

STUDY ON HIGH PERFORMANCE ANTI—WEAR ADDITIVES FROM WATER—SOLUBLE POLYMERIC LUBRICANT*

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ABSTRACT

A series of high performance lubricants of water-soluble polymers with telechelic or star structures has been studied. Their average molecular weights $\bar{M}$ are 1800—6000. The chemical structures of the lubricants are characterized by their hydrophilic groups ($-\text{CH}_2\text{CH}_2\text{O}-$), $-\text{COOH}$, $-\text{OH}$, $-\text{CONH}_2$ and antiwear active elements (S, P, Zn and Mo). The results of assessing for the anti-wear property indicate that this kind of water-soluble polymeric lubricants possesses excellent watersolubility, lubricity and anti-wear property. A preliminary study on the anti-wear mechanism of the polymers is performed by means of electron probe and scanning electron microscopy (SEM).

INTRODUCTION

High water base fluid (HWBF) is composed of 5% additives and 95% water. It was first used in industry in the 1970's as a replacement of mineral oil for hydraulic transmission medium and also as a lubricant for metal machining. It has the advantages of conservation of petroleum resources, non-flammability, low cost and low pollution. However its low viscosity and poor lubrication result

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in reduced service life of hydraulic elements. Hence, it is an important task to develop HWBF hydraulic transmission technology in the efforts to improve the lubricity of HWBF.

At present, oil-soluble anti-wear additives are conventionally added to water in cooperation with surface active agents to form emulsion, so as to improve the lubricant property, but the solution formed is not stable and the effects are not ideal. The anti-wear additives generally used are fatty acid esters and organic compounds containing active elements, i. e. sulfur, phosphorus, chlorine and so on.

This paper reports the high anti-wear and lubricant properties of a series of water-soluble polymers which have the telechelic or star structures containing some active elements (e. g. Zn, Mo, Pr, Sb, N, P and S) and are prepared through the molecule design approach. These high water base fluids containing 0.2 – 1% additive and 99.8% – 99% water possess not only good water solubility and lubricity but also excellent anti-wear properties.

EXPERIMENTAL

Preparation of polymeric lubricants

As we know, a good water-soluble lubricant should contain, besides

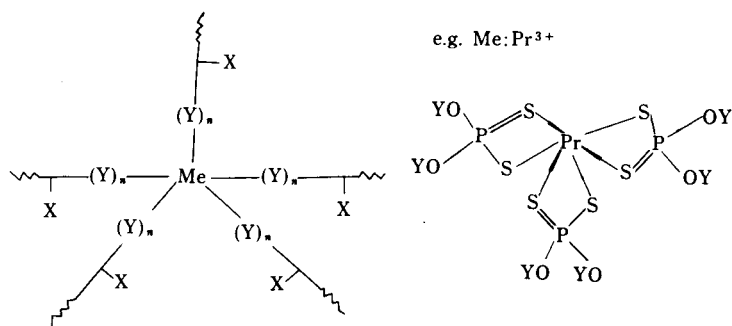


Fig. 1 Schematic illustration of the molecular structures of polymers

Me: Pr, Zn, Mo, B, Sn, Cr and so on.

X: $-H$, $-OH$, $-COOH$, $-\overset{\text{NH}_2}{\underset{|}{C=O}}$ and so on. Y: $-\underset{\text{COOH}}{\underset{|}{CH}}-$, $-(CH_2-CH_2O)-$.

hydrophilic groups, antiwear active elements and an excellent anti-shear structure. Therefore, we can first synthesize some prepolymers with a definite molecular weight containing the hydrophilic groups, $R-(CH_2CH_2O)_n-$, $-OH$, $-COOH$, $-CONH_2$ by means of the anionic polymerization method. The prepolymers then react with P_2O_5 , $SiCl_4$, P_2S_5 and Me_xO_y (Me: Cu, Zn, Mo, Pb, Pr) to form some telechelic and star polymers. According to the above method and referring to the relative patent U. S. P. 4,557,037 we have synthesized a series of water-soluble polymeric lubricants with the molecular structure as shown in Fig. 1.

Their average molecular weights have been measured by VPO method. The elemental analyses and IR analyses have also been carried out.

The lubricants synthesized are:

(1) ZDTP, a polymer with the star structure (Fig. 1) containing the active elements S, P and Zn, of which the center element is Zn, Y: $(-CH_2CH_2O-)_8$, $\bar{M}$:2174.

(2) ZDOP, a polymer with the star structure (Fig. 1) containing the active elements P and Zn, of which the center element is Zn, Y: $(-CH_2CH_2O-)_8$, $\bar{M}$:3757.

(3) MZDTP, a polymer with the star structure (Fig. 1) containing the active elements S, P, Zn and Mo.

Me: $-Mo-Zn$, Y: $(-CH_2CH_2O-)_8$, X: $-COOH$, $\bar{M}$:5400.

(4) MZDOP, a polymer with the star structure (Fig. 1) containing the active elements P, Zn and Mo, Me: $-Mo-Zn$, Y: $(-CH_2CH_2O-)_8$, X: $-COOH$, $\bar{M}$:2300.

Property tests

HWBF is usually composed of 5% additives and 95% water. However, our present HWBF is composed of only 0.2—1.0% additives and 99.0—99.8% water and it still possesses a good lubricant property. Results of the tests on lubricant anti-wear properties are as follows:

(A) Results of four-ball tests in Table 1 show that the anti-wear properties of the lubricants containing the above polymers are superior to those of lubricants with small molecules and that of American commercial products.

(B) Cutting property test of water soluble lubricate additives.

Cutting conditions:

Cutting method end -face cutting for a cylinder

Cutted material $\Phi 29\text{mm}$, thickness 2mm, S45C

Tool MITSUBISHI super hard chip TNPR331 (P super hard STi20,

Fig. 2)

Cutting speed $N=354\text{rpm}$ (30.0m/min, Fig. 2)

Feed $f=0.04\text{mm/rev}$ (Fig. 2)

Table 1 Results of four-ball anti-wear test (load: 400N,
revolve speed: 1500 rpm, revolve time: 30 min)

Sample	40-hydraulic oil	HWBF (1)	HWBF (8)	HWBF (9)	HWBF (10)	HWBF (12)	HWBF (13)
WSD(mm), D_{30}°	0.45	0.73	0.64	0.62	0.45	0.43	0.55

Note: HWBF(1)—0.2% organic sulphur molybdenum and 0.8% auxiliary additive A

HWBF(8)—Sunsol (Sun Refining & Marketing Co. U. S. A.)

HWBF(9)—U. S. P. 4,138,346

HWBF(10)—0.2% ZDTP and 0.8% auxiliary additive A

HWBF(12)—0.2% MZDTP and 0.8% auxiliary additive A

HWBF(13)—0.2% MZDOP and 0.8% auxiliary additive A

A: RNH_2 , its function is to adjust the pH value of the solution to 8—10

WSD: Wear scar diameter

in which HWBF(1), (10), (12), and (13) were synthesized by our laboratory and
HWBF(9) is an American commercial product

Samples:

Additives 7 types of the water-soluble lubricant additives

Consistence 1wt% (25°C pure water solution)

Fluid temperature 25°C

Flooding 6.9ml/min (supply to the cutting point by an injector, (Fig. 2))

Appraised terms:

Tool wears (Flank wear, Fig. 2)

Results of the tool-wear test are shown in Fig. 3. It can be seen from the figure that the order of flank wear is as follows:

$$\text{Excellent} - \begin{bmatrix} \text{MZDOP-4} \\ \text{MZDOP-9} \\ \text{ZDTP-2} \\ \text{MZDTP-2} \end{bmatrix} > (W_{2-1}) \geq \begin{bmatrix} \text{ZDOP-2} \\ \text{MZDOP-71} \\ \text{MZDOP-B}_2 \end{bmatrix} > \begin{bmatrix} \text{pure} \\ \text{water} \end{bmatrix} - \text{bad}$$

From these results it can be seen that MZDOP-4, MZDOP-9, ZDTP-2, MZDTP-2 can be expected to be good anti-wear additives.

(C) Vane pump test (by ASTM D2882). Results of the V 104C vane pump test are shown in Table 2. It can be seen from these results that the order of the vane pump wear for different HWBF is as follows:

Excellent- $[ZDOP] > [ZDTP-2] > [MZDOP-4] > EMBB$

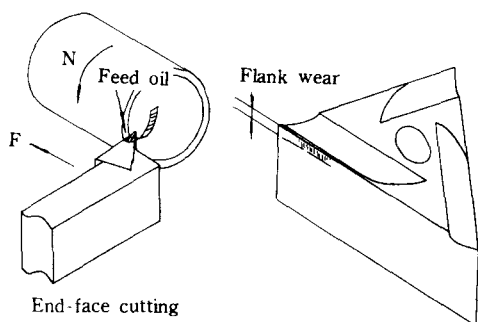


Fig. 2 Flank wear

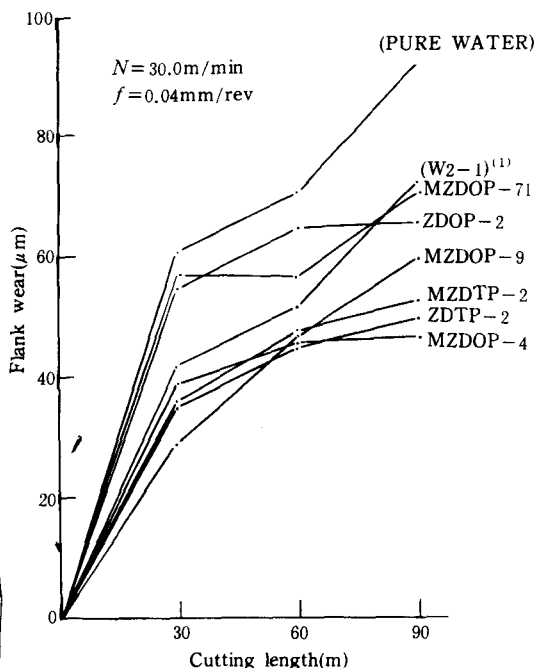


Fig. 3 Tool wear test note: 1 JIS W2-1

Table 2 Vane pump test (by ASTM D2882) (pump: V104c, output pressure: 2.0 MPa, revolve speed: 1200 rpm., temperature: 30°C)

Test time	Wear(mg)					
	24h		96h		240h	
Sampler	Vane	Ring	Vane	Ring	Vane	Ring
HGA	0	156	1	354		
OPZ2A	6	99	7	256	7	824
OPMZG	0	107	6	480	8	680
EMBB	5	264	22	888	10	1031

Note: HGA-0.2% ZDTP+0.8% auxiliary additive A+0.2% corrosion inhibitor+water

OPZ2A-0.2% ZDOP+0.8% auxiliary additive A+0.2% corrosion inhibitor+water

OPMZG-0.2% MZDOP

EMBB-German HWBF (97.5% water),

A: RNH_2 , its function is to adjust the pH value of the solution to 8-10

in which ZDOP, ZDTP-2, MZDOP-4 contain 0.2% Zn, P additive, 0.2% Zn, P, S additive and 0.2% Mo, Zn, P additive, respectively. EMBB is a German HWBF containing 2.5% additive. It is evident that the present additives, ZDOP, ZDTP-2 and MZDOP-4 are superior to EMBB, a German product.

(D) Lubricant experiment of the polymeric additives in the petrolic drilling fluid.

The experimental results are shown in Table 3

Table 3 Lubricant experiment of additives in muds

Sample	Medium	Added quantity(%)	Lubricant properties	
			Lubricant coefficient	Reduced rate of lubricant coefficient (%)
Mud %			0.640	
N. S. B resin	mud	2	0.336	56.3
Zn. P polymer(1)	mud	1	0.1717	73.2
Zn. P polymer(2)	mud	1	0.1789	72.1
ZDOP-2	mud	0.5	0.156	75.6
ZDOP-2	mud	1	0.159	75.2
ZDOP-4	mud	0.5	0.090	85.9
ZDOP-4	mud	1	0.082	87.2

Lubricant properties were measured by using the instrument BAROID E-P mud tester

Preliminary analysis on anti-wear mechanism

On anti-wear mechanism of high water base fluids a few scholars presented some preliminary theories. They postulated that anti-wear property of this type of fluid is due to its viscosity near to that of water and forming boundary lubricant film.

Organic zinc dialkyldithiophosphates is a usual oil soluble, anti-wear, anti-oxidative and anti-corrosive additive. We modified it and rendered it water soluble in order to obtain a high water base fluid.

From the EDS result of a wear scar in Fig. 5 and the SEM photo in Fig. 4, it can be seen that

(1) Molecules of the additives are first adsorbed on the metal surface to form an adsorbed film. Under the boundary lubricant state, the active elements in the film react with the surface metal due to temperature raising at contact parts and having some loading, and a non-crystalline state film is formed. This

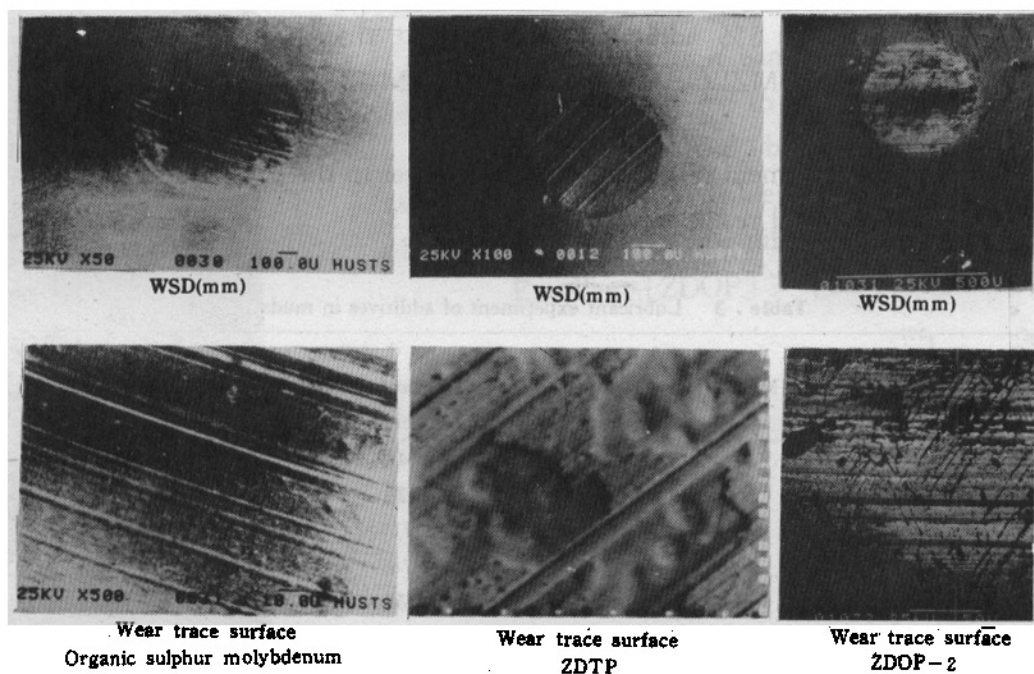


Fig. 4 SEM photo

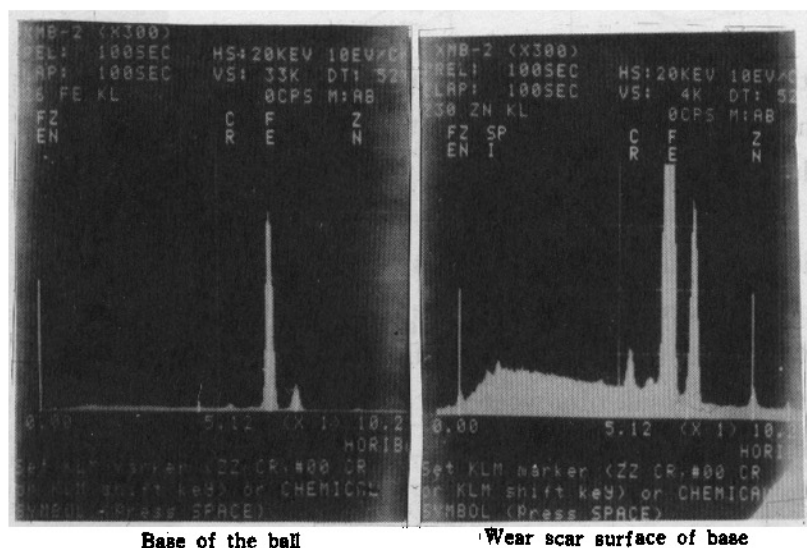


Fig. 5 Electron probe energy spectrum ZDTP-2

strong anti-wear film formed on the wear surface has been confirmed by means of irradiating the surface with the electron beam by the authors and the map distribution of Zn and P on the film has also been measured^[4].

(2) An electron scanning photo of a wear scar of sample ZDTP-2 shows that there exist polymers. Molecular weight of the polymer additives containing Zn, S, P is $\bar{M} = 2174$. Under the boundary lubricant state polymer films have viscoelasticity which is more tough than elastic film and whose thickness is not affected by loading. So the film lubrication is formed.

(3) Under the boundary lubricant state, $-S-Zn-$ and $-O-Zn-$ bonds of the additives containing Zn can be broken. Element Zn can form a solid lubricant film on the metal surface and so the wear is reduced. This inference is based on the following fact: from Table 1 and Table 4 it can be seen that the anti-wear effect of sample ZDTP-2 is the best, and its electron probe energy spectrum of the wear scar shows that the Zn content is 1.12% higher than that of samples MZDOP-5, ZDTP-4 and ZDTP-3.

(4) From Table 4, it can be seen that there exists some correlativity between the magnitude of the wear scar diameter and the content of the active elements. Elements N, S, P, Zn have a synergistic effect in improving anti-wear properties.

Table 4 Electron probe energy spectrum

Sample	Element content on wear scar surface			Diameter of wear scar D_{30}^{40} (mm)
	P(%)	S(%)	Zn(%)	
MZDOP-5	0.00	0.00	0.66	0.67
MZDOP-4	0.49	0.00	0.96	0.44
ZDTP-3	0.39	0.16	0.08	0.67
ZDTP-2	0.28	0.00	1.12	0.43
ZDTP-4	0.21	1.95	0.00	0.70

CONCLUSION

It can be seen that the anti-wear properties of HWBF containing our additives are superior to those of HWBF which are available domestically and internationally. It can be expected that HWBF containing the additives reported in this paper could be used as a replacement of mineral oil for hydraulic transmis-

sion medium, a lubricant for metal machining and an additive of the petrolic drilling fluid. Its application prospects are promising.

Keywords:

Antiwear; Lubricant; Friction; Water-soluble polymer; Star structure

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