Rheological, Stability and Antiwear Properties of Water-in-Oil Emulsion Hydraulic Fluids

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Water-in-oil 에멀젼 압축유의 유동성, 안정성 및 내마모성에 관한 연구

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Abstract—제철산업과 광산산업에서 난연성 압축유로써 water-in-oil (W/O) 에멀젼의 사용이 점차 증가하고 있다. 이러한 관점에서, 기유의 점도, 물과 오일의 배합비율 및 음이온성 emulsifier의 농도 변화에 따른 W/O 에멀젼의 점도, 안정성 및 내마모성을 조사하였다. 에멀젼의 점도는 기유의 점도에 비례해서 증가하였으며 물의 배합비율에 따라 지수함수적으로 증가하였다. 에멀젼의 안정성은 에멀젼 점도와 대수함수 관계임을 보여주고 있다. 에멀젼 점도와 다른 요소와의 상관관계는 매우복잡하며 이러한 상관관계를 해결하기 위해서는 더 많은 연구가 진행되어야 한다. 에멀젼의 점도는 에멀젼의 내마모성에 거의 영향이 없으며 기유의 점도에 따라 영향을 받으며 물의 배합비가 너무 커지게 되면 마모에 심각한 나쁜 결과를 초래하였다.

1. Introduction

There has been a growing legistative mandate for the use of fire-resistant fluids as lubricants in applications where there is a special fire hazard, as in the mining and steel industry. Synthetic fluids such as phosphate esters and perfluoropolyethers have been developed but these tend to be significantly more expensive and toxic than mineral oils. In view of this, the alternative approach has been to render combustible oils less flammable by including a high percentage of water either by preparing water-in-oil (W/O) or oil-in water (O/W), or by dissolving water-in-suitable polyalkyleneglycol (W/G). These produce reasonably inexpensive fire-resistat lubricants, although their use is limited to temperatures below the boiling point of water and above pour point. Additionally, each of the fire-resistant fluids desired has its own performance deficiencies such as rheological property and stability for the (O/W) emulsion fluid, stability for the (W/O) "invert" emulsion fluid, and antiwear property and health   hazards for the (W/G) fluid. In spite of these limitations, the (W/O) "invert" emulsion fluid is widely used as fire-resistant hydraulic fluid in the mining and steel industry because of its good rheological, corrosion and antiwear properties [1]. Much has been invented, innovated and reported in (W/O) emlusions hydraulic fluids [2,3]. However, to the best of authors knowledge, no systematic work has been done on this class of hydraulic fluids.

The present work, therefore, is an attempt to study the emulsion viscosity, stability and antiwear properties of (W/O) "inverted" emulsion hydraulic fluids, particularly relating to the effects of water concentration, base oil viscosity and emulsifier content. Little such information is available in the literature, although the knowledge on these effects is generally considered critical in assessing the performance capability of (W/O) emulsion hydraulic fluids.

2. Experimental

Water-in-oil emulsion hydraulc fluids were pre-

Table 1. Physical Property of Base Oils

	Oil A	Oil B	Oil C
Specific Gravity @ 15°C	0.846	0.863	0.871
Kinematic Viscosity, cSt @ 40°C	11.72	24.55	36.30
Pour Point, °C	-10	-7	-4

pared from distilled water and mineral oils which contain functional additives such as antiwear agent, corrosion inhibitor and pour point depressant. The emulsion fluids were stabilized with an anionic emulsifier by passing through a Greerco laboratory homogenizer/mixer for 10 minutes while maintaining their temperature below 60°C. An emulsifier concentration of 5.0 percent by weight was used throughout this study unless otherwise specified. Typical properties of the test oils used are shown in Table 1.

Emulsion viscosity and antiwear characteristics were measured using ASTM Method D445 (at 40°C) and D4172, respectively. Emulsion stability was determined in the following manner: Place an emulsion sample in a 100 mL graduated cyclinder and store it in an oven at 93°C. Check the sample on a daily basis. Terminate the test and record the number of days either when the percent water separation is 10 or when the percent of oil and water separation is 25 whichever occurs first. The determinations were made with the emulsions prepared from at least two separate batches for each sample.

3. Results and Discussion

Initial experiments investigated the effect of mixing time and shear rate on the property of emulsions produced with a 0.369 volume fraction of water in Oil B (24.55 cSt). Results are plotted in Fig. 1. The plot shows that the effects of longer mixing time and higher shear rate were to reduce the number of larger water droplets, thereby producing a stable emulsion. Only relatively small changes in the emulsions were observed after about 10 minutes mixing with 100 percent power input, so this was adopted as a standard manufacturing proceure throughout this study.

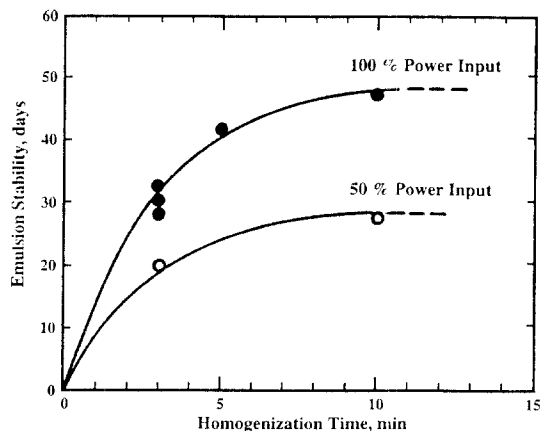Fig. 2 is photomicrograph of a typical emulsion sample. Droplet sizes were estimated to be 1.0 - 1.5 μm.

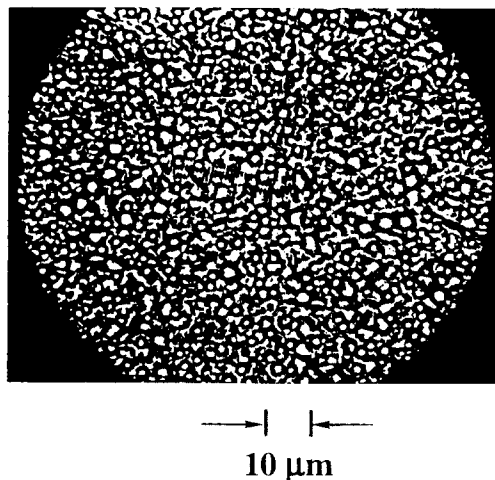**Fig. 1. Effect of homogenization time on emulsion stability.**

$$10\ \mu m$$

Fig. 2. Typical photomicrograph of (Water/oil) emulsion.

3-1. Effects of Oil Viscosity and the Volume Fraction of Water

Fig. 3 represents the variation of emulsion viscosity (η_e) as a function of oil viscosity (η_o) for a given the volume fraction (φ) of water. The emulsion viscosity progrssively rises with increasing oil viscosity for a given water concentration. An straight-line relationship implies that the emulsion viscosity is directly proportional to the oil viscosity. The straight lines are constant irrespective of changes in the volume fraction of water.

The results from Fig. 3 are re-plotted in a semi-log chart to more clearly illustrate the effect of the
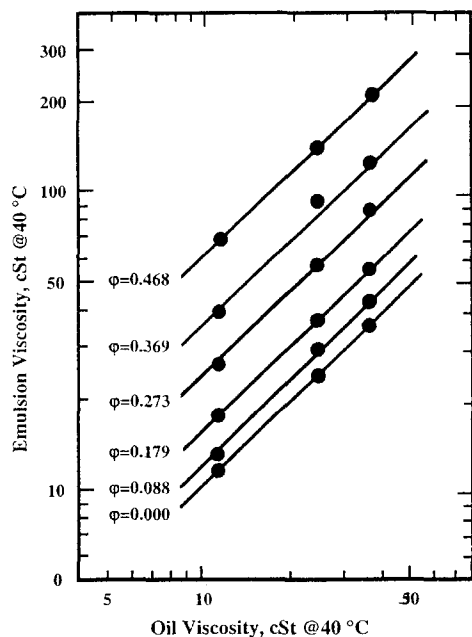
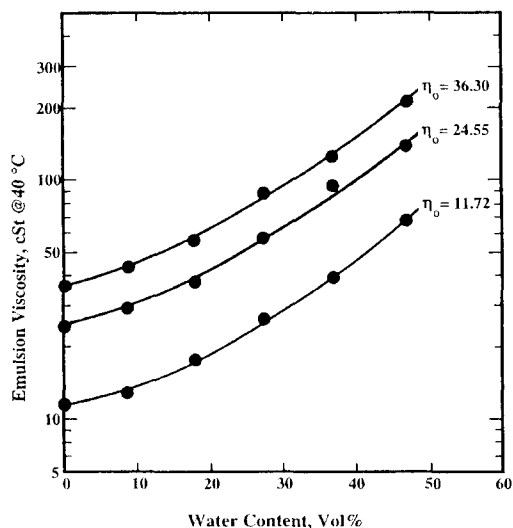**Fig. 3. Effect of oil viscosity on emulsion viscosity.**

Fig. 4. Effect of water content on emulsion viscosity.

volume fraction of dispersed water phase on emulsion viscosity for a given oil viscosity. As given in Fig. 4, the emulsion viscosity, unlike depicted in Fig. 3, increases exponentially with increasing the volume fraction of water for all three base oils, indicating that the viscosity of (W/O) emulsions is pri-

Table 2. Effective viscosity relations

Theory	Relationship	
Einstein	$\eta_e/\eta_o = 1 + 2.5\varphi$	$\varphi \leq 0.02$
Eilers	$\eta_e/\eta_o = \left[1 + \dfrac{1+2.5\varphi}{2(1-1.35\varphi)}\right]^2$	
Sibree	$\eta_e/\eta_o = \dfrac{1}{1-\sqrt[3]{1.3\varphi}}$	
Empirical	$\eta_e/\eta_o = 1 + \dfrac{2.5\varphi}{1-1.63\varphi}$	$1.35 < f < 1.91$

marily a function of the volume fraction of the dispersed phase. In addition to the effects of oil viscosity and the volume fraction of dispersed phase, variations in the emulsifier and droplet size have some impact on the emulsion viscosity. But, it has been reported that these seem to be second-order effects, when the concentration of the dispersed phase is high [4].

3-2. Emulsion Viscosity

As indicated in the previous section, the usual way of characterizing the rheological behavior of (W/O) emulsions is through the use of emulsion viscosity. The emulsion viscosity is related to the viscosity of continuous phase (oil) by a factor which is a complex function of the volume fraction of water.

Several well-known emulsion viscosity equations are given in Table 2 and graphically shown in Fig. 5 along with the experimental data sourced from Fig. 3. The classic work of Einstein [5], derived on hydrodynamic grounds, is valid only for dispersed phase fractions of below 0.02. Although a variety of "improved" models [6,7] were developed for higher concentrations, they all retain the initial assumption that the dispersed phase is rigid. Thus, none of the models takes any account of the viscous properties of dispersed phase in a (W/O) emulsion.

When the predictions of various theoretical models are compared with the experimental emulsion viscosity measurements, both Sibree and Eilers models tend to overestimate the emulsion viscosity at the entire concentration ranges of dispersed phase. On the other hand, Einstein equation accurately predicts the emulsion viscosity at lower concentrations, but it largely underestimates at higher concentrations.
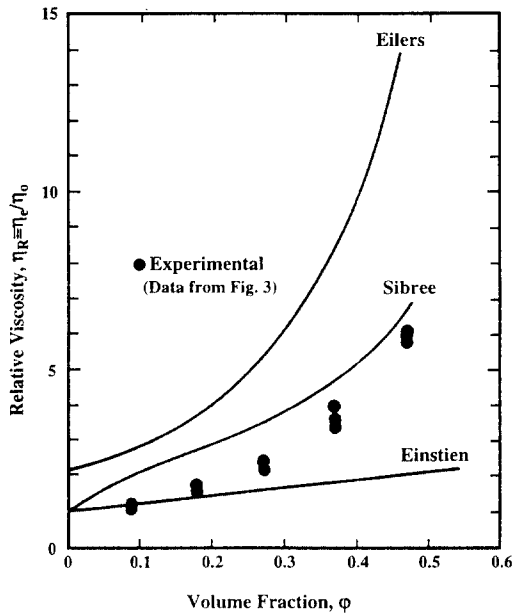
Because of the discrepancies, several semi-em-

Fig. 5. Relate viscosity as a function of volume fraction of dispersed phase.

Fig. 6. Relation between $\left(\dfrac{\eta_e}{\eta_o} - 1 \right)$ **and** $\left(\dfrac{\varphi}{1-1.63\varphi} \right)$.

pirical equations have been proposed which take the general form [8],

$$\frac{\eta_e}{\eta_o} - 1 = \frac{a\varphi}{1 - f\varphi} \qquad (1)$$

where a is a constant, usually of value 2.5 and 1 - $f\psi$ is the "free volume" of continuous phase. When Equation (1) was applied to the present emulsion viscosity study with a swelling factor value, f, of arbitrarily selected 1.63 (Equation (1) is valid only for 1.35< f<1.91). With these selected values, Equation (1) then becomes

$$\frac{\eta_e}{\eta_o} - 1 = \frac{2.5\varphi}{1 - 1.63\,\varphi} \qquad (2)$$

A comparison between the present experimental observations and Equation (2), shown in Fig. 6, indicates that the equation accurately predicts the emulsion viscosity. Accordingly, Equation (2) appears well suited for use in estimating the viscosity of (W/O) emulsion up to an "inversion" point of this type of emulsions. The "inversion" point may come when (1-1.63 φ) approaches zero. It must be remineded, however, that the value of f may vary dependent upon the emulsifier, mixing time and shear rate employed.
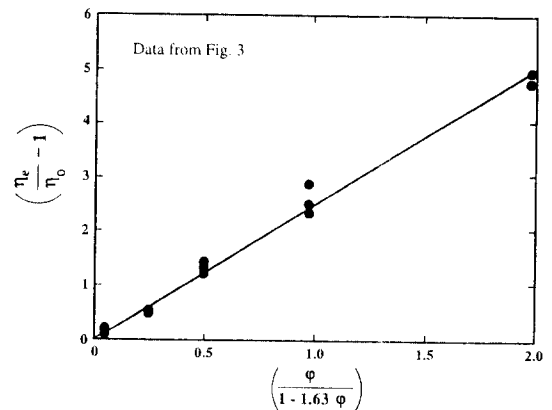
To investigate the viscosity change in (W/O) emulsions during aging, three emulsion samples with the water volume fractions of 0.088, 0.273 and 0.378 were aged at 25°C for 30 days. Relative viscosity (η_e/η_o) versus aging time was used to characterize emulsion stability, which is shown in Fig. 7. The relative viscosity data shows that the emulsion viscosity hardly changes for the water volume fraction of 0. 088, whereas it decreases about 10 percent for the water volume fraction of 0.378. All in all, little change in the emulsion viscosity on aging was observed with the emulsion samples, indicating that they provide excellent emulsion stability.

3-3. Changes in Emulsion Stability on Emulsion Viscosity

To examine the emulsion viscosity effects on emulsion stability, the stability was determined on many emulsion samples prepared by varing the volume fraction of water, the oil viscosity and the emulsifier concentration. Test results are presented in Fig. 7 by plotting in a log-log chart the stability as a function of emulsion viscosity for different emulsifier concentrations. The results give a straight line relation for a given emulsifier concentration.

According to Fig. 7, the emulsion stability (E.S.) is related which takes an empirical form:

$$E.S. = b\,(\eta_e)^k \qquad (3)$$

where b and k are constants which may be related to emulsifier concentration in a certain form. By substituting Equation (2), Equation (3) now becomes
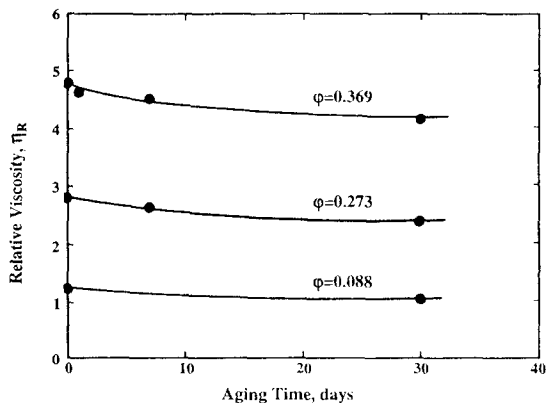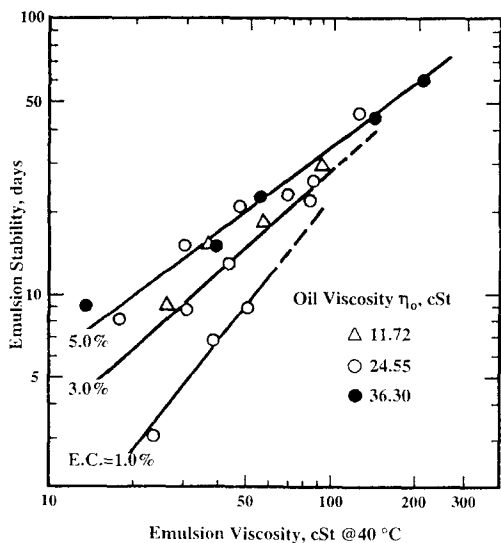
Fig. 7. Changes in relative viscosity on aging.

Fig. 8. Change in emulsion stability on emulsion viscosity.

$$E.S. = b\left[\eta_o\left(1 + \frac{2.5\varphi}{1 - 1.63\,\varphi}\right)\right]^k \quad (4)$$

Using Fig. 7, Equation (4) for an emulsifier concentration of five percent can be written as

$$E.S. = 0.81\left[\eta_o\left(1 + \frac{2.5\varphi}{1 - 1.63\,\varphi}\right)\right] \quad (5)$$

With Equation (5), E.S. values can be estimated if η_o and φ values are given. Similar expressions can be developed for other emulsifier concentrations. It is clear from Fig. 7 that the emulsifier concentration
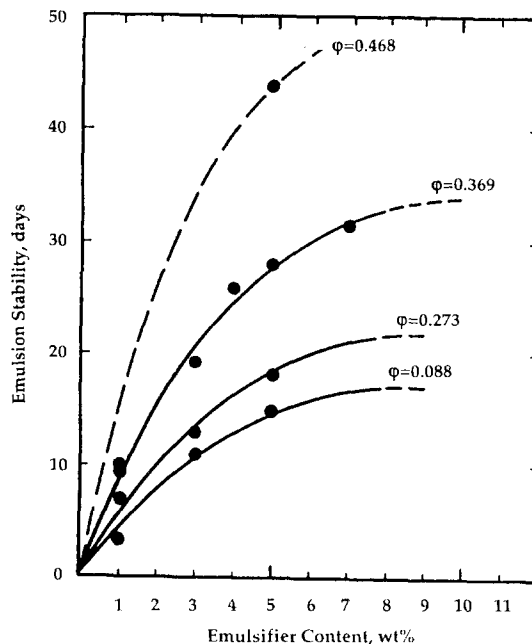

Fig. 9. Influence of emulsifier content on stability of emulsions with different amounts of dispered phase.

plays a major role in the determination of emulsion stability. In order to expand and generalize the application of Equation (4), more extensive study is needed to include other emulsifier systems, manufacturing procedure and other related factors.

3-4. Emulsifier Concentration Effects on Emulsion Stability

To further examine the effects of emulsifier concentration on emulsion stability, a series of fresh emulsion samples were produced with Oil B varying emulsifier concentration and the volume fraction of water. Stability data are presented in Fig. 9.

Fig. 9 shows that the emulsion stability improves and appears to approach an asymptotic value for a given water content with increasing emulsifier concentration. For example, the asymptotic values are 15 days at five percent emulsifier and 0.088 fraction of water, and 33 days at seven percent emulsifier and 0. 369 water volume fraction. Also, it can be seen from Fig. 8 that the emulsion stability dramatically improves with increasing the volume fraction of water for a given emulsifier concentration. This dramatic improvement may be attributable mainly to the in-

Table 3. Effect of water content on antiwear properties

	A	B	C	D	E	F
Water Content, vol%	0.0	8.8	17.9	27.3	36.9	46.8
Viscoity, cSt @ 40°C	24.65	32.95	40.34	57.32	89.52	140.7
Four-Ball Wear Test, mm scar						
(20 kg, 1200 rpm, 49°C, 1 h)	0.38	0.45	0.50	0.50	0.55	0.74
(40 kg, 1200 rpm, 49°C, 1 h)	0.62	0.65	0.80	0.83	0.85	1.02
Vickers 104C Vane Pump Wear Test						
(10 Mpa, 65°C, 100 h), mg wt loss 57/72	57/72	61	56	74	123	514

crease in emulsion viscosity. Equation (4) clearly signifies this relation.

3-5. Antiwear Property

A series of the emulsion samples prepared using Oil B at different volume fraction of water was evaluated to investigate water content effects on the antiwear characteristics of (W/O) emulsion hydraulic fluids. In addition to Four-Ball wear test (ASTM D 4172), Vickers V-104C vane pump wear test (ASTM D2882) was used to rate the antiwear property. Test results are summarized in Table 3.

Four-Ball wear results show that the wear scar diameter increases gradually with increasing water content: Under 20kg load, the wear scar is mildly affected by the increase in water content, even though the emulsion viscosity almost quarterlipled. But, the wear finally starts to accelerate when the water content reaches 46.8 percent. Under 40kg load, the wear shows similar trend, but higher levels of wear.

Vickers V-104C vane pump wear also demonstrates similar characteristics, showing that large increases in the emulsion viscosity has a minor effect on pump wear. But, the pump wear starts to rise rapidly when the water content exceeds 36.9 percent.

These results suggest that the emulsion viscosity has little effect on the wear characteristics of (W/O) emulsion hydraulic fluids; i.e. the oil viscosity plays a key role in the wear behavior, not the emulsion viscosity. On the other hand, at higher levels of water content, the water has an adverse effect on the wear chracteristics of (W/O) emulsions. It is unclear how the water damages surface of contact points in the Four-Ball and Vickers vane pump wear tests. It may be speculated that turbulences in the inlet region of the contact point could mold the water droplets into flat platelets which will be drawn through the contact, thereby causing surface damages.

Hamaguchi et.al [9] concluded from the first major study of the elastohydrodynamic (EHD) properties of (W/O) emulsions that the EHD film thickness was determined almost entirely by the properties of base oil so that although, when water was added, bulk emulsion viscosity increased, this had no effect on EHD film thickness, thereby minor impact on wear protection.

4. Conclusions

The rheological, stability and antiwear properties of (W/O) emulsion hydraulic fluids were investigated under various conditions by systematically changing base oil viscosity, the volume fraction of water and emulsifier concentration. The investigation reveals the followings:

1. The emulsion viscosity rises exponentially with increasing the volume fraction of water for a given oil, while it increases progressively with increasing the viscosity of base oil.

2. A semi-empirical equation has been proposed for use in estimating the viscosity of (W/O) emulsions. The equation can predict with a reasonable accuracy the emulsion viscosity if the viscosity of base oil and the volume fraction of water are known.

3. The emulsion stability is a logarithmic function of the emulsion viscosity. Their inter-relation appears to be very complex. The types of emulsifier and their concentration probably play an important role in the emulsion stability. Also, manufacturing (mixing time and shear rate) is a factor as well.

4. The emulsion viscosity has little effect on the wear characteristics of (W/O) emulsion hydraulic fluids. The wear was impacted primarily by the viscosity of base oil. However, at the high level of water content, the water has a marked adverse effect on the wear.

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