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Thermodynamic Properties of Ferrofluid: Preparation, Stability and Statistical Mechanics

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ABSTRACT

Ferrofluids are known as magnetic liquids that are colloidal suspensions of ultrafine, single domain magnetic particles in either aqueous or non-aqueous liquids. For such fluids, the problem arises in calculating thermal conductivity, viscosity, and thermodynamic properties on nanoparticles and ferrofluids. Thus, the main objective is to determine thermal conductivity and viscosity for ferro-nanoparticles and ferrofluids. For this study, the ZnO and Fe_3O_4 *are checked for mechanical properties such as SEM, TEM and XRD. Then, being suspended into the diesel engine oil SAE-50 as base fluid and surfactant, Triton-100, in preparation of two-step method. Ferrofluids are prepared for 0.1%, 0.4% & 0.7% w/v and stability of nanofluids are being observed for 5 days. From the results obtained experimentally, the nanoparticles were found to be in good stability as no coagulate occur. This is because the EDLRF acts as the opposite to Van der Waals attractive force which separates the particles from each other. Finally, the thermal conductivity and viscosity for ferro-nanoparticles and ferrofluids were successfully obtained and demonstrated. Statistical mechanics are then discussed to calculate the properties of ferrofluids. The analytical results from statistical mechanics are potentially be used to compare with the experiment data.*

Keywords: Ferrofluid, ZnO nanofluid, Fe_3O_4 *nanofluid, stability of nanofluid.*

INTRODUCTION

Lubrication acts as a very important role in economic and continuous movement. The use of lubricant is to keep the surface of the two materials, that separates them from each other by creating a preferable layer on the surfaces with friction, and then eliminate the heat and abrasive particles. Lubrication is the process or technique to reduce the friction and wear for two relative moving surfaces by using lubricant. The benefits provided by lubrication include rust, water, and dust prevention and as an insulator in transformer (Mobarak et al. 2014). Wear and friction can cause machinery failure (for example in the engine, shaft, bearings, gears) and energy losses. Hence, it is essential to have sufficient lubrication to overcome these issues. Hence, it is essential to have sufficient lubrication to overcome these issues (Jason et al. 2020).

Lubricants are classified into three physical appearances: solid, semisolid, and liquid form. Generally, lubricants are synthesized from three different types of base oils. They are mineral oil, synthetic oil, and bio-lubricant. The American Petroleum Institute (API) classified lubricant base oil quality and the necessary information of different groups of base oils under API 1509 (Jason et al. 2020). Synthetic oil is artificially made from hydrocarbons or other chemicals. This lubricant can be manufactured by chemically modifying petroleum products instead of using whole crude oil. The formulation of synthetic oil provides superior properties over mineral oils, including the ability to lubricate in extremely low or high temperatures and offers better wear protection and in addition, synthetic oils also provide several economic benefits including reducing energy consumption and maintenance costs, and improving energy efficiency, etc. Additionally, synthetic lubricants are designed to fulfil the high demands of modern machinery (Jason et al. 2020).

Hence this research involves preparation nanoscale magnetic particles and their dispersion within a carrier fluid and to observed the impact of surfactants on the stability.

LITERATURE

There have been several ground-breaking advancements achieved in the field of nanotechnology since Nobel Laureate Richard P. Feynman first used the term in this well-known 1956 lecture “There’s Plenty of Room at the bottom”. Materials of all kinds were created at the nanoscale through nanotechnology (Bayda et al. 2020). Nanotechnology deals with the preparation, design, and characterization of materials and devices on the nanoscale besides nanotechnology is an emerging field, which plays an important role in the development of innovative technology to produce new products with improved performance and utilize less energy and reduce harm to the environment (Mansoori & Saelaiman, 2005).

Nanoparticles are tiny materials having size ranges from 1 to 100 nm. Nanoparticle technology is of considerable interest for many practical applications (Liu et. Al 2006). The nanoparticles suspended in the nanofluids can be the nanostructured materials below 100 nm in diameter (Liu et. Al 2006). They can be classified into different classes based on their properties, shapes, or sizes. The different groups include fullerenes, metal NPs, ceramic NPs, and polymeric NPs. NPs possess unique physical and chemical properties due to their high surface area and nanoscale size. Their optical properties are reported to be dependent on the size, which imparts different colors due to absorption in the visible region. Their reactivity, toughness and other properties are also dependent on their unique size, shape, and structure. Due to these characteristics, they are suitable candidates for various commercial and domestic applications, which include catalysis, imaging, medical applications, energy-based research, and environmental applications. Heavy metal NPs of lead, mercury and tin are reported to be so rigid and stable that their degradation is not easily achievable, which can lead to many environmental toxicities besides nanoparticles (NPs) are a wide class of materials that include particulate substances, which have one dimension less than 100 nm at least (Khan et. Al 2019). Depending on the overall shape these materials can be 0D, 1D, 2D or 3D (Tiwari et al. 2012). NPs are not simple molecules themselves and therefore composed of three layers i.e. (a) The surface layer, which may be functionalized with a variety of small molecules, metal ions, surfactants, and polymers. (b) The shell layer, which is chemically different material from the core in all aspects, and (c) The core, which is essentially the central portion of the NP and usually refers the NP itself (Khan et al. 2019). The importance of these materials was realized when researchers found that size can influence the physiochemical properties of a substance e.g., the optical properties. A 20- nm gold (Au), platinum (Pt), silver (Ag), and palladium (Pd) NPs have characteristic wine-red color, yellowish gray, black and dark black colors, respectively (Kahn et.al 2019).

Nanofluid, a name conceived by Choi, in Argonne National Laboratory, to describe a fluid consisting of solid nanoparticles with size less than 100nm suspended on it with solid volume fractions typically less than 4% (Prasher 2005). Nanofluids are defined as the dispersion of metallic or non- metallic nanoparticles with principal dimensions of less than 100 nm in a liquid. Different studies by various researchers were conducted with nanofluids prepared in different base fluids and concentrations such as water, ethylene glycol, and engine oil using metal or metal oxide nanoparticles (Yu et. al 2012). Nanofluids are a new class of fluids engineered by dispersing nanometer-size structures (particles, fibres, tubes, droplets) in base fluids (Wan & Fan, 2010). Nanofluids are dilute colloidal suspensions of nanoparticles in a base fluid that shows excellent enhancement in heat transfer performance in various applications. However, nanofluids preparation and stabilization are indeed a matter of concern since the properties of nanofluids are dependent on the stability of the suspensions (Fuskele & Sarviya 2017). The nanofluids are made by adding some solid nanoparticles to the base fluid (Wang et. al, 2020). The NPs usually used in the NFs are oxides, metals, nitrides, and non-metals like carbon nanotubes and graphene, while the BF are often water, ethylene glycol, oils and polymer solutions (Gonçalves et. al, 2021). Nanofluids play a vital role in automobile industries to remove excess energy generated from fuel combustion. Nanofluids can lose heat to the surrounding air through the walls when it flows through the radiator tubes. The conventional fluids used in any manufacturing process that involves heat transfers can be substituted with nanofluids. Understanding the fundamental mechanisms that result in the enhancements requires investigating the properties and flow characteristics of nanofluids.

One application of magnetic nanoparticles is to prepare ferrofluids, which are stable colloidal dispersions of nanosized ferro- or ferromagnetic particles suspended in a liquid carrier, thereby constituting a magnetic functional material with fluidity (Meng et. al, 2019). Ferrofluids are known as magnetic liquids that are colloidal suspensions of ultrafine, single domain magnetic particles in either aqueous or non-aqueous liquids (Genc & Derin, 2014). Ferrofluids (FFs) are stable and quite homogeneous colloidal dispersions of ferromagnetic nanoparticles in a solvent referred to as the carrier. The particles are coated with a surfactant to avoid agglomeration and coagulation. Brownian motion, however, keeps the nanoparticles from settling under gravity (Kaloni & Mahajan, 2010).

These materials have the properties of both of their components: (i) the magnetic nanoparticles (MNPs), which confer a paramagnetic behavior to the suspension; and (ii) the carrier, which is responsible for the fluidic nature of the material (Socoliuc et. al, 2020). Ferrofluids are colloidal liquids possessing strong magnetic features whose physical properties can be altered or controlled when exposed to a magnetic field (Raj et.al. 1995). Iron oxide (usually magnetite and maghemite) nanoparticles are mostly used as magnetic particles in ferrofluids due to their high saturation magnetization and high magnetic susceptibility (Maity & Agrawal, 2007). Magnetic nanoparticles tend to aggregate due to a strong magnetic dipole–dipole interaction (Amara et. a 2009). The stability of FFs can be clearly affected by the agglomeration of the MNPs, due to Van Der Waals interactions and magnetic attractions, among others (Vollmer & Janiak 2011). Thus, ferrofluids need to incorporate a stabilizer or a dispersing agent to prevent such aggregation. Magnetic particles are also applicable in the microscopic manipulation of nano- and micro-sized objects (Bessalova 2016). There are three components that combine to form a ferrofluid, which are dispersion medium also known as carrier liquid, a surface-active agent, or dispersant and magnetic nano particles. As one homogenous system, the fluid responds to applied magnetic field. Commonly, a ferrofluid is composed of (by volume) of 85% liquid, 10% surface active agent and 5% solid component. A model of ferrofluid is shown in Fig.1 which each application brings its own challenges of design and selection of magnetic liquid. The choice of carrier, being the most dominant component of a ferrofluid, governs the overall physical properties besides the advancement in ferrofluids has mostly occurred along the lines of new carriers achieving specific combinations of magnetization, viscosity, and volatility values (Raj et. al 1995).

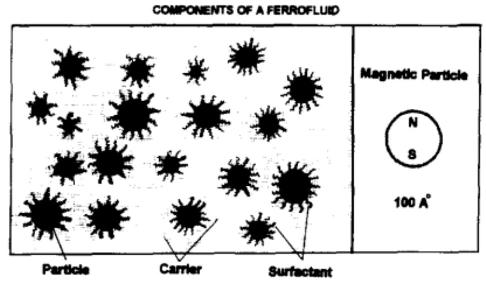


FIGURE 1. Three components of a ferrofluid: carrier, surfactant, and magnetic particles.

The problem that is highlighted in this study is the boundary layer flow due to a stretching or shrinking surface in fluids which arises in calculating thermal conductivity, viscosity, and thermodynamic properties on nanoparticles and ferrofluids. For the objectives that need to be obtain are to determine thermal conductivity and viscosity for ferro-nanoparticles and ferrofluids besides to identify the thermodynamic properties for ferro-nanoparticles and ferrofluids and to establish the analytical computation by comparing with experimental data which also lead to the contribution of this research to the real-life application.

METHODOLOGY

This study is to improve the characteristics of the lubrication of multigrade diesel engine oil using ZnO and Fe_3O_4 nanoparticles. The SAE50 diesel oil has been used as the base fluid for this experiment. Nanolubricants can be synthesized by the one-step method or two-step method. For the one-step method, the nanolubricants directly formulate through a chemical process. In the two-step method, the first procedure is the nanomaterials are synthesized in dry powder form by either physical or chemical methods, and the second procedure is to disperse them into base oil by mixing techniques with or without dispersants or surfactants. An illustration of nano-lubricants synthesis is shown in Figure 2. To prepare the nano lubricants, the two-step method has been used. The ZnO and Fe_3O_4 are merged with the diesel engine oil on a diverse weight percentage at 0.1%, 0.4% and 0.7%. The SAE 20W50 multigrade diesel oil (Grantt) has being use as the base fluid for this experiment which is supplied by UMW Grantt International Sdn Bhd, Singapore. The ZnO and Fe_3O_4 were purchased from Korea and Malaysia, respectively. The material characteristics for both nanoparticles and the diesel engine oil are shown in Table 2. To prepare the nano lubricants, the two-step method has been used. The ZnO and Fe_3O_4 are merged with the diesel engine oil on a diverse weight percentage at 0.1%, 0.4%

and 0.7%. The surfactant that being used is Triton X-100 (Grainger Industrial Supply, United States of America), which as the surface modifier in diesel engine oil to give scattering durability of the additives. The amount of surfactant use was 50 wt.% of each nanoparticle. The non-ionic surfactants such as Triton X-100, do not give any negative effects on the oil quality based on the varies of studies conducted. A stirrer (WT500 Homogenizer, Malaysia) was used for 30 minutes which is to obtain a steady suspension of nanoparticles in the diesel engine oil. The amount of each nanoparticle required was weighed by using a precision digital scale (Kern, Germany) which then being added to the diesel engine oil. The scanning electron microscope (SEM) by using MERLIN Compact model (Zeiss, Germany) was used to observe the nanoscale topographic details on the surface and the composition analysis of specimen besides to survey the morphology of the nanoparticles. The X-ray diffractometer (XRD) by using D8 Advance (Bruker, Germany) was employed to identify chemical phase present in a crystalline material besides to examine the crystal structures of the ZnO and Fe_3O_4 nanoparticles.

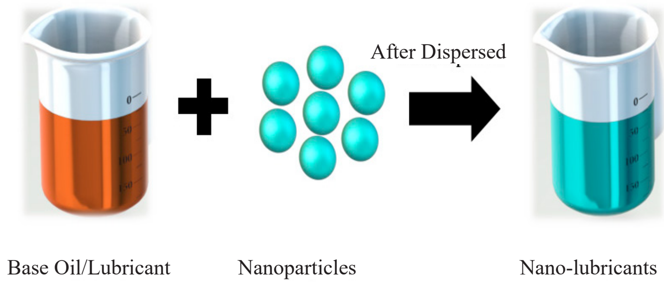


FIGURE 2. Synthesis of nanolubricant

EXPERIMENT DETAILS

The process contains two steps: firstly, synthesis of the nanoparticles, Zinc Oxide (ZnO) and Iron(iii) Oxide (Fe_3O_4) in the powder form, then disperse the nanoparticles into the base fluids of multipurpose diesel engine oil, SAE50 to form a stable and homogeneous solution. By the two-step method, most of the nanofluids are produced by using oxide particles and carbon nanotubes. However, in preparing nanofluids by using the two-step method, having some challenges due to the agglomerations and the nanoparticles tend to settle down quickly. This method is usually produced in large scales because nano powder synthesis techniques have already been scaled up to industrial production levels.

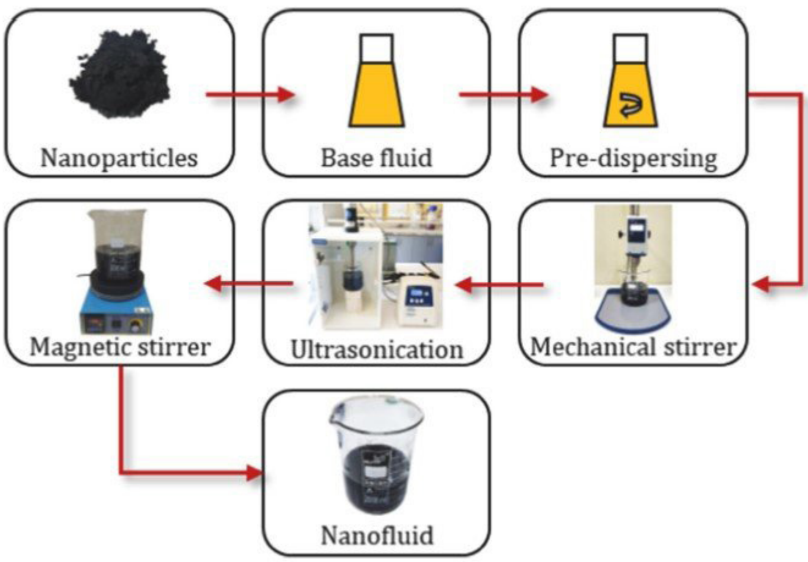


FIGURE 3. shows the flow chart of producing nanofluid

EXPERIMENT DETAILS

Table 1 shows the amount required (gram) for every 250ml SAE50 used to prepared the volume fraction for ZnO and Fe_3O_4.

TABLE 1. Amount required (gram) for every 250ml SAE50 used for different volume fraction.

Concentration (%)		ZnO (g)	Fe3O4
For every 250ml of base fluid	0.1	1.607 1.	483
	0.4	6.445	5.950
	0.7	11.313	10.445

The equation use is for volume fraction formula which to get the amount of ZnO and Fe_3O_4 required for the use of the experiment. From the equation used here, "m" stands for nanoparticles, i.e., ZnO or Fe_3O_4, and "f" is for base fluid which is the diesel engine oil SAE50 in this study. The material characteristics for ZnO, Fe_3O_4 and SAE-50 are shown in Table 2. Equation (1) of volume fraction for ZnO and Fe_3O_4. Amount required.

$$\varphi = \frac{\left(\frac{w}{\rho}\right)_m}{\left(\frac{w}{\rho}\right)_m + \left(\frac{w}{\rho}\right)_f} \tag{1}$$

STATISTICAL MECHANIS

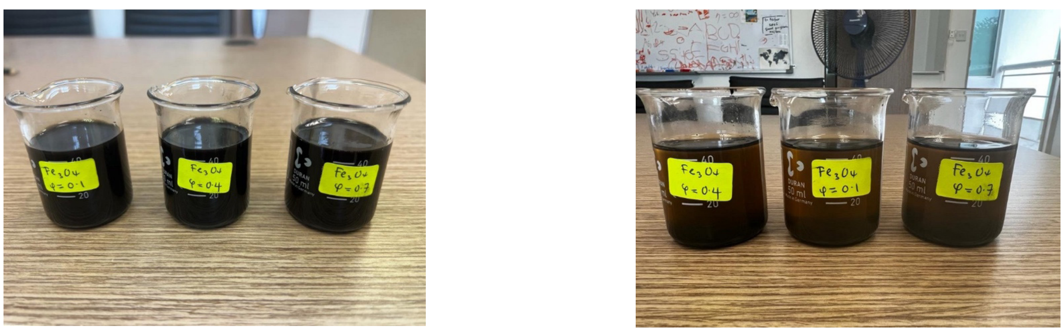
Calculation of properties for ferrofluids is possible by statistical mechanics. Statistical mechanics, calculates the properties of state based on molecular motions and intermolecular Interactions. Equation (2) show the thermal conductivity of basic nanofluids.

$$\lambda = \lambda_0 \left\{ \frac{\lambda_p + (n-1)\lambda_0 - (n-1)\alpha(\lambda_0 - \lambda_p)}{\lambda_p + (n-1)\lambda_0 + \alpha(\lambda_0 - \lambda_p)} \right\} \tag{2}$$

RESULTS AND DISSCUSSION

For the nanoparticle preparation Initially, nanoparticles being dispersed in the base fluid. Figure 5 shows observation result of Iron (iii) Oxide (Fe_3O_4) with concentration of 0.1%, 0.4%, and 0.7% on day 1 (5a) and day 3 (5b). However, from the third days, the nanoparticles being settle down at the bottom of container due to gravity. From the experiment, the nanoparticles are in good stability due to there is no coagulate occur because of the Electrical Double Layer Repulsive Force (EDLRF) acts as opposite to Van der Waals attractive force which separates the particles from each other.

FIGURE 4. shows observation results of Zinc Oxide (ZnO) for concentration of 0.1%, 0.4%, and 0.7% on day 5



(a) (b)

FIGURE 5. Fe_3O_4 with concentration of 0.1%, 0.4%, and 0.7% on day 1 (a) and day 3 (b).

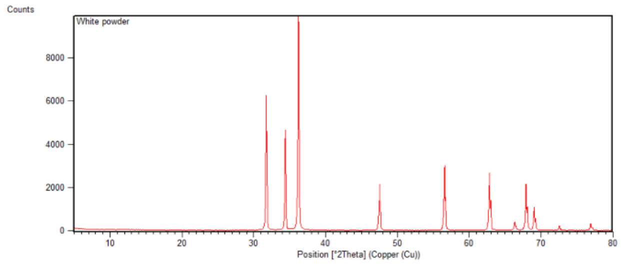


FIGURE 6. XRD for ZnO

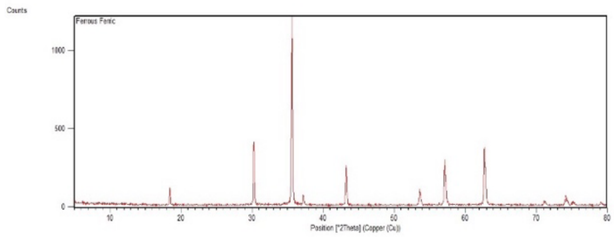


FIGURE 7. XRD for Fe_3O_4.

Both graphs above show the XRD analysis for Zinc Oxide (ZnO) and Iron (iii) Oxide Fe_3O_4 sample which give the result of the sample is crystalline due to the graph have visible and regular peak.

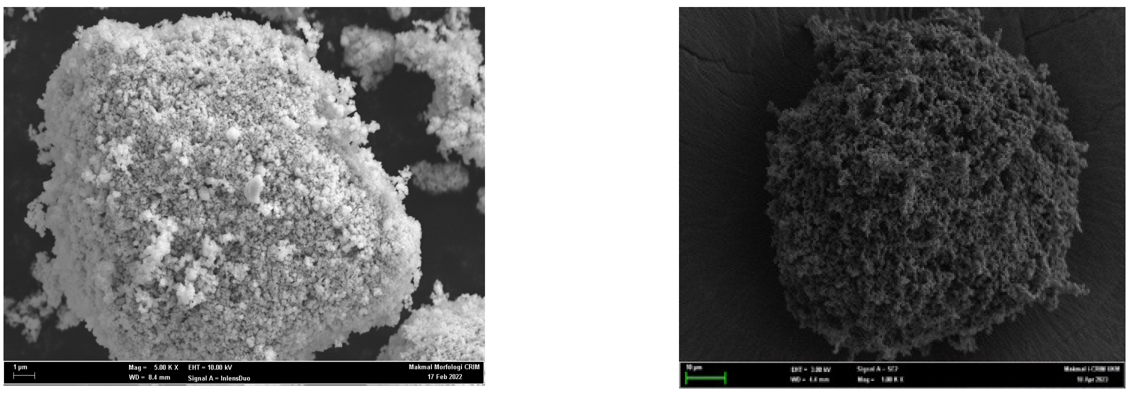


FIGURE 8. Scanning electron microscope (SEM) of ZnO with different magnification

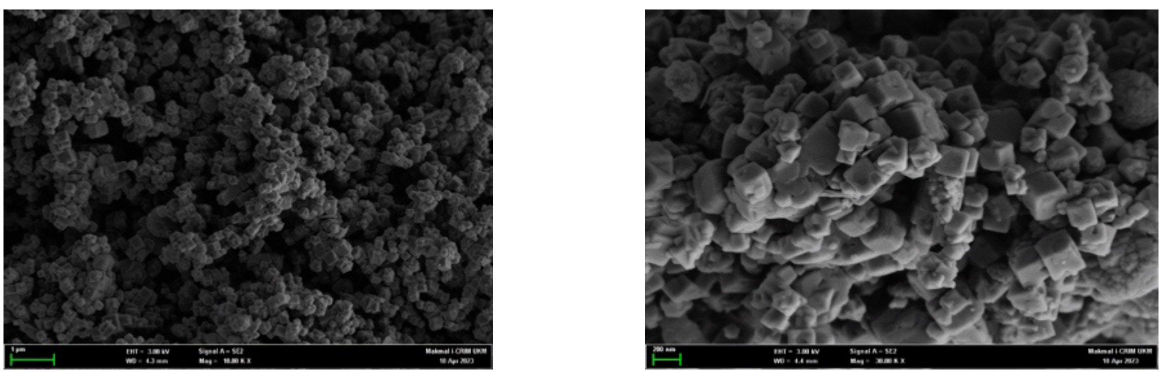


FIGURE 9. Scanning electron microscope (SEM) of Fe_3O_4 with different magnification

The SEM micrograph reveals that zinc oxide nanoparticles have an almost spherical shape with an average diameter of 30 nm while for Iron (iii) Oxide, SEM micrograph reveals that the nanoparticles have rod shape with average diameter of 23 nm.

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From the experiment obtain, the nanoparticles are in good stability due to there is no coagulate occur because of the EDLRF acts as opposite to Van der Waals attractive force which separates the particles from each other. In conclusion, the objective of this study was successfully achieved due to the thermal conductivity and viscosity for ferro-nanoparticles and ferrofluids successfully obtained and demonstrated in this study. Statistical mechanics are then discussed to calculate the properties of ferrofluids. The analytical results from statistical mechanics are potentially be used to compare with the experiment data.

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DECLARATION OF COMPETING INTEREST

None

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