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STUDIES OF ANTICORROSIVE PROPERTIES MOTOR OILS AND WAYS TO IMPROVE

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ABSTRACT: - The purpose of this work is to study how to improve the anticorrosive properties of lubricants. With an increase in temperature, the combined action of oxygen, air and water present in the lubricating oil causes rusting of the crankshaft, the walls of the sleeves, the cylinders of the internal combustion engine.

We have studied anticorrosive additives as an additive to improve the anticorrosive properties of oils. dialkylphenyldithiophosphoric acid additive was used as such additives. The anticorrosive activity of these substances is associated with their ability to orient themselves on the oil–water surface so that hydrophilic groups bind firmly to water, and the hydrocarbon radical remains in the oil.

KEYWORDS: Anticorrosive additives, hydrophilic groups, hydrocarbon radical, protective properties, corrosive effect.

INTRODUCTION

In recent years, increased requirements for protective properties have been imposed on petroleum oils for various purposes. One of the functions of the oil is to protect the surface of the parts from corrosion. The corrosive effect becomes especially intense when the engine is operated in humid hot climate zones. Oil in this case plays a double role: on the one hand, it protects the surfaces of the parts from the aggressive influence of the external environment; and on the other, the oil itself causes corrosion due to the presence of substances with a corrosive effect in it.

The reason for the corrosive properties of oils is that they contain organic and inorganic acid peroxides and other oxidation products, as well as sulfur compounds, alkalis and water. The source of water in the lubricating oil is condensation on the cold walls of its vapors formed during the combustion of fuel, or atmospheric moisture. Corrosion is especially intensified after the engine is stopped, since when it cools, moisture condenses on the parts, lubricating oil, flowing down from the lubricated surface, is not able to protect the metal from corrosion.

Organic acids are present in any fresh oil in the form of naphthenic acids. Their content in oil usually does not exceed 0.4 mg KOH per 1 g of oil. Among the various oxidation products, there are low-molecular-weight carboxylic acids with increased corrosion due to their solubility in water.

The acid content increases during the application of the oil: three to five times or more. The amount of acids formed depends on the chemical stability of the oil, the presence of antioxidants in it and the conditions of use of the oil. During the combustion of oil, high-molecular organic acids are formed, which in the presence of oxygen have a detrimental effect on metals. Oxygen is a part of peroxides, therefore, in the presence of oxygen and water, the metal undergoes electrochemical dissolution.

Corrosion under the action of organic acids consists in electro-chemical dissolution of metals. Cadmium, lead, and iron are easily corroded. The dissolution of the metal in high-molecular acids precedes the formation of an oxide. The dissolution of cadmium proceeds according to the equation:

$$Cd + RCOOH \longrightarrow CdO + RCOH,$$
$$CdO + 2RCOOH \longrightarrow Cd(RCOO)_2 + H_2O.$$

The indicator of the corrosion resistance of the oil is the acid number, which should not exceed 0.4 mg of caustic potassium KOH (potassium hydroxide) per 1 g of oil. Due to the high molecular weight, the acids in fresh oil dissociate weakly, and the acids formed during the oxidation of oil become the most dangerous, since their low molecular weight has increased corrosive aggressiveness due to good solubility in water and better dissociation.

The mechanism of corrosion action consists in the initial formation of a complex metal compound with a sulfur compound deposited on the bearing surface and having a protective effect. Under temperature conditions, the resulting complex decomposes with the release of sulfide, which, being hard and brittle, breaks up into individual particles, which leads to the loss of metal.

RESEARCH ANALYSIS

In recent years, increased requirements for protective properties have been imposed on petroleum oils for various purposes. One of the functions of the oil is to protect the surface of the parts from corrosion. The high protective effect is based on the ability of oils to quickly displace active compounds from the metal surface, retain it in the volume of the lubricant and form strong adsorption and chemisorption films on it, preventing the development of electro-chemical processes. Base oil oils are not capable of protecting metals from electrochemical corrosion for a long time. The main means of increasing the anticorrosive properties of the lubricant is the use of corrosion inhibitors.

The nature of oil oxidation is influenced by the specific conditions of its operation in the engine: large oil-air contact surfaces (oil films, fog, oil foaming in the crankcase). Oxidation is most intense in relatively thin layers of oil located on highly heated metal surfaces. Corrosion of bearing liners made of non-ferrous metals is especially dangerous, which can be caused by acidic oxidation products, sulfur compounds. At high temperatures, sulfur compounds become especially aggressive towards silver, copper and lead.

The corrosion aggressiveness of the oils in relation to the lead bronze from which the crankshaft bearing liners are made is assessed by a breakdown on a lead plate. At the same time, the loss of its mass is determined under conditions of its being in oil for 50 hours at 140°C.

The corrosive effect becomes especially intense when the engine is operated in humid hot climate zones. Oil in this case plays a double role: on the one hand, it protects the surfaces of the parts from the aggressive influence of the external environment; and on the other, the oil itself causes corrosion due to the presence of substances with a corrosive effect in it. The temperature factor especially affects the rate of general corrosion. With an increase in temperature in the presence of moisture, corrosion increases. The presence of aggressive gases in the surrounding atmosphere (SO_2, H_2S, NO_2, chlorine and bromine compounds, etc.) increases corrosion.

The study shows that an increase in temperature from 20 to 80°C at 5% water causes an increase in corrosion from 0.1 to 0.25 mm/ year. If we assume that the permissible corrosion rate is 0.2 mm/ year, then this value is reached at a temperature of 80°C by 2%, and a further increase in the water content in the oil leads to a significant increase in the corrosion rate. Corrosion processes in engines are suppressed in the following ways: by neutralizing acidic products; slowing down oxidation processes; creating a protective film on the metal. Therefore, the main barrier to their path are surfactants and chemically active substances - corrosion inhibitors that contribute to the formation of adsorbed or chemical films on metal surfaces.

In order to combat corrosion, special additives are added to the oils. Anticorrosive additives are mainly polar substances that are easily adsorbed on metal surfaces.

Substances used as anticorrosive additives are salts of organic acids, metal phenolates, and various thiophosphoric compounds. Nitrogen, phosphorus containing compounds, aromatic amines $C_6H_5NH_2$, which are ammonia derivatives, deserve considerable attention as an anticorrosive additive.

Corrosion inhibitors also include oxy-acids and their esters, synthetic fatty acids, oxidized mother-of-pearl (MNI-5) and oxidized ceresin (MNI-7). All of them are used in the composition of petroleum oils, but they worsen the chemical stability, detergent and other properties of the oil. Before giving recommendations on the use of any additives, it is necessary to study their mechanism of action, without knowledge of which their effective use is impossible.

RESEARCH METHODOLOGY

Corrosion protection by a layer of lubricant located on the metal surface consists of its simple physical isolation from corrosion aggressors and the ability of the active components of corrosion inhibitors to form a water-resistant adsorption or chemical film on the metal surface.

In general, the protective layer consists of three parts (Fig. 1) the lower one formed as a result of chemical interaction of lubricant components with metal, the middle one resulting from the adsorption of surfactants and the upper volume layer.

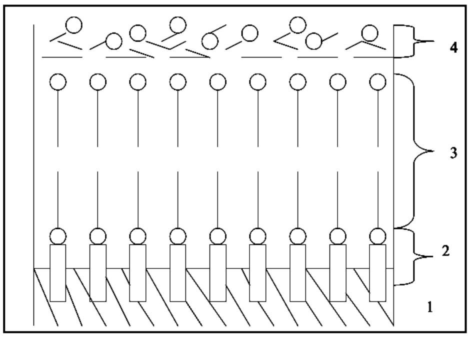


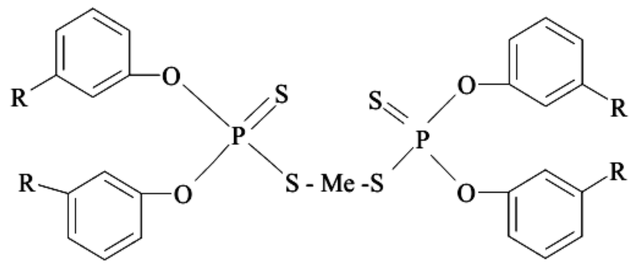
Fig. 1 Diagram of the structure of the protective oil coating

1 - metal; 2 - chemisorption layer; 3 - adsorption layer; 4 -volumetric oil layer

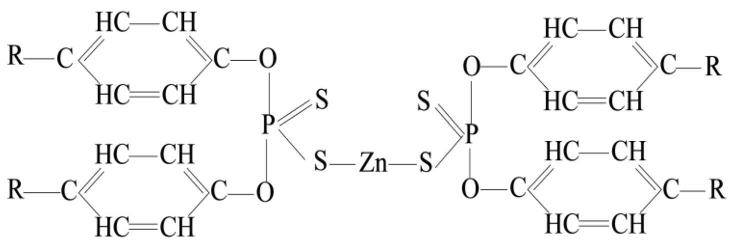
The lower layer is the result of the interaction of chemical components of oil with metal, the middle layer is the adsorption of surfactants. The upper layer is a volumetric layer of oil that does not protect metal surfaces from moisture and gases to the necessary extent.

The bulk layer formed by hydrocarbons does not provide reliable protection of the metal from corrosion, since it passes moisture and gases to the metal surface quite easily. An increase in the thickness of the hydrocarbon layer to 5 mm or more does not significantly affect the diffusion of water and gases.

The most active additives are surfactants, such as sodium salts of petroleum sulfonic acids, some nitrogen-and phosphorus-containing compounds (for example,compounds such as RSO2NHCOO4H9, dicyclohexylamine nitrite, etc.) and metal phenolates, as well as numerous compounds containing phosphorus, sulfur and alkaline earth metal. Such additives are obtained, for example, by the reaction of alkylphenol with phosphorus pentasulfide and salts of calcium, barium, zinc, etc. These compounds have the formula:



As an anticorrosive additive, we studied a mixture of zinc salt alkylphenolate: dialkylphenylcinc dithiophosphoric acid (ZnDP) containing complex and internal esters.



We analyzed motor oils M-10G2 and the anticorrosive additive dialkylphenylcinc dithiophosphoric acid (ZnDP). The study showed that this compound has a number of advantages over other additives. The anticorrosive activity of these additives is related to their ability to orient themselves on the oil–water surface so that the hydrophilic groups bind firmly to water, and the hydrocarbon radical remains in the oil. Polar groups that are able to hydrate, dissolve and orient themselves in polar solvents are called hydrophilic; they have an acidic character:

-COOH, -OSO3H, -SO3H, -OH, -NH2, -NHR, -N(R)2-N+(R)3,R2O, R-CONHR

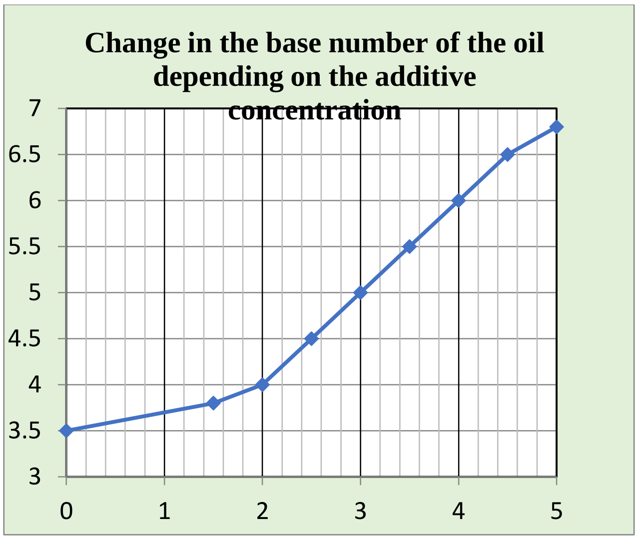
Hydrophobic nonpolar structural elements soluble in nonpolar organic solvents are most often alkyl chains, aromatic mono- or polycyclic groups or alkylaromatic radicals. The mechanism of their action consists in creating a protective monomolecular layer on the metal, preventing the effect of acidic and other active agents on the metal and reducing it to preventing contact of water and gases with the metal. When ZnDP is introduced into motor oils, the wetting ability is manifested by the formation of strong hydrogen bonds with water and the displacement of water from the metal surface. Water permeability decreases due to the formation of their colloidal structure with hydrocarbons, which repels water, blocking access to metal surfaces. Displacement of water from the metal surface can occur as a result of its binding: due to solvation by metal cations, inclusion of hydrophilic components of additives in the hydrate shells, as well as due to solubilization or emulsification and stabilization in the form of water-oil emulsions. At the same time, the activity of water molecules adsorbed on the metal surface will be significantly reduced.

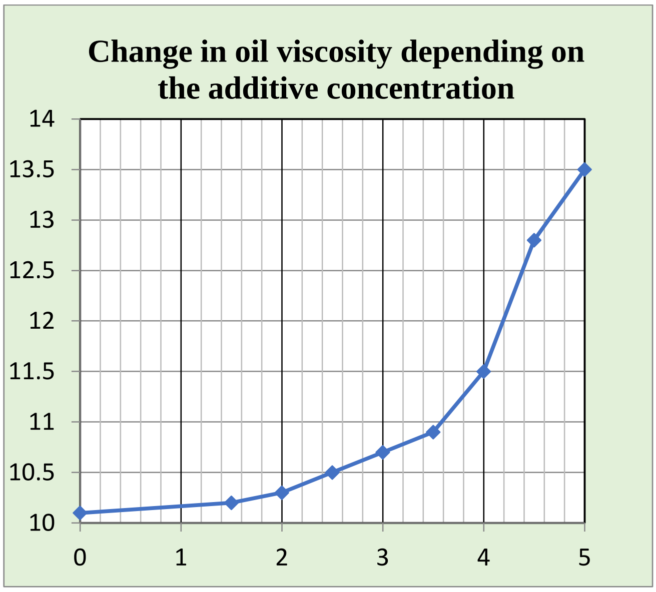
To achieve the desired effect, it is required to apply ZnDP in quantities of 2-5%. The greater the activity of the inhibitor, the more hydrocarbon atoms the radical contains. After the introduction of 2-5% of the additive concentration into the oil, the physico-chemical parameters of the engine oil for different concentrations of additives were determined.

CONCLUSION

According to the results of laboratory tests, when the additive was introduced into the M-10G2 engine oil, they gave a positive result. Thus, the mechanism of action of the proposed corrosion inhibitors based on dialkylphenylcinc dithiophosphoric acid (ZnDP) is reduced to their ability to orient themselves on the oil–water surface so that hydrophilic groups bind firmly to water, and the hydrocarbon radical remains in the oil. At the same time, the activity of inhibitors is greater, the more hydrocarbon atoms the radical contains.

From the results of the analysis, the alkaline number increased from 3.5 to 6.8, which indicates the effectiveness of the added additive. Engine oil with such an alkaline number can be used not only in medium-powered, but also in high-powered engines. It is known that with an increase in the neutralizing ability of the oil, the wear of the piston rings decreases sharply.





From the results of the analysis, we selected the content of the ZnDP additive 3.5%, which shows the optimal value of the alkaline number (5.5) and viscosity (10.9 mm2/sec). With a further increase in the concentration, the viscosity increases greatly, which can lead to increased friction losses.

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