

The Dielectric Constant of Lubrication Oils

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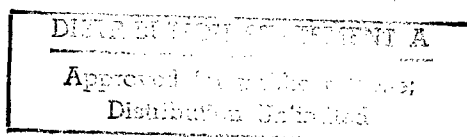
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Abstract: The values of the dielectric constant of simple molecules is discussed first, along with the relationship between the dielectric constant and other physical properties such as boiling point, melting point and refractive index. The Debye equation shows the relationship of dielectric constant with the polarizability and dipole moment of materials. The interpretation of the Debye equation as it applies to lubrication oils is considered. The effect of base oil (paraffinic versus naphthenic) and additives on the dielectric constant of oils is included in this paper. The temperature and electric field frequency dependence of dielectric constant on lubrication oils is discussed.

Key Words: Additives; Debye equation; dielectric constant; lubricant properties; temperature dependence of dielectric constant.

Introduction: Several companies such as Computational Systems Inc. (Knoxville, TN), Kavlico (Moorpark, CA) and Control Devices (Standish, ME) manufacture a capacitance sensor for measuring oil quality. The capacitance of the oil sensor is directly proportional to a property of the oil called a dielectric constant. This paper discusses the dielectric constant of materials, the Debye equation and its application to lubrication oils.

What is a dielectric constant? A dielectric constant is a fundamental property of a material, along with: boiling point, melting point, viscosity, and refractive index. A dielectric constant measures the interaction of an oscillating electric field (that is an electric field that oscillates between positive and negative values at a certain AC frequency) with a molecule. A dielectric constant is a dimensionless number. In pure simple compounds, the values of boiling point, melting point, viscosity, and refractive index are strongly influenced by their dielectric constant. We can compare three simple molecules (of approximately the same molecular weight) like lithium fluoride (LiF), ethane (C_2H_6), and nitrogen (N_2) with various physical properties:



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Table I: Dielectric constant and physical properties of simple compounds [1]

Property	LiF	C ₂ H ₆	N ₂
Dielectric constant	9.00 (5 °C)	1.9356 (-178 °C)	1.4680 (-210 °C)
Melting Point °C	845	- 172	-210
Boiling Point °C	1676	-88	-196
Molecular weight g/mole	26	30	28

Table I shows that there is a relative simple relationship between dielectric constant and boiling and melting points for compounds of approximately the same molecular weight. Namely as the dielectric constant increases, so does the melting and boiling point of simple molecules. Later we will extrapolate these concepts when going to large molecules like lubrication oils. The viscosity of a substance is related to dielectric constant by way of its boiling point. The boiling point of most substances (including lubrication oils) occurs when the viscosity is within 0.4 to 1.4 centistoke. In the case of boiling, it is heat that supplies the energy to overcome the forces between molecules and permits expansion to a gas. The dielectric constant is (partly) a measure of the forces between molecules which must be overcome by heat. In summary, a dielectric constant measures the forces between molecules of a substance. This is relevant to oils where the interaction between molecules is weak (which gives it lubricating properties) and the dielectric constant of oils is relatively small (because the interaction between molecules is small). We will discuss the relationship between dielectric constant and refractive index later.

Table II: Dielectric constant of common materials [1]

Vacuum	1 (exactly)
Metals	Infinite
Gases	1.00xx (at one atmosphere)
Water	87.9 (0 C) to 55.5 (100 C)
Hexane	1.8865 (20 C)
Benzene	2.285 (20 C)
Lubrication oils	2.1 to 2.8 (room temperature)

The dielectric constant of a vacuum is exactly one by definition, whereas metals have an infinite dielectric constant because they are conductors (Table II). The density of gases is about one thousandth the density of solids and liquids and therefore have relatively small dielectric constants (1.00xx). Water has an anomalously large and temperature dependent dielectric constant. Hexane is a simple six carbon paraffinic type compound and has a lower dielectric constant than benzene which is also a simple six carbon aromatic (napthenic) compound. Hydrocarbon lubrication oils have a dielectric constant from 2.1 to 2.8, which depends on the viscosity of the oil, the paraffinic/napthenic content, and additive package.

A molecule contains a positive charge (the nucleus which is relatively massive) and negative electrons which surround the nucleus and are involved in forming chemical bonds. The negative electrons are moving at near the speed of light around (or between) atoms. When a dielectric constant is quoted for a material, the value depends on the electric field frequency and the temperature of the substance. The values of dielectric constant reported in Tables I and II are extrapolated to a zero frequency electric field.

A dielectric constant (also known as permittivity) represents the sum of two different component properties of materials (including lubrication oils): the polarizability, and the dipole moment.

Polarizability is a fundamental property of all atoms and molecules and therefore all material objects. Polarizability measures the interaction of the electrons in a molecule with an electric field. All atoms and molecules are composed of a positively charged nucleus surrounded by negatively charged electrons. Imagine a single hydrogen atom (one proton and one electron) between two parallel plates. If an electric potential is created between the plates, the nucleus is displaced towards the negative plate and the electron is displaced towards the positive plate, in other words the atom (or molecule) is polarized. This displacement is proportional to the electric field until (at sufficiently high voltages) dielectric breakdown occurs. Dielectric breakdown occurs when electrons (rather than electric fields) travel between the capacitor plates. The magnitude of the potential difference between the plates when dielectric breakdown occurs is called the dielectric strength. The magnitude of the proportionality (α) between the induced dipole and electric field (before dielectric breakdown occurs) is called polarizability [2].

$$\mu_{\text{induced}} = \alpha E \quad 1$$

Where μ_{induced} represents the induced dipole moment, α is the polarizability and E is the electric field. The polarizability term (α) has dimensions of cm^3 . The electrons in aromatic compounds (naphthenic) are more polarizable than the electrons in paraffinic compounds. Therefore naphthenic oils should have larger dielectric constant than paraffins.

A dipole moment measures the center of gravity of the positive and negative charges in a molecule. If these two centers do not coincide, then the molecule is electrically unsymmetrical and has a net polarity and therefore a permanent dipole. In a compound like water (H_2O), the oxygen atom shares electrons with the hydrogen atom. However, the oxygen atom holds the negative electrons more strongly than the hydrogen atoms. Thus, the oxygen atom has a more negative charge and the hydrogen atoms are more positive, in other words the molecule is polar. The dipole moment, μ , is defined as the magnitude of a unit charge e (in esu) times the distance r between charges (in cm), and it is expressed in Debyes ($1 \text{ Debye} = 10^{-18} \text{ esu-cm}$). Molecules with a dipole moment have two physically separated charge centers. In an electric field the charge centers align themselves to oppose the field. If the electric field oscillates, the entire molecule has to

rotate. In microwave cooking, the water molecules are rotating at such a frequency (10^9 Hz) that they dissipate energy in the form of friction, causing the heating. Almost all materials (including lubrication oils) show a decrease in dielectric constant at higher electric field frequencies. At higher electric field frequencies there is not sufficient time for the molecule to rotate, and therefore only the polarizability term contributes to the dielectric constant.

The Debye equation: The dielectric constant (ϵ) is related to the polarizability (α) and the dipole moment (μ) by the Debye equation. The relationship is rather messy but we can break it down into simpler parts.

$$(\epsilon - 1)/(\epsilon + 2) = (\alpha + \mu^2/3kT)(L\rho/3MW) \quad 2$$

ϵ = permittivity (dielectric constant) of oil

α = polarizability of oil

μ = dipole moment of oil

k = Boltzman constant = 1.31×10^{-23} joules/degree Kelvin

T = temperature degrees Kelvin = $273 + \text{degrees centigrade}$

L = Avogadro number = 6.02×10^{23} molecules of oil/mole

ρ = density of oil = grams/cm³

MW = molecular weight of oil = grams/mole

The term $(L\rho/3MW)$ represents the volume of a single molecule. The term kT represents the amount of thermal energy available (thermal energy gives molecules random motion). Thus, the dielectric constant is a direct result of the polarizability (α) and dipole moment (μ) of a molecule. Base oil makes only a small contribution to the dipole moment term in the Debye equation, and therefore shows a relatively small change in dielectric constant.

Almost all additives (antiwear compounds, antioxidants, detergents, dispersants etc) contain compounds with dipole moments. This is the reason why additives increase the dielectric constant of lubrication oils. Moreover, as the Debye equation indicates, the dipole moment contribution to the dielectric constant shows a direct inverse temperature relationship. Therefore, additives show direct temperature dependence, whereas the base oil does not.

The Debye equation works well with gases because the large distance between molecules causes weak interaction between dipoles. In solids, because of constraints imposed by the crystal structure, the Debye equation gives useful information. In solids the crystal structure 'freezes' the dipoles in a fixed geometric orientation, and direct solution of the Debye equation is possible. In liquids, thermal motion is continuously changing the orientation of dipoles

The polarizability term at optical frequencies can be determined simply by measuring the refractive index of the oil sample. The equation for determining the

polarizability from refractive index is:

$$\alpha = (n^2 - 1)/(n^2 + 2) * (L\rho/3MW) \quad 3$$

Where n is the refractive index. As can be seen, this equation is similar to the Debye equation. Thus the polarizability term in the Debye equation for dielectric constant is related to the refractive index of the oil.

The Debye equation works well with gases because they are dilute and the distance between molecules is large. The large intermolecular distance implies that there is no dipole-dipole interaction. The Debye equation works only approximately in solids because they have a rigid crystal structure that restricts the molecular orientation. Nevertheless, there is an enormous amount of literature on the dielectric behavior of plastics both as a function of frequency and temperature [3]. Changes in dielectric behavior of plastics are usually associated with localized motion in the polymer systems, that is, side-group rotation, short order motion in the main chain, and so-on. Thus, orientation and movement of dipoles present in the system cause dielectric changes in solids. The Debye equation is complicated in liquids because of dipole-dipole interactions produced by polar materials while thermal motion is continuously reorienting the molecular dipoles.

Lubrication oils: Although the Debye equation does not work exactly for liquids, it is still useful for interpreting the dielectric behavior of lubrication oils. First, the oil base stock contains no polar materials and therefore does not have a dipole moment (μ) contribution. That is, the oil base stock only contains a polarizability (α) term in the Debye equation, which is related to the refractive index. The polarizability of aromatic (naphthenic) compounds is higher than paraffinic because of the delocalized electrons in the aromatic nucleus are more polarizable [4]. Since there is no dipole moment contribution in the oil base stock, there is no direct temperature dependence to the dielectric constant. However, the dielectric constant in the Debye equation contains a term for the density of the oil, and therefore should show temperature dependence due to changes in the density of the oil with temperature. To a first approximation, the temperature dependence of the dielectric constant of the oil base stock is affected by changes in density of the oil. The change in density with temperature varies from 0.716 to 0.658 mg/ml K for oils with 40 C viscosity of 10 and 1500 cSt respectively [5]. As a matter of fact, the dielectric constant of hydrocarbon fuels (which contain smaller carbon chains than lubrication oils) correlates with fuel density, within an accuracy of 2%, according to the equation

$$\epsilon = 0.001667\rho + 0.785 \quad 4$$

Where ρ is the fuel density in kg/m³ at the temperature of interest [5]. Typical densities of lubrication oils vary from 0.829 to 0.908 g/ml with 40 C viscosity of 10 and 1500 cSt respectively.

The temperature dependence of dielectric constant of oils shows a hysteresis using several different dielectric sensors. Figure 1 shows the temperature dependence of the dielectric constant of pure mineral oil (no additives) using a sensor manufactured by Kavlico. This sensor operates at an electric field frequency of about 100 kHz. The figure shows that there is a slight difference in dielectric constant of the oil at a particular temperature during warm up and cool down. This hysteresis effect was found to occur with all oils tested. The effect could be caused by out gassing of water (or dissolved gases) during heating and cooling. Other explanations include electrical effects occurring in the sensor during warming and cooling or molecular relaxation in the fluid. The precise shape and value of the dielectric vs. temperature curve for any oil is probably dependent on the oil base stock and additive package present.

The dielectric constant of almost all additives (especially those containing nitrogen or oxygen atoms) are larger (often 6 to 10) than the base oils stock (2.1 to 2.4). These additives have a dipole moment and should show a different temperature dependence on the dielectric constant than oil base stock. Common additives used in lubrication oils are compounds belonging to the zinc dialkyl dithiophosphates (ZDDP) used in many formulations. Figure 2 shows the dielectric constant vs. temperature during cool down of mineral oil with 1700 ppm of ZDDP. The ZDDP used in this experiment had a dielectric constant of 3.92 at room temperature. The figure shows an increase in dielectric constant at low temperature due to the presence of ZDDP, while the dielectric constant at higher temperature is approximately the same as neat mineral oil.

Synthetic oils such as polyol esters (POE), polyalkyleneglycols (PAG), and phosphate esters have higher dielectric constants. For synthetic oils the value of the dielectric constant depends to a large degree on the oxygen content.

Experiments have shown that the dielectric constant of used lubrication oils is higher than unused oils. The exact increase depends on the amount of water and other contaminants present in the system as well as the amount of oxidation/degradation products present in the oil. Further tests are required to quantify this increase.

Conclusions: The accurate measurement of dielectric constant is an excellent method for measuring oil quality. It is believed that measuring the temperature dependence of the dielectric constant will provide a useful real-time method of measuring oil quality in operating systems.

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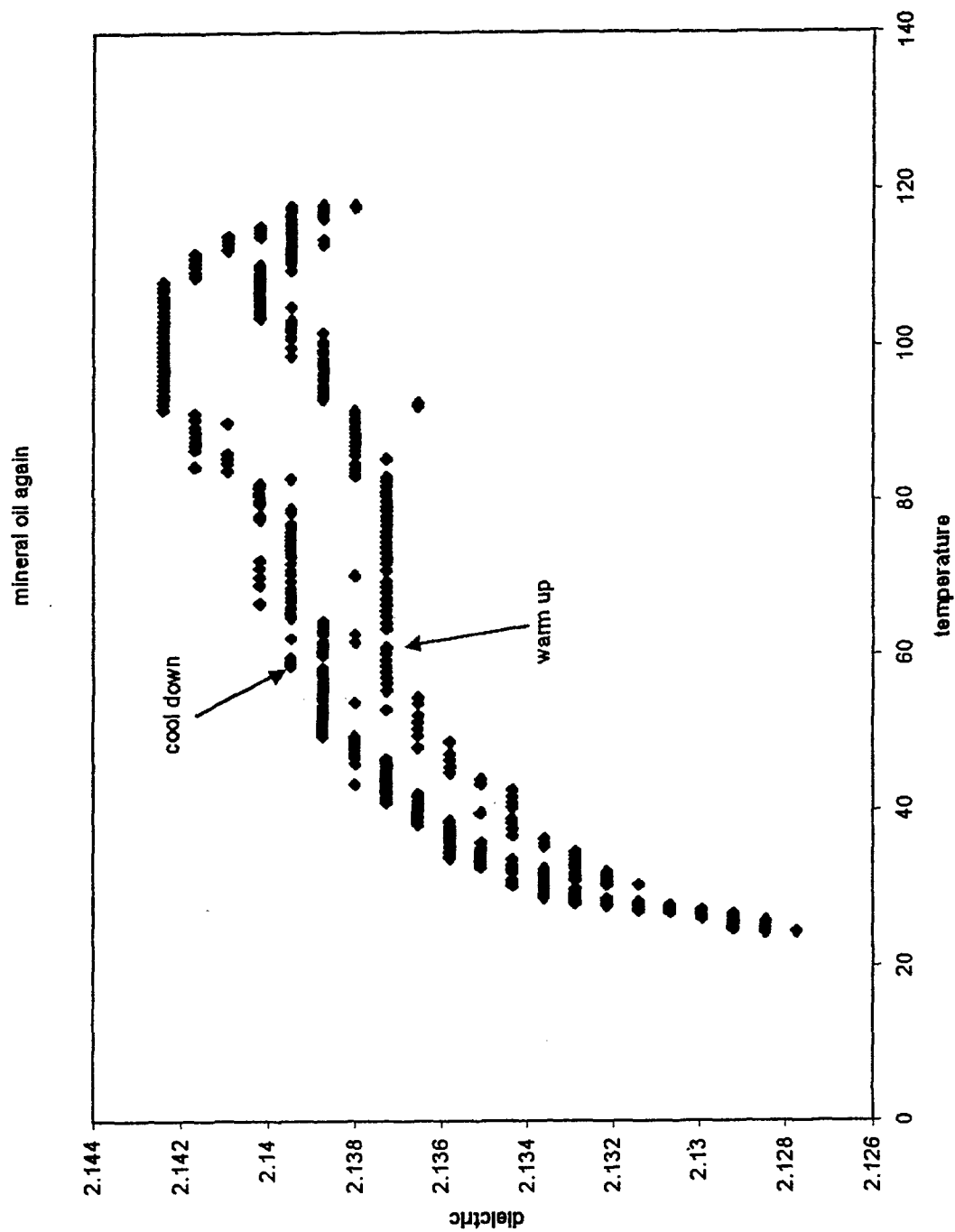


Figure 1: Temperature dependence of dielectric constant of mineral oil (Kavlico sensor)

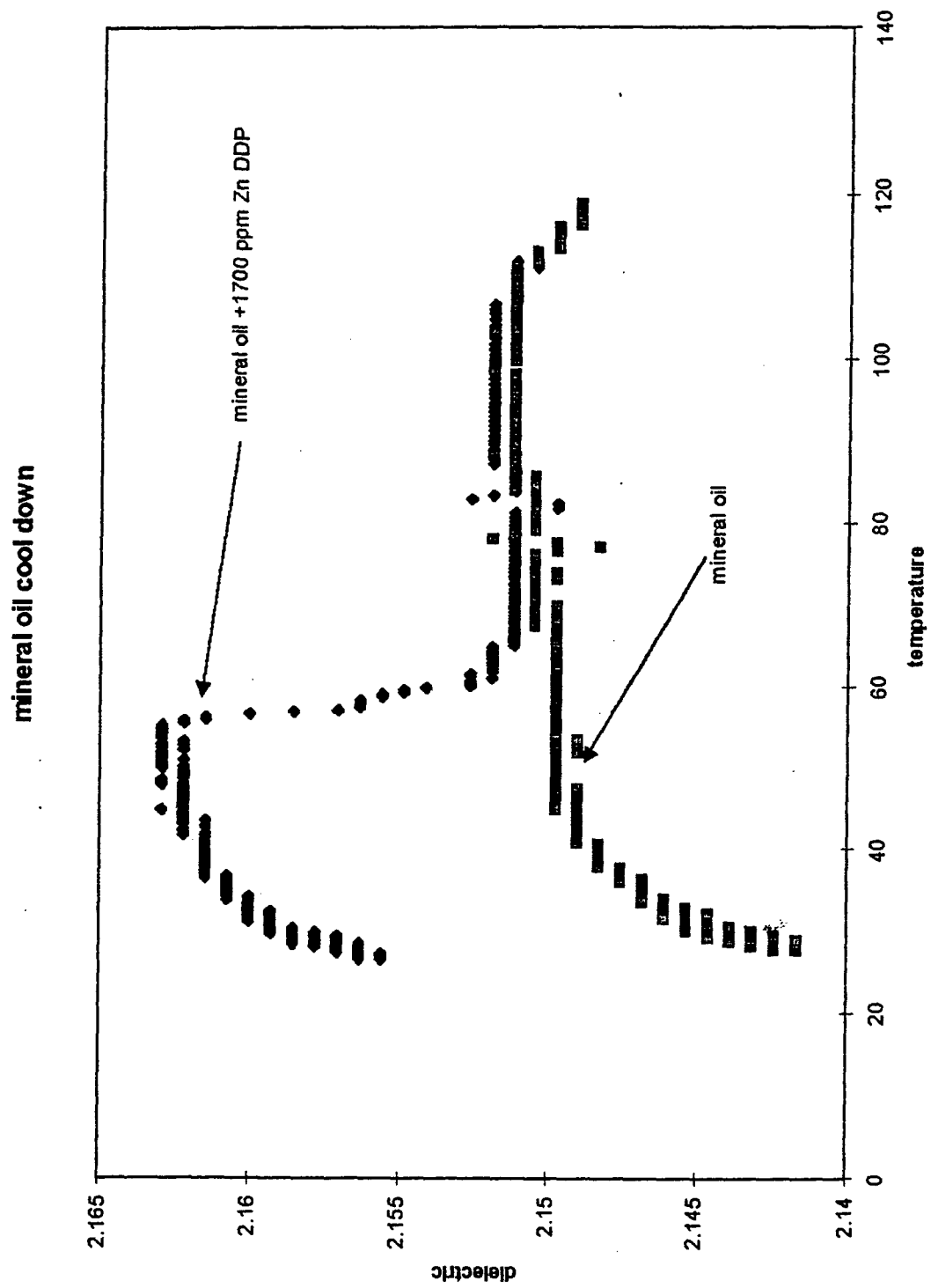


Figure 2: Temperature dependence of dielectric constant of mineral oil with 1700 ppm ZDDP (cool down)