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Influence of the Structure of Polysulphide Additives on the Shiftability of Manual Transmissions

Abstract

The shiftability of manual transmissions is known to be strongly affected by the nature of the transmission oil. When conventional sulphur–phosphorus (SP) additives are used in the oil, gear clashing, sticking, and other problems occur. As reported previously, these problems are caused mainly by the polysulphide used in the SP additives. This paper reports on a study of the effect of the structure of the polysulphide's hydrocarbon chain on the synchromesh characteristics. It is found that polysulphides with long hydrocarbon chains have high kinematic friction coefficients and low static friction coefficients. It is also shown that this phenomenon occurs because of the adsorption of the polysulphide on to the copper alloy of which the gear synchroniser ring is made. By using a polysulphide with a long hydrocarbon chain it is possible to develop transmission oils that have superior load-carrying capacity and better shiftability even when compared with the latest transmission oils that contain metallic detergents.

Keywords

shiftability, polysulphide, manual transmission, additive

INTRODUCTION

Shiftability is one of the principal types of performance required of manual transmissions.[1,2] It is well known that the transmission oil affects this. When additives are selected during the development of the oils, it is necessary to consider not only their extreme-pressure (EP) properties and oxidation stability but also the frictional properties.[3]

The shiftability is greatly affected by the frictional properties between the synchroniser ring and gear cone. During the first stage of shifting, the gear and the synchroniser ring, which have been rotating at different speeds, are synchronised to the same speed. At this stage a high kinematic friction coefficient (μ_d) means a shorter shifting time or less shifting force. A low μ_d sometimes causes clashing due to non-synchronous

Table 1 Structure of polysulphides

Designation of polysulphide	*Structure*	*Carbons in R*	*Main R structure*
A	R–S_x–R R–S_x–R–S_x–R	4	Isobutene
B	R–S_x–R	4	Isobutane
C	R–S_x–R R–S_x–R–S_x–R	8	Isobutene dimer
D	R–S_x–R	9	Propylene oligomer
E	R–S_x–R	12	Isoparaffin
F	R–S_x–R	16–18	Linear paraffin

Table 2 Conditions of the synchroniser test

	Inertia test	μ_s*	μ_d†
Oil temperature, °C	80	80	80
Gear rotating speed, rpm	1200	1	1200
Load, N	400	400	400
Inertia, kg m^2	0.06	–	–
Pressing time, s	0.5	2	0.5
Release time, s	9	5	1

*The value of μ_s was the maximum friction coefficient after the inertia test and after the 1 rpm slip test was begun. The inertia test was run 100 times.
†The values of μ_d was the average friction coefficient in the 0.5 s fixed-speed slip test at 1200 rpm after the measurement of μ_s. The μ_d measurement was run 10,000 times.

speed conditions between the synchroniser sleeve and gear clutching teeth. When the synchronisation has finished and the gear is fixed in place, the sleeve must move the stationary synchroniser ring slightly, so a low static friction coefficient (μ_s) is required. A higher μ_s causes a 'second bump' or 'sticking' because of the greater effort required for movement.

Sulphur–phosphorus (SP) additives are commonly used in gear oils. These additives have very good antiwear and antiseizure properties. However, in manual transmissions, SP additives tend to cause gear clashing and/or sticking during shifting. In a previous study, it was reported that such phenomena are caused by the polysulphide used in the additives.[4] If a polysulphide having good frictional properties for a synchromesh mechanism can be found, gear oils with good shiftability and superior load-carrying capacity can be developed.

In this paper, the effect of the length of the polysulphide's hydrocarbon chain on the frictional properties between the gear cone and synchroniser ring is investigated, and the mechanism of this effect is discussed. This study seeks ways to improve the shiftability of manual transmission gear oils with a polysulphide that could improve the EP properties.

EXPERIMENTAL

The structures of the polysulphides used in this study are summarised in **Table 1**. Polysulphides A and B are conventional additives that are commonly used in gear oils. The others are rarely used as additives in gear oils but have been commercialised for other applications. The base oil was a hydrocracked oil with a viscosity of 4.1 mm^2/s at 100°C and a viscosity index (VI) of 123. The concentration of polysulphide in the base oil was adjusted to a sulphur content of 0.5 wt.%.

A synchromesh tester was used to measure the kinematic and static friction coefficients between a gear cone made of steel and a synchroniser ring made of copper alloy. **Table 2** lists the test conditions. The kinematic friction coefficient and the static friction coefficient were measured with this tester.

LFW-1 was used to study the causes of the frictional properties. The rings used as the test specimens were as prescribed in ASTM D 2714. Steel blocks having a Rockwell hardness of HRC 60 and copper alloy blocks specified by JIS C 6782 were used. The tests were conducted at 25 rpm, a load of 50 N, and an oil temperature of 80°C for 3 min while the frictional force was measured. The shapes and elemental compositions of the wear scars on the surfaces of the tested blocks were measured.

RESULTS

The properties of the test oils used for measuring the frictional performance are given in **Table 3** (overleaf). The letter

Table 3 Oils for testing frictional properties of polysulphides

	S-A	*S-B*	*S-C*	*S-D*	*S-E*	*S-F*
Viscosity, mm^2/s						
at 40°C	18.00	17.65	18.22	18.07	18.07	17.28
at 100°C	4.04	4.00	4.06	4.04	4.04	3.94
S, wt.%	0.52	0.51	0.51	0.57	0.55	0.56
LWI*, N	394	412	347	477	606	326
WL*, N	2452	3089	3089	3089	3923	2452
Wear-scar diameter†	0.8	0.84	0.69	0.77	1.84	0.83

*ASTM D 2783.
†ASTM D 4172, 1800 rpm, 392 N, 1 h.

following the 'S-' in each name indicates the corresponding polysulphide in **Table 1**. **Table 3** also gives the results of four-ball tests. The sulphides in S-A and S-B are conventional types, while the other polysulphides have equal or superior load-carrying capacity to the conventional polysulphides.

Synchroniser test

Figure 1 shows the kinematic friction coefficient at 1200 rpm during the synchroniser test. The kinematic friction coefficient decreased only with S-A and S-B, which contained conventional polysulphides having shorter hydrocarbon chains. The other polysulphides with longer hydrocarbon chains maintained higher kinematic friction coefficients.

Figure 2 shows the wear behaviour of the synchroniser ring during the test. Wear was heavy only with S-A and S-B, and corresponded to the behaviour of the kinematic friction coefficient. Thus the decrease in the kinematic friction coefficient seems to be caused by the synchroniser ring wear. The wear is thought to be caused by the different structures of the polysulphides' hydrocarbon chains; a short hydrocarbon chain causes increased wear, resulting in a decrease in the kinematic friction coefficient due to conformity.

Figure 3 (p. 138) shows the results of the static friction coefficient measurements. Only S-F, which contained the polysulphide that had the longest hydrocarbon chain, showed a low static friction coefficient. Thus, while a hydrocarbon chain with eight or more carbons was sufficient for preventing

Figure 1 Kinematic friction (μ_d) test

● S-A
■ S-B
□ S-C
▲ S-D
◇ S-E
○ S-F

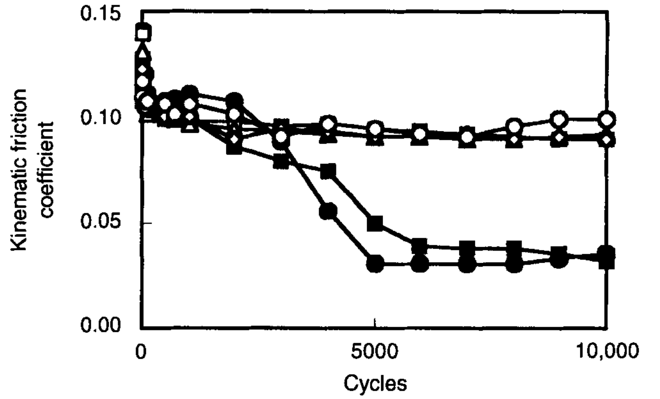


Figure 2 Wear of synchroniser ring during kinematic friction test

● S-A
■ S-B
□ S-C
▲ S-D
◇ S-E
○ S-F

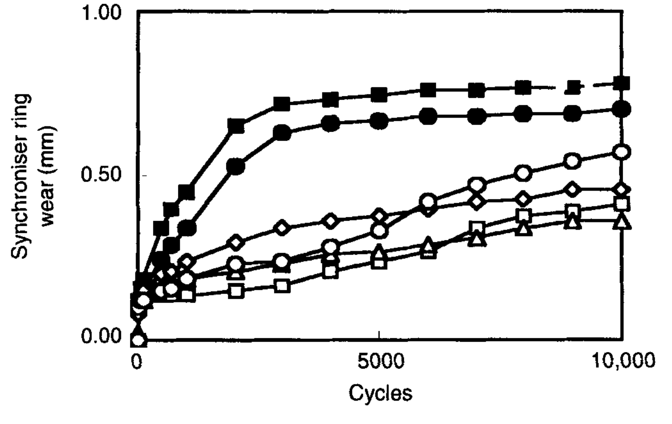
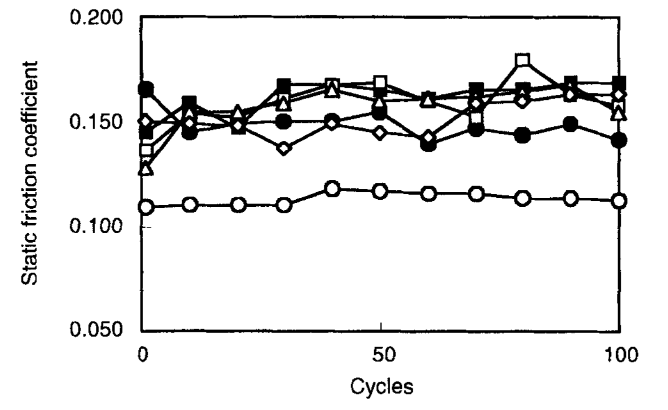


Figure 3 Static friction (μ_s) test

● S-A
■ S-B
□ S-C
▲ S-D
◇ S-E
○ S-F



synchroniser ring wear, even one with 12 carbons was not enough to reduce the static friction coefficient. These results show that a hydrocarbon chain with at least 18 carbons is needed to reduce the static friction coefficient.

LFW-1 test

An LFW-1 friction test was conducted in order to determine the frictional mechanism in the synchroniser test. The test conditions were as described above. The oils used in the test were S-A, which was made with a four-carbon polysulphide that reduced the kinematic friction coefficient in the synchroniser test but had a high static friction coefficient, and S-F, which was made with an 18-carbon polysulphide that maintained a high kinematic friction coefficient and a low static friction coefficient.

Figure 4 shows the results of measurements of the friction coefficient using a steel block. In this case, the friction coefficient of S-A was greater than that of the base oil and slightly less than that of S-F, but the overall behaviour was nearly the same and the changes over time were small.

Figure 5 shows the results of a test using a block made of copper alloy that is nearly identical to the material of the synchroniser ring. In this case, S-A showed nearly the same frictional properties as the base oil, while S-F maintained a lower friction coefficient. The frictional characteristics of the copper alloy block are the same as the static friction coefficient

Figure 4 Friction coefficient on LFW-1 with steel block

◆ Base (steel)
● S-A (steel)
○ S-F (steel)

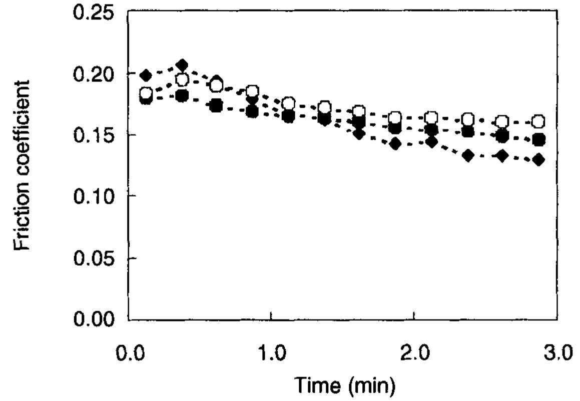


Figure 5 Friction coefficient on LFW-1 with copper alloy block

◆ Base (Cu)
● S-A (Cu)
○ S-F (Cu)

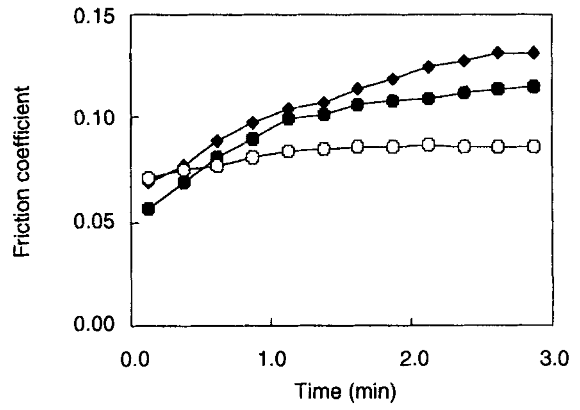


Table 4 Wear depth after LFW-1 test

	Steel block, μm	*Cu block, μm*
Base	1.7	6.1
S-A	0.4	5.7
S-F	0.8	6.6

of the synchroniser ring. Thus, it is believed that the frictional properties of polysulphide in the synchroniser test are caused by the adsorption or the reaction of the polysulphide on to the surface of the synchroniser ring, which is made of copper alloy.

Table 4 shows the results of measurement of the wear depth on the blocks after the LFW-1 test. On the steel block, there was a large amount of wear with the base oil alone, but little wear with S-A or S-F, which contained polysulphide. The friction coefficient with the base oil decreased during the LFW-1 test. This frictional behaviour seems to be caused by the enlargement of the hydrodynamic lubrication region. While there was slightly more wear with S-F than with S-A, the friction coefficient with S-F was higher. Thus it is thought that the enlargement of the hydrodynamic lubrication region caused by this wear did not have so much effect on the friction coefficient with S-A and S-F.

On the copper alloy block, there was a large amount of wear compared with the steel block. However, the friction coefficient with each oil increased during the test. Therefore it seems that the effect of enlargement of the hydrodynamic lubrication region on the friction coefficient can be ignored in the discussion of the frictional properties of the polysulphides. It is thought that the low friction coefficient with S-F depends on the properties of the polysulphide F. However, it was not possible in this test to simulate the wear to the synchroniser ring in the synchroniser test. This test was conducted for only 3 min, which may have been too short, or the load during the test may have been too small.

Table 5 shows the results of an X-ray photoelectron spectroscopy (XPS) analysis of the wear surface of each block after the LFW-1 test. To avoid any effect from contaminants on the surface, the elemental concentrations were measured after 1 min of argon sputtering. More sulphur was present on the

Table 5 Elements* on wear surface after LFW-1 test

Element	*Block*	*Base*	*S-A*	*S-F*
S	Steel	–	1.0	0.1
	Cu	–	3.5	0.6
C	Steel	38.7	51.5	13.7
	Cu	9.5	11.9	6.3
O	Steel	16.5	10.5	12.3
	Cu	18.1	4.7	4.7

*XPS analysis: at.% after 1 min of argon sputtering.

Table 6 Properties of transmission oils containing polysulphides

		RGO	*RGO-SA*	*RGO-SF*
Viscosity, 40°C	mm^2/s	66.41	66.43	65.05
Viscosity, 100°C	mm^2/s	13.65	13.62	13.41
TAN	mg KOH/g	2.38	2.42	2.46
TBN	mg KOH/g	5.25	5.15	5.04
Ca	wt.%	0.23	0.23	0.23
P	wt.%	0.14	0.14	0.14
Zn	wt.%	0.12	0.12	0.12
S	wt.%	0.39	0.84	0.83
N	wt.%	0.01	0.01	0.01

copper alloy surface than on the steel surface, thus supporting the hypothesis that the polysulphide had a major effect on the copper alloy. The block tested with S-F had less sulphur and less carbon than the S-A block, suggesting that S-F has either less reactivity or less adsorptive force than S-A. Polysulphide A, because it has higher reactivity with copper alloy, may form copper sulphides more easily, thus bringing about increased wear. This hypothesis needs to be confirmed in the future through adsorption tests and detailed analyses of the substances formed on the metal surface.

Table 7 Extreme-pressure properties

	RGO	*RGO-SA*	*RGO-SF*
LWI* (N)	481	606	620
WL* (N)	2452	2452	3089
LNSL* (N)	490	490	490
Wear-scar diameter† (mm)	0.34	0.36	0.32

*ASTM D 2783.
†ASTM D 4172, 1800 rpm, 392 N, 1 h.

An attempt was made to measure the reflective infrared spectrum in order to determine the condition of the adsorbed polysulphide. However, a spectrum could not be obtained, perhaps because not enough polysulphide had been adsorbed.

While there is no definite proof, it does seem clear that polysulphide adsorbs on the copper alloy surface and that the polysulphide's hydrocarbon chain affects the synchromesh characteristics.

Performance of transmission oil

Since, as discussed above, polysulphide F reduces the static friction coefficient in the synchroniser test without reducing the kinematic friction coefficient, it could perhaps be used in the development of manual transmission oils that have superior synchromesh characteristics when compared to oils made with conventional polysulphides.

Table 6 shows the properties of oils containing polysulphides A and F when the oils were used as manual transmission oils. The starter oil, RGO, was blended from 75W–90 base oil, VI improvers, and additives that provide the performance required of transmission oils. RGO contained calcium sulphonate and zinc dialkyldithiophosphate (ZDTP), which are effective for improving the synchromesh characteristics.[5] RGO also contained a phosphorus-type additive with ZDTP as EP agents, but it contained no sulphur-type additives. RGO-SA and RGO-SF were blended from RGO with the addition of 0.5 wt.% sulphur of polysulphides A and F, respectively.

Table 7 shows the EP properties of each oil. The polysulphide-containing RGO-SA and RGO-SF showed better performance than RGO alone. The LWI and WL of RGO-SF

Figure 6 Kinematic friction (μ_d) test

◆ RGO
● RGO-SA
o RGO-SF

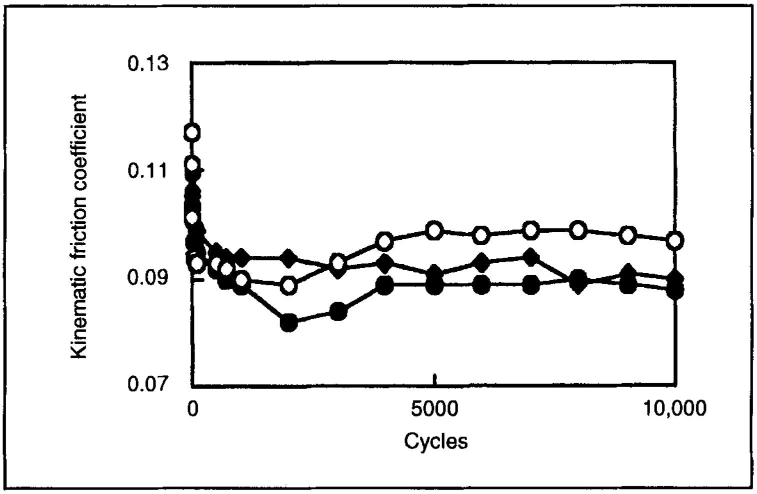
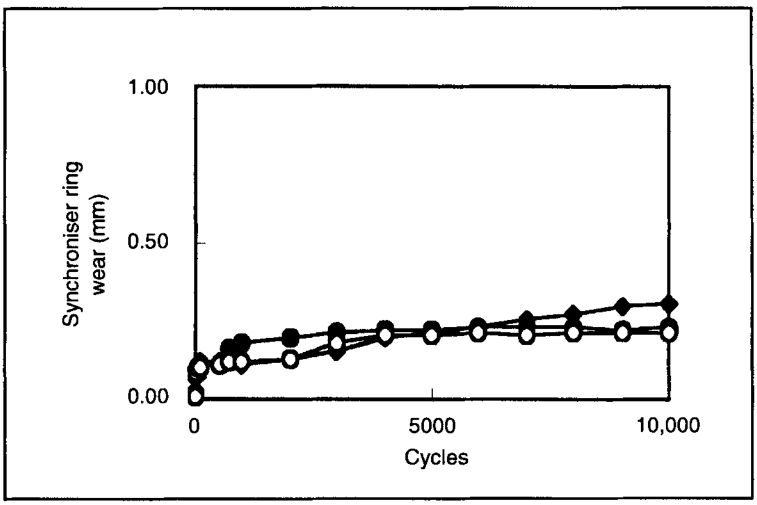


Figure 7 Wear to synchroniser ring

◆ RGO
● RGO-SA
o RGO-SF

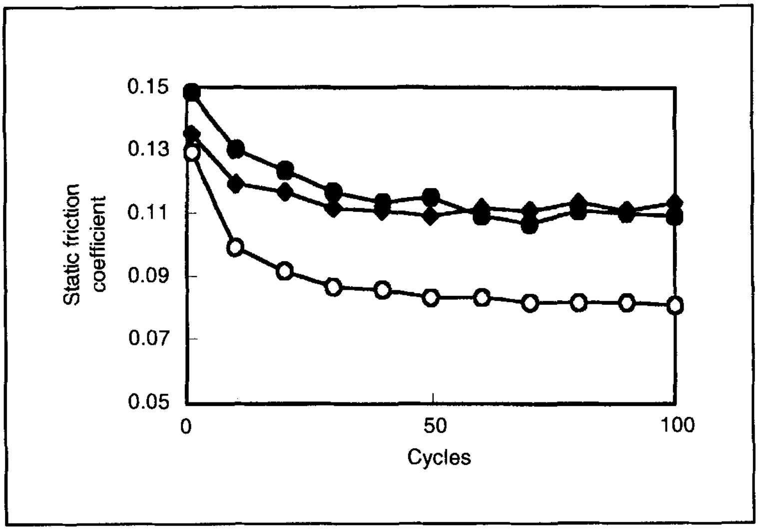


were particularly improved, showing that the basic purpose for adding polysulphide, that is, better EP performance, had been achieved.

Figure 6 shows the results obtained for the kinematic friction coefficient in the synchroniser test. RGO-SA was expected to have a much lower kinematic friction coefficient due to the addition of the conventional polysulphide, but in fact there was little decrease. This is likely to be due to the fact that

***Figure 8* Static friction test**

◆ RGO
● RGO-SA
o RGO-SF



the ZDTP and calcium sulphonate already in the RGO limited any further decrease. As expected, RGO-SF maintained a much higher friction coefficient than RGO alone, thus showing the improvement.

As shown in **Figure 7**, the wear to the synchroniser ring was very low for each oil. This wear behaviour also corresponded to the kinematic friction coefficient behaviour.

Figure 8 shows the static friction coefficient as determined by the synchroniser test. While RGO-SA had about the same static friction coefficient as RGO alone, that of RGO-SF was much lower. These results indicate that it is possible to avoid the sticking phenomenon during shifting.

When polysulphide is added to conventional manual transmission oils in order to improve the load-carrying capacity, problems arise, such as gear clashing during synchronisation and sticking after synchronisation. However, the above results show that the use of polysulphides with long hydrocarbon chains makes it possible to develop transmission oils with both high load-carrying capacity and superior shiftability. The results also show that it is possible to develop transmission oils with not only better load-carrying capacity but also better shiftability than the latest transmission oils that have their shiftability improved with ZDTP and metallic detergents.

CONCLUSIONS

Polysulphides with longer hydrocarbon chains reduced the wear of synchroniser rings, maintained higher kinematic friction coefficients, and reduced the static friction between the synchroniser ring and gear cone compared with conventional polysulphides. These effects were found to be caused by the adsorption or the reaction of the polysulphide on to the copper alloy. By using polysulphides with long hydrocarbon chains, it is also possible to develop transmissions oils that have superior load-carrying capacity and shiftability when compared to the latest oils that contain metallic detergents and ZDTP.

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