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The use of Zinc Dialkyl Dithiophosphate as a Lubricant Enhancer for Drilling Fluids particularly Silicate-based Drilling Fluids

Zen-Yu Chang, Lubrizol Corp., David Breeden, Newpark Drilling Fluids, Michael McDonald, PQ Corp.

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Abstract

As well profiles become more challenging, drilling fluids and lubricants face the need to provide further reductions in torque and drag. Tightening environmental regulations have placed further pressure on operators who now look more frequently to water based fluids to solve these challenges despite their higher coefficients of friction.

One of the most commonly used methods for reducing toque and drag is the addition of a lubricant to the drilling fluid. Lab results show that the addition of a minor amount of zinc dialkly dithiophosphate (ZDDP) is an effective means of improving the performance of most classes of lubricants including those used with water base fluids. Under downhole conditions the ZDDP decomposes to form a polyphosphate film on the surface of the drill string and casing. This film is proving to serve multiple roles, reducing wear and corrosion on the underlying metal surface while working synergistically with other lubricants used.

This paper focuses on the use of ZDDP/lubricant combinations in potassium and sodium silicate-based drilling fluids. Silicates were chosen as the drilling fluid for this evaluation because of their reputation for shale inhibition, clean environmental performance and because these fluids are often disadvantaged with high coefficients of friction. Lab testing has shown that a small addition of ZDDP can improve performance to a number of lubricants demonstrated by 15% to 60% reductions in coefficient of friction versus the unmodified lubricant. Of the various lubricants tested with ZDDP, the base lubricant was selected for field trials using the criteria of performance and health, safety & environmental characteristics.

Introduction

Lack of lubricity is a major concern with using water-based drilling fluids. Oil-based drilling fluids have the inherent advantage of significantly lower coefficients of friction (CoF). The typical CoF for an oil-based drilling fluid is 0.10 or less (metal to metal). As comparison, water has a CoF of 0.34 and water-base drilling fluids typically range from 0.2 to 0.5. Within this range, silicate-based drilling fluids have a CoF equal or slightly greater than that of water[1]. There is a perception that silicate-based fluids can cause higher torque and drag than would be anticipated by its CoF. Often, cases of high torque and drag can be attributed to the shale stabilization characteristics of silicate-based drilling fluids with holes in near guage condition. Bottom hole assembly design, hole cleaning and hole geometry need to account for a gauge borehole to minimize impact on torque and drag.

Sodium and potassium silicate chemistry has been well documented as it pertains to soluble silicate reacting with shale[2]. The accepted theory is soluble silicates at pH 11 to 12 exist in a drilling fluid in the form of monomers, dimers, trimers and oligmers (figure 1). These negatively charged, soluble silica species react by gelation, precipitation and van der Wall forces on contact with shale. This results in a thin physical and chemical barrier at the shale surface. To a lesser extent, the corrosion mechanism of silicate-based drilling fluids has been studied for drill pipe[3]. The same soluble silica species reacting with the shale are also reacting with cationic metals and metal surfaces.[4] This phenomenon is illustrated in Figure 2. Monomeric silica $(H_2SiO_4)^{2-}$ is absorbed onto the metal drill pipe surfaces at anodic sites, to form a monomolecular layer.

Figure 1: Silica Species

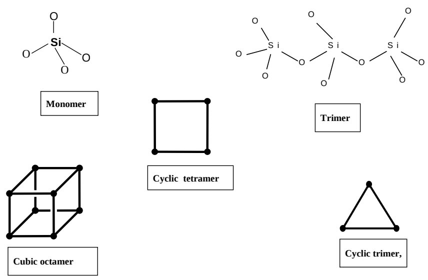
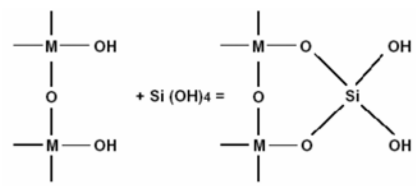


Figure 2: Deposition of Silica on Metal Surface



Microscopic and X-ray examination of iron coated with silica show two layers.[5] At the drill pipe interface is a metal silicate overlaid by an amorphous silica layer. Once the silica film has been formed, deposition stops. The film does not build on itself. The film is an electrical insulator and blocks the electrochemical reactions. It is highly likely that the silica film being formed on the drill pipe makes it very difficult for most lubricants to deposit via adsorption, chemisorption or tribochemical reactions.

As the protective silica film is continually eroded by turbulent flow and abrasive action of drill solids and drilling fluid additives surface sites do become available on the steel. The strategy taken for improving lubricant performance was to find a chemical that would act as a boundary layer for the lubricant to deposit on the steel surface. Desired attributes for a boundary coating would include;

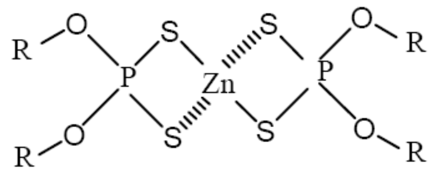
-high affinity for steel
-high affinity for a lubricant
-have durability greater than that of the silica film
-deposit at a thickness greater than the silica film

Looking at the desired attributes, zinc dialkyldithiophosphate (ZDDP) emerged as the molecule of interest, or more accurately, class of molecules. The focus of this paper is on silicate-based drilling fluid; however, an improvement in lubricity and wear resistance would also have potential application for other water-based systems or even oil-based fluids.

Identity and Chemistry of Zinc Dialkyl Dithiophosphates

Historically, silicates were introduced as a drilling fluid additive in the 1930's and are arguably the most effective shale inhibitor. In a similar fashion, ZDDP was introduced into engine oils in the 1930s and can be argued to be one of the most effective lubricant additives. Originally added to lubrication oil as an antioxidant, it was discovered to be a highly effective antiwear, extreme-pressure additive and corrosion inhibitor. Decades of research has led to an in-depth understanding of ZDDP chemistry and mechanism as an extreme pressure additive for engines. It is postulated that some of these mechanisms can also take place on the drill string and casing.

Zinc dialkly dithiophosphate (ZDDP) consists of zinc bound to diphosphordithioic acid with alkyl or alkaryl ester substituent groups. The alkyl groups are saturated hydrocarbons that vary in length from C3- C12. The basic chemical structure of ZDDP is shown in figure 3. The chemical category of ZDDP can be divided into twelve products that share similar structure types.

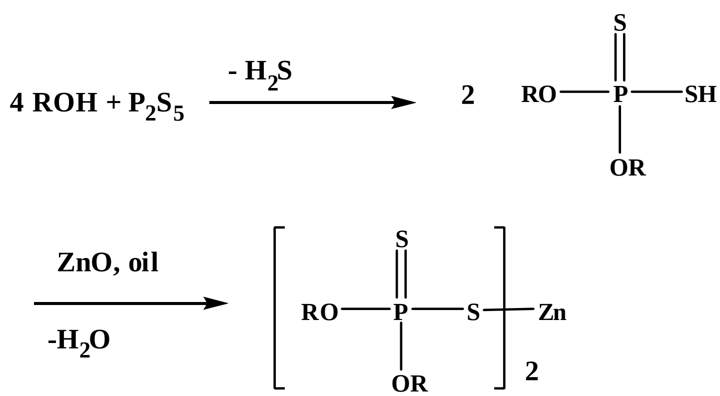


R = C_3 – C_{10} (linear and/or branched) alkyl or C_{12} (branched) alkaryl

Synthesis

The synthesis of ZDDP is straightforward as shown below. Alcohols can be primary, secondary, alkylphenol or mixtures.

Zinc Dithiophosphate synthesis



Mechanism

The history and mechanisms of ZDDP actions in lubricating oil additive application has been reviewed by H. Spikes[6]. ZDDP also serves as an antioxidant and its mechanism has also been reviewed by M. Rasberger[7]. Most of the research and development work were conducted in automotive lubricant applications. The structure activity relationships shown below have been well documented.

ZDDP Structure Performance Comparisons

Parameter	Aryl	Primary Alkyl	Secondary Alkyl	Mixed Alkyl
Thermal Stability	Best	Good	Lowest	Medium
Hydrolytic Stability	Worst	Medium	Best	Good
Antiwear Protection*	OK	Good	Best	OK

* Based on data obtained from Sequence IVA antiwear engine

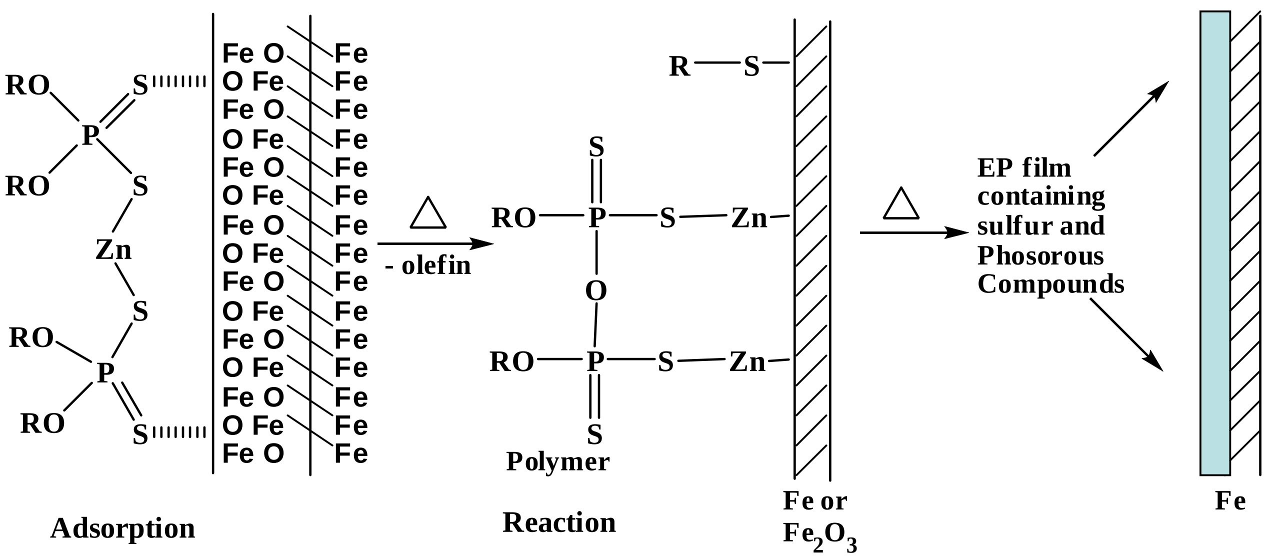
The antiwear mechanism of ZDDP is to react with the metal surface to form a solid protective film and the reaction layer formation follows a four-step process.

- Break in
- Physical or chemical adsorption
- Additive-surface reaction
- Reaction layer growth

The formation of the reaction then prevents welding, friction and surface wear. The tenacity, shear strength and compressive strength of the reaction film also affect the performance, especially under boundary lubrication regime. Adsorption of ZDDP to iron surface occurs first followed by the chemical reaction to form a zinc metaphosphate film. Under extreme pressure, an EP film containing sulfur and phosphorous forms. Further reaction can lead to iron-organosulfide and iron sulfide formation on the surface.

Interactions with Metal Surfaces

Antiwear Mechanisms of Boundary Film Formation by Dithiophosphate Derviatives



Lab Testing

The lubricity of the drilling fluid and lubricant was measured using an Extreme Pressure Lubricity Tester (i.e. surface to surface drag test). This is one of the most common apparatus for screening drilling fluid lubricants (reference or more info on apparatus?). The standard test consists of the following: 150 inch-pounds of torque are applied to two hardened steel surfaces, a block and ring rotating at 60 RPM. The test sample is completely immersed between the ring and block. The apparatus runs for 5 minutes in order to coat the metal test pieces with the sample fluid. The torque adjustment handle is then turned until 150 inch-pounds of torque have been applied to the test block. The machine again runs for a 5 minutes stabilization period. A friction coefficient reading is then taken. Additional readings are taken every 5 minutes until two consecutive readings agreed within ±2 units. Several hundred EP tests were run in the lab to investigate the three main composition variables;

-silicate drilling fluid formulation
-type of ZDDP molecule
-choice of lubricant

Silicate Drilling Fluid

Over the last decade, several different types of silicate-based drilling fluids have come onto the market. These fluids have been formulated to meet specific regional and drilling conditions. The majority of testing was done with potassium silicate since it is the soluble silicate of choice for on-land drilling in North America. The preference for potassium silicate is environmentally driven. As a fertilizer and a low salinity K based product, most jurisdictions allow for on-site and/or surface disposal methods of potassium silicate-based drilling fluids[8,9]. Testing was done with drilling fluids formulated in the lab as well as obtained at various well sites. Table 1a indicates the potassium and sodium silicate used to formulate the lab mud. Table 1b represents a workhorse formulation with a robust concentration of alkali silicate. In all the testing, the drilling was hot rolled for a minimum of 16hrs at 40C.

Table 1a: Properties of potassium and sodium silicate

Silicate	Weight: Ratio SiO_2:Alkali	%Na_2O	% K_2O	% SiO_2	% Solids	Density	pH	Visc cps
K Silicate	2.5	-	8.30	20.8	29.1	1.259	11.3	40
Na Silicate	3.2							

Table 1b: Base Drilling Fluid

Water	920 m
Potassium/Sodium Silicate	80 ml
Xanthan gum	2 g
Starch	2 g
PAC	2 g
Rev Dust	30 g

ZDDP

As was previously discussed, ZDDP is a class of chemicals with 12 distinct constituents. Lab screening looked at different ZDDP molecules prepared from different alcohols, including primary, secondary alcohols and alkylphenol. While not all 12 ZDDP molecules were tested, the selected ZDDP molecules gave similar levels of reduction in CoF under lab conditions. Given similarities in efficacy, the preferred ZDDP molecule was selected using the criteria of cost and HS&E characteristics.

For liquid lubricants, ZDDP was preblended into the lubricant at load levels of 5% and 10% weight to weight. In the case of a 5% loading this would equate to 5.0 g of ZDDP into 95g of lubricant. In all cases, ZDDP easily mixed into the lubricant and showed no signs of separating with time. In the case of solid lubricants such as graphite and polymers, ZDDP was added directly to the drilling fluid.

Lubricant

The industry trend to directional drilling has led to a proliferation of lubricants for water-based drilling fluids and lubricants marketed specifically for silicate-based fluids. Several lubricants were selected from a broad cross section of different chemical families. Tables 2a and 2b indicate the chemical class of lubricant and the effect of ZDDP on reducing CoF in a sodium silicate as well as a potassium silicate drilling fluid. Lubricants were tested in the drilling fluid at a concentration of 2% wt/wt (i.e. 10 g lubricant into 500g drilling fluid). The total amount of ZDDP going into the drilling fluid would be 0.1% for potassium silicate and 0.2% for sodium silicate. Lubricant & drilling fluid were shear mixed and then hot rolled for a minimum of 16hrs at 40C prior to lubricity testing.

Table 2a: Coefficient of Friction in a Sodium Silicate Drilling Fluid

Lubricant	No ZDDP	Lubricant:ZDDP (9:1)
No Lubricant	0.48	0.48
2 % blend of fatty esters and specialties	0.33	0.18
2% phosphate ester	0.43	0.23
2% di-ester	0.46	0.27
2% Treated vegetable oil and paraffin oil	0.34	0.25
2% polyalphaolefin (PAO)	0.48	0.34
2% Vegetable oil additives	0.43	0.36
0.5% High molecular weight, anionic polymer	0.44	0.33

Table 2b: Coefficient of Friction in a Potassium Silicate Drilling Fluid

Lubricant	**No ZDDP**	**Lubricant:ZDDP (9:1)**
Drilling Fluid (No Lubricant)	0.48	
2% ZDDP	0.32	
2 % blend of fatty esters and specialties	0.33	0.18
2% Fatty acid ester	0.37	0.24
2% Biodiesel	0.37	0.26
2% gylcerol monoleate	0.39	0.29
2% Modified vegetable ester	0.33	0.26
2 % blend of fatty esters and specialties	0.36	0.23
2% Phosphate ester	0.38	0.16
2% di-ester	0.18	0.15
2% Graphite	0.38	0.32
2% Sulferized olefin	0.24	0.24
2% Esters, sulphonated additive, phosphate additive	0.17	0.16

With the notable exception of the sulphur-based lubricants, a small amount of ZDDP imparted a significant reduction in CoF over the unmodified lubricant. The lack of efficacy with sulphur-based lubricants is thought to be related to the mechanism of formation of the polythiophosphate film onto the metal surface. ZDDP chemistry suggests that under conditions of temperature and pressure, ZDDP decomposes to give an organosulphur species that play a key role in the formation of the polythiophosphate film. It is believed that the composition and/or quantity of organosulphur lubricant interfere with the proper deposition and formation of a functioning film.

ZDDP was tested as a stand alone lubricant. Results show a modest reduction in CoF supporting the theory that ZDDP is acting more as a lubricant enhancer.

The effect of ZDDP on the lubricant efficiency was tested using a phosphate ester lubricant. For this set of tests, a potassium silicate drilling fluid was taken from a completed well in Alberta.

Table 3: Improved Efficacy: Field Mud containing 6.5% v/v potassium silicate

	CoF Phosphate Ester	**CoF Phosphate Ester+ZDDP (19:1)**
Drilling Fluid (no lubricant)	.45	.45
0.5 % lubricant (wt/wt)	.35	.29
1.0 % lubricant (wt/wt)	.34	.24
2.0 % lubricant (wt/wt)	.29	.21
4.0 % lubricant (wt/wt)	.25	.19

Conclusion

Research is moving from the lab to the field. Field trials will allow metal coupons to be placed on the drill pipe and later examined by X-ray diffraction to determine. This will help determine if the ZDDP is forming a polyphosphate film on metal under downhole conditions. Field trials will also measure the depletion rate of ZDDP.

Based on the lab work to date, it can be concluded;
-ZDDP appears to be a highly effective additive for almost all classes of drilling fluid lubricants.
-it is anticipated that ZDDP modified lubricants will allow the expanded use of silicate-based drilling fluids in deeper, more deviated wells that have traditionally relied on oil-based drilling fluids
-it is thought that ZDDP mechanism for improved lubricity is similar to the way it functions as an antiwear and corrosion inhibitor in engine oil.

While the focus of this paper has been on silicate-based drilling fluids, other water-based systems and oil-based systems have also seen reductions in CoF with the addition ZDDP. The use of ZDDP as a lubricant enhancer is covered by patent

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