Preparation and properties of low temperature fluidity polyether polyol ester antiwear agent

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Abstract: Polyether polyol ester was obtained by esterification reaction with tall oil fatty acid and propoxylated pentaerythritol, and then the viscosity was adjusted by adding a depressant, thus the diesel antiwear agent with better low temperature fluidity was obtained. The structure of the product was characterized by FTIR. The results showed that the esterification rate reached 98.9% when the reaction temperature was 190℃, the reaction time was 3.5h and the amount of catalyst was 4% of the total mass of acid alcohol. After the reaction of propoxylated pentaerythritol with tall oil fatty acid, the fluidity of the product at low temperature was significantly improved, and the product had better anti-emulsification and lubricating properties. When the addition amount was 150ug/g, the spot diameter decreased to 408μm. According to the kinetic analysis, the antiwear molecules are adsorbed to the metal surface through diffusion. On the surface of each iron atom, there are about 1.975×1010 antiwear molecules, forming a protective film with a dynamic equilibrium of adsorption-desorption, thus ensuring the lubricity of diesel oil.

1. Introduction
With the widespread use of diesel engines, diesel consumption is increasing year by year, but a large amount of diesel consumption will inevitably lead to further aggravation of vehicle emissions of harmful substances. The VI standard for vehicle gasoline and diesel has carried out on January 1, 2019 in China[1].The sulfur content of diesel would be falled below 10 ug/g and the content of polycyclic aromatic hydrocarbons was also limited stringently.

The existing technology is usually to add anti-wear agents to low-sulfur diesel oil, which can be adsorbed on the metal surface to form a protective film on the metal surface, reduce the friction between metals, and effectively improve the lubricity of low-sulfur diesel oil. According to the technical requirements of diesel anti-wear agent formulated by Sinopec, there are mainly two types of unsaturated fatty acids and unsaturated fatty acid esters [2].With poor quality of oil extraction, more and more high sulfur and high acid crude oil was exploited, after deep hydrotreating, polar compounds content in diesel oil was greatly reduced, grinding spot was far greater than 700 microns in diameter, although not saturated fatty acid type anti-wear agent could enhance the lubricity of diesel fuel, adding 300 ppm far could not satisfy the low sulfur diesel oil mill spot dropped to below 420 microns in diameter technical requirements. With the increase of the amount of fatty acid antiwear agent added, the acidity of diesel oil was often greater than the standard of 7mgKOH/100mL. At this time, fatty acid antiwear agent could not meet the technical requirements of diesel standard, so the addition of unsaturated fatty acid ester antiwear agent was needed.
At present, some scholars\cite{3-5} have been used molecular simulation method to study the anti-wear agent molecules on the mechanism of the surface of the metal. Many institutions at home and abroad have carried out the application research of single ester\cite{6-8}, double ester or multi-ester\cite{9} class antiwear agent, which could also meet the use standard of the ester type antiwear agent $< -16$ $\degree C$ using point specified in the Q/SHCG 57-2014 standard. However, in the process of use, it would be found that although the condensation point of these ester antiwear agents was very low, the liquidity at low temperature was very poor, and the pump body could not transport it to the diesel tank for mix, especially in the cold north, which was more difficult to transport. Therefore, a polyether polyol ester type antiwear agent was synthesized in this study. Propoxylation molecules were introduced into the molecule, which could not only improve the solubility of the product, but also reduce the viscosity \cite{10}, and did not affect other indicators of diesel oil. It had good lubricity and could solve the problem of difficult transportation under low temperature conditions.

2. Experimental part

2.1 Reagents and instruments
Pentaerythritol, Chemical Pure.; Propoxypentaerythritol (4PO/8PO/12PO), Ltd.; Para-toluene sulfonic acid, xylene.; Tall oil fatty acid.; Polyethylene vinyl acetate,; DF-101S heat-collecting magnetic agitator.; Constant speed agitator (S312-90), rotary evaporator (R503D), Shimazu IRprestige-21 Fourier Infrared Spectrometer,; SYD-3000 petroleum products kinematic viscosity tester.

2.2 Methods
Add tall oil fatty acids (56.4 g, 0.2mol), propoxylated pentaerythritol (containing 4PO) (73.6g, 0.2mol), 5.2g p-toluenesulfonic acid and 39g xylene to a 250 mL four-mouth bottle. Dimethyl benzene as water carrying agent, reaction 3.5 h, 190 $\degree C$ after the reaction at 0.098 Mpa, 145 $\degree C$ under the condition of vacuum residue of xylene in out bottle, add 130 g distilled water bath products, repeated three times, 0.098 Mpa, 115 $\degree C$ under the condition of reduced pressure extraction product residues in distilled water, add 0.1 g polyethylene vinyl acetate and get 100 g red brown liquid product, yield of 80%.

2.3 Structural characterization and performance testing

2.3.1 FTIR
FTIR test using potassium bromide tablet product, wave number range: 4000 ~ 400 cm$^{-1}$.

2.3.2 Viscosity
In accordance with GB/T265-1988 "Petroleum Product Kinematic Viscosity Measurement and Dynamic Viscosity Calculation Method" \cite{11}.

2.3.3 Spot diameter
According to SH/T0765-2005 Diesel Lubricity Evaluation Method (High Frequency Recipient Testing Machine Method) \cite{12}.

2.3.4 Acid value
According to GB/T264-1983 "Determination of Acid Value of Petroleum Products" \cite{13}.

2.3.5 Demulsification
According to Appendix C of Q/SHCG 57-2014 Technical Requirements for Diesel Antiwear Agents.
3. Results and discussion

3.1 Influence of reaction conditions on esterification rate

The reaction product was mainly to prepare single ester, so the molar ratio of acid and alcohol was fixed at 1:1. The alcohol was propoxylated pentaerythritol containing 4PO. The effects of reaction temperature, reaction time and the amount of catalyst on the esterification rate were investigated. The results were showed in Figure 1, Figure 2 and Figure 3.

![Figure 1: Effect of reaction temperature on esterification rate](image1)

![Figure 2: Effect of reaction time on esterification rate](image2)

![Figure 3: Effect of catalyst dosage on esterification rate](image3)

The reaction time was fixed at 3.5h and the amount of catalyst was 4% of the total mass of acid and alcohol. With the increase of reaction temperature, the esterification rate increased gradually. At 160°C, the esterification rate was 90.3%, and at 190°C, the esterification rate was 98.9%. The esterification rate could not be improved significantly with the increase of reaction temperature. The reaction temperature was fixed at 190°C, the amount of catalyst was 4% of the total mass of acid and alcohol. With the prolongation of reaction time, the esterification rate increased gradually. When the reaction time was 3.5h, the esterification rate was 98.9%, and when the reaction time was 4h, the esterification rate was 99.2%. The reaction degree was gentle and close to the end of the reaction. The reaction temperature was fixed at 190°C and the reaction time was 3.5h. With the addition of p-toluenesulfonic acid, the esterification rate increased gradually. When the amount of p-toluenesulfonic acid was 4% of the total weight of acid and alcohol, the esterification rate was 98.9%, and the increase was not obvious.

3.2 FTIR

![Figure 4: FTIR spectra](image4)

Infrared spectrum comparison of synthetic ester antiwear agent is shown in Figure 4. The characteristic absorption peak of OH hydroxyl group appeared at 3300cm⁻¹, which is brought by the reaction of pentaerythritol with propoxylated. The C=C stretching vibration absorption peak of the synthesized product at 2925 cm⁻¹ is the unsaturated double bond brought by the fatty acid reaction. The characteristic strong absorption peak of C=O carbonyl group is 1742cm⁻¹ and the characteristic strong absorption peak of long chain alkyl -(CH₂)ₙ - is 720cm⁻¹ of the synthesized product were carried by the reaction of fatty acids. Based on the above analysis, the product can be judged as ester type product.
3.3 Influence of structure on viscosity
Tall oil fatty acid and pentaerythritol respectively, including propoxy of 4 PO, 8 PO and 12 PO of pentaerythritol respectively were got product, 0.1% of polyethylene vinyl acetate and was added in the propoxy of 4 PO of pentaerythritol with tall oil fatty acid esterification products. According to the requirements of solidification point of ester antiwear agents < -16℃ in Technical Requirements for Diesel Antiwear Agents issued by Sinopec, the viscosity at -16℃ was taken as the basic observation condition. The viscosity of 5 samples at -16℃ was measured respectively. The experimental results are shown in Table 1.

| Example | Viscosity (-16℃) (mPa·s) |
|---------|--------------------------|
| 1       | no liquidity             |
| 2       | 335                      |
| 3       | 331                      |
| 4       | 329                      |
| 5       | 273                      |

The pentaerythritol mono-fatty acid ester is a paste solid at room temperature and has no fluidity at low temperature. The data in table 1 showed that after the introduction of epoxy propane in molecules, the product viscosity was greatly reduced, because the epoxy propane ring opening access to the molecules, it made the individual molecules bigger, the molecular spacing changed, the intermolecular forces reduced, it also made the whole chain of neat degrees lower when the epoxy propane was accessed which made more than a side chain in methyl, not easy to crystallization, so compared with excluding epoxy propane molecules, viscosity was greatly reduced. With the increase of the degree of propoxylation, the monomer viscosity showed a decreasing trend, but the decreasing amplitude was not large. Polyethylene vinyl acetate is a kind of better pour point depressant, when the addition amount of 0.1%, the product viscosity was dropped further, because the polyethylene vinyl acetate could change the lubricity improver molecular crystal shape and size, and prevent the molecular bond with each other, the inhibition of form a larger crystal blocks to achieve the purpose of improve the low temperature fluidity. Compared with the common triglyceride oleate antiwear agent, the viscosity of the prepared polyether polyol ester antiwear agent was also greatly reduced.

3.4 Demulsification
Study of emulsifying phenomenon of phosphate buffer and antiwear agent of diesel mixed, respectively for blank diesel fuel and the product of propoxy of 4 PO of pentaerythritol contained 0.1% polyethylene vinyl acetate emulsion in diesel fuel, 1 min, 5 min, 10 min were recorded respectively emulsifying phenomenon, the results shown in figure 5.

From Fig.5 showed that, blank base diesel oil and water were stratified with water layer after 1min, no emulsifying layer appears, and the water layer was not turbidity, with a volume of 10mL. After adding ester type antiwear agent for 1min, it was layered with water layer about 8mL, and the water layer was slightly turbidized. After 5 min, the diesel oil and water layer were separated into about 9mL layers, and the water layer was not turbid. After 10min, it was layered with the water layer, and the water layer was not turbid, with a volume of 10mL. It could be seen that the synthetic ester type antiwear agent had good demulsifying performance and met the requirements of antiwear agent after addition.
3.5 Influence of addition amount on lubricity

From Figure 6 showed that with the increase of the amount of antiwear agent added, the lubricity of diesel oil became better. The wear scar diameter of blank diesel oil was 598 μm, and decreased to 443 μm when the dosage was 80 μg/g, and 408 μm when the dosage was 150 μg/g, which met the technical requirements of no more than 420 μm in Q/SHCG 57 -- 2014. It showed that this lubricating improer had good application effect. When it added dose of 200 μg/g, the wear scar diameter further down to 376 μm, when added dose of 250 μg/g, the wear scar diameter down to about 329 μm, and when added dose of 300 μg/g, the wear scar diameter was 325 μm, anti-wear effect change was leveling off. It suggested that, with the increase of the dose abrasion resistance within a certain range was getting better and better, but when the addition amount continues to increase, because the antiwear agent molecules on the surface of the steel ball, adsorption and stripping balance, formed a relatively stable protective film, so the wear scar diameter would not decline further.

3.6 Kinetic analysis

The adsorption reaction process of antiwear agent molecules on metal surface consists of the following steps [15].

1. The antiwear agent molecule diffuses from the fluid body to the outer surface of the metal through the fluid film outside the carbon steel (the distance is X₁), when the antiwear agent molecule diffusion, the concentration decreases from Cₐ to Cₐ₁, the concentration gradient is constant;

2. The antiwear agent molecules diffuse from the outer surface of the metal through the surface atoms to the interface of the active site (distance x₂), when the antiwear agent intramolecular diffusion process, the concentration of the antiwear agent decreases from Cₐ₁ to Cₐ₂, and its concentration gradient is constant.

3. The chemisorption reaction between the antiwear agent molecule and the atoms at the active site is carried out on the interface with a distance of x₃, it is the surface adsorption process.

The above concentration distribution is shown in Figure 7.
The equations of external diffusion rate, internal diffusion rate and surface chemical reaction rate were shown in Equations (1), (2) and (3) respectively.

\[
\frac{dn_A}{dt} = -D_{as} \frac{dc_{as}}{dx} = D_{as}(C_{as} - C_{ac}) \quad (1)
\]

\[
\frac{dn_A}{dt} = -D_{as} \frac{dc_{as}}{dx} = D_{ac}(C_{as} - C_{ac}) \quad (2)
\]

\[
- \frac{dn_A}{dt} = - \frac{1}{b} \frac{dn_A}{dt} = kC_{ac} \quad (3)
\]

Therefore, the reaction process of antiwear agent molecules on the metal surface is affected by antiwear agent molecules and diffusion coefficient. In liquid-solid phase system, the basic theoretical formula for the diffusion coefficient of solute molecules is [16].

\[
D_{AB} = \frac{kT}{6\pi\mu r_A^2}
\]

The radius of molecule A of RA solute, m; The dynamic viscosity of \( \mu B \) solvent B, \( \text{Cp} \) (1\( \text{Cp} = 1\text{mPa}\cdot\text{s} \)); K Boltzmann constant (K = 0.1380J/K); T thermodynamic temperature, K. The diffusion coefficient is a function of temperature. Therefore, when the temperature increased, the molecular diffusion coefficient \( D_{AB} \) increased, and the number of molecules diffusing to the metal surface per unit area increases. For the diesel system containing antiwear agent, because the antiwear agent molecules were oil-soluble molecules, it was easy to diffuse in the diesel system. When the temperature increased, the number of antiwear agent molecules diffusing to the metal surface increased, so that the effective collision probability increased. Therefore, it could be considered that the rate of external diffusion and internal diffusion was much higher than the rate of surface adsorption reaction, and the anti-wear effect is affected by the rate of adsorption of antiwear agent molecules on the metal surface. According to Equation (3), the increase of reaction rate constant K and anti-wear agent concentration \( CAC \) could accelerate the reaction rate. Therefore, under the condition of a certain temperature, the anti-wear effect increases with the increase of anti-wear agent concentration, which was consistent with the experimental results. According to the theoretical analysis of kinetics, the increase of the concentration or temperature of antiwear agent would accelerate the adsorption rate between antiwear agent and metal surface, reduce the friction of metal surface, and play an anti-wear effect.

From the microscopic point of view, we regard the iron atom as a sphere. According to the iron density \( \rho = 7.8 \times 10^3\text{kg/m}^3 \), molar mass \( M = 5.6 \times 10^2 \text{kg/mol} \), Avogadro constant \( N_A = 6.0 \times 10^{23} \text{mol}^{-1} \), it can be estimated that the diameter of the iron atom is about \( 2.8 \times 10^{-10} \text{m} \), then the surface area of the
test ball with a diameter of $6 \times 10^{-3} \text{m}$ is $1.13 \times 10^{-4} \text{m}^2$, and the surface contains about $4 \times 10^5$ atoms. In 2mL diesel oil, when the amount of antiwear agent was 150mg/L, according to the molecular weight of antiwear agent, the number of antiwear agent molecules in diesel oil could be estimated to be about $7.9 \times 10^{15}$, that was each iron atom had about $1.975 \times 10^{10}$ antiwear agent molecules that could be adsorbed. When the metal ball was put into the diesel oil, it was first covered by the adsorbed diesel molecules. A large number of antiwear agent molecules needed to reach the surface of the metal through diffusion. The antiwear agent molecules first needed to exclude the adsorbed diesel molecules on the iron surface before they could be adsorbed on the active site, and adsorption and desorption occur simultaneously. Because there were enough antiwear agent molecules in the system, when the antiwear agent molecules desorbed from the metal surface, other antiwear agent molecules would quickly adsorb on the metal surface, forming a dynamic equilibrium.

4. conclusion
(1) When the reaction temperature was 190℃, the reaction time was 3.5h, and the amount of catalyst was 4% of the total mass of acid and alcohol, the esterification rate reached 98.9%, and the acid value of the product was 1mgKOH/g. The infrared spectrum showed that the product was ester type target product.

(2) The pentaerythritol mono-fatty acid ester had no fluidity at low temperature. When propylene oxide was introduced into the pentaerythritol molecule and 0.1% polyethylene vinyl acetate was added, the viscosity of the esterified product was greatly reduced, and the viscosity (-16℃) was 273mPa *s. The fluidity was good at low temperature, which solved the problem of transportation difficulty at low temperature.

(3) When the dosage was 150ug/g, the wear scar diameter decreased to 408μm, which met the technical requirements of Q/SHCG 57-2014 no more than 420μm, and had good anti-emulsification property.

References:
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