start conditions, using different lubricants. SAE 5W30 lubricants, formulated with polyalphaolefins (PAO), high viscosity index mineral base lubricants and the same additive pack were compared with SAE 15W40 lubricants formulated with regular mineral base lubricants. The lubricants containing PAO produced a significant reduction of particulate matter emissions in comparison with the lubricants formulated with regular mineral base lubricants and those with high viscosity index. SAE 5W30 lubricants demonstrated, in an average, 2 % better performance in comparison with SAE 15W40 lubricants.

Lower fuel consumption can be achieved by combining cylinder bore wall surface treatment with reduced lubricant viscosity as is shown by Fox. (2005). However, the author observed that the application of low-viscosity lubricants requires bore wall surface treatment to increase wear resistance at the same proportion to the increase of metal–metal contact severity. Fuel economy improvements of up to 4 % could be achieved with the use of surface treatment together with reduced lubricant viscosity, if the surface was protected against wear.

The effect of automotive lubricants on engine performance and exhaust emissions was investigated by Murtonen and Sutton (2005). Seven different lubricants were tested in a 9.6 litre bus engine. The average difference between the lowest and the better performance produced by the lubricants was of 1.6 %. A clear relation between lubricant viscosity and exhaust emissions was observed. The difference in hydrocarbon emission and on particulate matter emission varied from 0.6 % to 22 %.

The effects of different engine cylinder liner surface finish of friction and wear were verified by Tomanik et al. (2005). Ring and liner specimens removed from a production heavy-duty diesel engine were tested in a reciprocating bench test under two loads and six speed conditions. It was found that the friction coefficient was reduced with increasing lubricant viscosity.

2.3 Nanoparticles

Nanoparticles have great potential to more effectively improve the thermal transport properties of Heat transfer fluids (HTF) than micrometer and millimetre sized particles. This is mainly due to the tininess of nano particles or other nano structures, which not only improves the stability and the applicability of liquid suspensions, but also increases the specific surface area (SSA) and the diffusion mobility of Brownian motion of nano particles. Furthermore, the tininess of nano particles can provide nano fluids a potential to be used in miniaturized electronic cooling and micro channels where larger particles would either clog the channels or settle out from the carrying fluids quickly. In this chapter, experimental and theoretical efforts on synthesis process, experimental measurements of thermal conductivity, viscosity and friction, and wear detailed proposed theories for explaining the experimental results will be reviewed and discussed by Mohanraj and Chen (2006).

2.3.1 Influence of Nanoparticle Properties on Lubricant Performance

Lubricant with additive was extensively investigated by Xie et al. (2002); however, the temperature dependence of thermophysical properties of lubricant has been less studied as most of experimental data to date on nanolubricant were obtained at room temperature. In this section, the temperature-dependent enhancement of thermal conductivity is investigated in CNT with lubricant. The effects of the particle aspect ratio (the ratio of length to diameter) and the change of particle thermal conductivity on thermal transport in nanolubricant will be discussed.

Since solid materials have much higher thermal conductivities than fluids, as shown in Table 2.1, it is then a straightforward logic to increase the thermal conductivity and viscosity of fluids by adding solids on lubricants. However, if solid particles of micrometer, even millimeter magnitudes are added into the base lubricants to make slurries, the increase in thermal conductivity and viscosity of the slurries is insignificant even at high particle loading. Meanwhile, large particles cause many troublesome problems:

a) Large particles are easy to settle out from the base lubricants, especially in low speed circulation, not only losing the enhancement in thermal conductivity, but forming a sediment layer at the surface, increasing the thermal resistance and impairing the heat transfer capacity of the lubricants.

b) The large size of the particles or the agglomerates of these particles causes severe clogging problems, especially at the low circulation rate of fluids or in micro channels.

b) Large particles and the agglomerates in fluid flows carry too much momentum and kinetic energy, which may cause damage to the surface.

e) Noticeable conductivity enhancement is based on high particle concentration, which leads to an apparent increase in viscosity. The pressure drop in lubricants goes up considerably due to the increase of viscosity.

Table 2.1: Thermal conductivities and viscosity of common solids and liquids

Materials		**Thermal Conductivity (W/m-K)**	**Viscosity at 25℃ (mPa.s)**
Carbon	Diamond	2300	
	Carbon Nanotubes	~2000	-
	Graphite	110-190	
Metallic Materials	Silver	429	
	Copper	401	-
	Aluminum	237	
Non-Metallic Materials	Silicon	148	
	Silicon Carbide	120	-
	Alumina	40	
Heat Transfer Fluids	Water	0.613	0.89
	Ethylene Glycol	0.253	16.6
	Engine Oil	0.145	~20
	FC-72	0.057	0.64

Source: Zhao and Lu (2002)

Due to these disadvantages of the liquid suspension of large particles, the method of enhancing the thermal conductivity and viscosity by adding solid particles was not a preferred one until the emergence of nanolubricants. Modern material process and synthesis technologies provide us an opportunity to explore the dimensional bottoms of materials. A variety of nano structured materials have been produced possessing quite different mechanical, optical, thermal and electrical properties of the corresponding bulk materials. Several outstanding features of nano particles, such as the small size, large specific surface area, less particle momentum, and high mobility makes nano particles perfect candidate as the dispersed phases in liquid suspensions. At a junction of conventional thermal science and modern nano technology, now nano lubricants have shown great potential as advanced heat transfer fluids and reduce friction and wear with enhanced thermal properties as was extensively investigated by Zhao and Lu (2002).

2.3.2 Carbon Nanotubes

Previous studies on nanolubricant have focused on spherical nanoparticles or carbon nanotubes (CNTs) was extensively investigated by Chang et al. (2004) Yang et al (2006) found CNTs are very effective to increase the thermal conductivity of fluids attributed to their high thermal conductivity and high aspect ratio. However, CNTs are easy to be entangled and agglomerate due to their long length and low diffusive mobility in base fluids. Stable suspensions of CNTs are not easy to be made and usually the CNTs settle out from the liquid phases too soon, causing erosion and clogging problems as stated by Assael et al. (2005). The urchin-like nanoparticles can improve the diffusive mobility and the colloidal stability of nanotubes and they are also as effective as CNTs in enhancing the operational quality of conventional lubricants by the addition of CNT as an additive and then having its properties improved.

Carbon nanotubes have captured the imagination of researchers worldwide since they were first observed by Iijima. (1991), because of their small dimensions, unique structures, strength and remarkable physical properties. In the past decade, significant advances have been made on the synthesis method, chemical modification and potential applications of carbon nanotubes. Carbon nanotubes, consisting of only sp2 hybridized carbon atoms, are cylindrical nanostructures with a diameter ranging from 1 nm to several nanometers and a length of tens of micrometers. They are made of graphite sheets wrapped into a hollow cylinder and capped by fullerene-like structures.

There are two typical types of carbon nanotubes. High resolution transmission electron microscope (HRTEM) results showed that the first observed carbon nanotubes by Iijima 1991 were fullerene-like tubes consisting of coaxial multiple shells. These tubes were named multi-walled carbon nanotubes (MWNTs). Their inner diameter ranges from 1 nm to a few nm and the outer diameter varies from 10 nm to 20 nm depending on the number of layers. The interlayer spacing is 0.34 nm, which is slightly greater than that of graphite (0.335 nm) due to a combination of tubule curvature and van der Waals force interactions between successive graphene layers. This observation and analysis of the nanotube structure started a new direction in carbon research. The diameters of SWCNT's can be as small as 0.4 nm. However, the typical diameters change between 0.7-3 nm with a mean diameter at 1.7 nm the experiment done by Dresselhaus et al. (2001).

The thermal conductivity of nanotubes has been examined both theoretically and experimentally. Theoretical work predicts a room temperature thermal conductivity that is larger than graphite or diamond. Measurements show a room-temperature thermal conductivity over 200 W/m K for bulk samples of single-walled nanotubes (SWNTs) and over 3000 W/m K for individual Multi-Walled Nanotubes (MWNTs) reviewed and discussed by Sanchez-Portal et al. (1999).

2.3.3 Zinc Oxide

Zinc Oxide (ZnO) is an inorganic compound with the chemical formula ZnO. It usually appears as a white powder, nearly insoluble in water. The powder is widely used as an additive in numerous materials and products including plastics, ceramics, glass, cement, rubber, lubricants, paints, ointments, adhesives, sealants, pigments, food (source of Zn nutrient), batteries, ferrites, fire retardants etc. Their inner diameter ranges from 40 nm to 50 nm depending on the number of layers ZnO is present in the Earth's.