EFFECT OF MECHANICAL STRESS ON THE STRUCTURE OF LUBRICATING GREASE MIXTURES

by

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Introduction

In the practice of lubrication it is usually presumed that lubricating oils of different origin are not miscible, due to the possible mutual reactions of additives contained therein. However, lubricating greases were up to now considered to be miscible and little is known about the possible changes of their structure and properties, although this knowledge would be of great practical value. If e.g. motor vehicles or trains pass several frontiers and are serviced in different countries, it may well occur that bearings are lubricated with a lubricant differing in quality from the original.

RICHTHAMMER [1] reported on the miscibility of a few sodium, lithium-oxystearate, aluminium, calcium-complex and bentonit-base greases, as measured by penetration and dropping point changes before and after having been worked in the Shell-Roller equipment. It was found that some of the binary mixtures decidedly showed some increase in penetration and decrease of dropping-point as compared with the original components.

NEUMANN and VÁMOS [2] tested binary model mixtures of calcium-hydrate, sodium, lithium-calcium mixed, calcium-ricinoleate complex and aluminium-base greases by determining the change of penetration and dropping point before and after working them by up to 100,000 double strokes in the ASTM mechanical grease worker. Similar results to those of Richthammer were obtained.

The scope of the research work, reported hereafter, was to correlate changes of physical properties such as penetration, syneresis (bleeding tendency) and dropping point, with changes of structure as deducible from electron micrographs.

The tested substances were four typical lubricating greases of the Hungarian assortment, as listed below:

lime hydrate-base ball bearing grease	Zs-90
sodium-base, (Kalypsol) grease	Zs-175
lithium-calcium mixed base grease	Liton C-12/2
calcium-stearate-acetate-base complex grease	CaK

The greases were manufactured by the lubricating grease plant of the Komáromi Kőolajipari Vállalat (Petroleum Refinery Komárom). Physical properties of the tested samples are shown in Table 1.

Table 1

Substances investigated

	Zs-90	Zs-175	Li-C-12/2	CaK
Pen. unworked mm/10	198	203	231	256
Pen. worked 60 times	208	223	240	293
Pen. worked 10,000 times	254	282	315	264
Pen. worked 100,000 times	270	296	335	185
W.I. $^{60}_{10}4$	82	77	74	111
W.I. $^{60}_{10}5$	77	72	70	103
Drop. point °C	98	184	181	225
Syneresis at 60 °C%	0.0	0.0	0.0	0.0
Syneresis at 100 °C%	—	0.0	0.0	0.0
Stability at 90 °C unworked	no	passing	passing	passing
Stability at 100 000	no	passing	passing	passing

Six binary mixtures were prepared from these greases in a proportion of 1 : 1 as follows:

Zs-90 + Liton-C-12/2
Zs-90 + CaK
Zs-175 + Liton-C-12/2
Zs-175 + CaK
Liton C-12/2 + CaK

The mixtures were submitted subsequently to 60, 10,000 and 100,000 double strokes in the ASTM grease worker and penetration [3], dropping point [4] syneresis [5] were determined before and after having worked them. From these results the working index (W.I.$^{60}_{10^4}$ and W.I.$^{60}_{10^5}$) was calculated [6]. Finally electron micrographs were made of unworked and worked binary mixtures.

The W.I. was defined as follows:

$$W.I.^{60}_{10^4} = \frac{P_{60}}{P_{10^4}} \cdot 100 \qquad (1)$$

where $W.I.^{60}_{10^4}$ is the working index after 10,000 double strokes, P_{60} the penetration at 25 °C after 60 strokes and P_{10^4} the penetration after 10,000 double strokes.

$$W.I.^{60}_{10^5} = \frac{P_{60}}{P_{10^5}} \cdot 100 \tag{2}$$

where P_{10^5} is the penetration at 25 °C and $W.I.^{60}_{10^5}$ the working index after 100,000 double strokes, other symbols being the same as in [1]. According to this formula a W.I. of 100 denotes a grease which does not change its consistency, a W.I. of 0 one which fluidizes on working and if W.I. surpasses 100, the grease is rheopectic.

The stability of greases was determined at 90 °C in tests of 6 hours. After this time the sample was inspected as to oil separation, hardening of surface or formation of layers. If such changes occurred, the sample was denoted as "not passing" the test, if no change occurred, it was regarded as "passing".

Electron micrographs of unmixed samples after 60 double strokes are shown in Figs 1 to 4.

Fig. 1 shows the typical structure of a lime hydrate-base grease, i.e. a twisted fibrillic soap structure, well known from literature [7, 8].

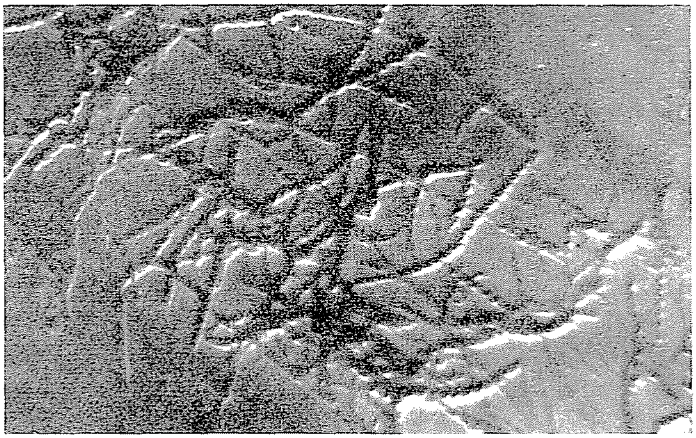

Fig. 1. Soap structure of lime hydrate-base ball-bearing grease Zs-90 (after 60 strokes)

Fig. 2 shows the typical large fibrilles of sodium-base greases, Fig. 3 the shorter soap fibrilles of the network of Li-base greases. There are no separate lime-soap and lithium soap particles in this micrograph, therefore it can be taken for granted that the lime-soap gives a common micelle with the lithium soap as usual in lithium-lime mixed base lubricating greases. Fig. 4 shows a structure of neutral calcium-stearate-acetate complex greases.

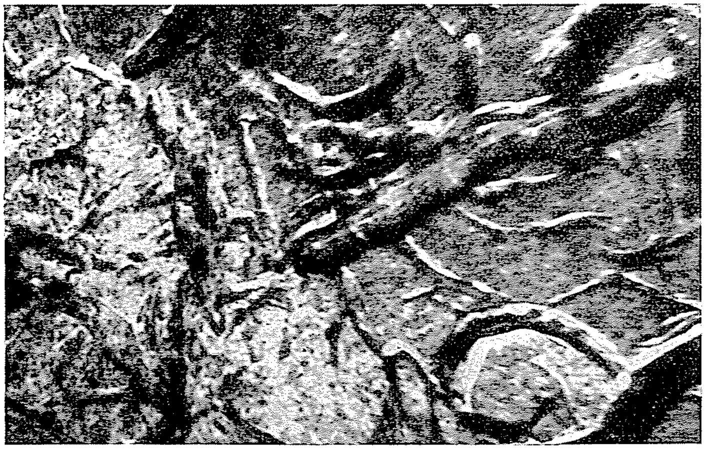

Fig. 2. Soap structure of sodium-base "Kalipsol" grease Zs-175 (after 60 strokes)

Fig. 3. Soap structure of lithium-calcium-mixed base grease Liton C-12/2 after 60 strokes

Fig. 4. Soap structure of calcium-stearate-acetate base complex grease CaK (after 60 strokes)

The electron micrographs of the soap structure of these commercial greases show good agreement with the soap structure of model greases known from literature [7, 8].

Results of tests on binary mixtures

Results of testing binary mixtures are shown in Table 2. Comparing these results, it can be shown that penetrations of mixtures are usually approximately as high as penetrations of the softer component in the binary mixture or even higher, indicating that leakage of grease from the bearing is liable to occur if greases are mixed during the lubrication period. However, no definite tendency can be shown in respect to changes of W.I.

Dropping points of high-dropping-point greases Zs-175, Liton-C-12/2 and CaK are substantially reduced with the only exception of the binary mixture of Zs-175 + CaK.

Table 2

Mixtures

	Zs-90 Zs-175	Zs-90 Li-C-12/2	Zs-90 CaK	Zs-175 Li-C-12/2	Zs-175 CaK	Li-C-12/2 CaK
Pen. unworked, 25 °C mm/10	195	244	209	198	194	300
Pen. unworked, 60× °C mm/10	216	253	223	221	240	324
Pen. unworked, 10,000× °C mm/10	262	286	284	286	291	342
Pen. unworked, 100,000× °C mm/10	286	292	302	333	295	329
W.I.$^{60}_{10^4}$	82	88	80	77	82	95
W.I.$^{60}_{10^5}$	76	86	74	66	81	98
Drop. point °C unworked	107	107	115	187	144	154
Drop. point 60× °C unworked	100	106	110	188	150	155
Drop. point 10,000× °C unworked	120	108	117	172	129	141
Drop. point 100,000× °C unworked	105	111	114	173	137	142
Syneresis at 60 °C	2.0	2.0	1.8	0.1	0.0	0.0
Syneresis at 100 °C	16.3	9.2	21.8	0.4	4.7	0.1
Stability unworked 90 °C	no	no	no	passing	no	passing
Stability unworked 100,000 °C	no	no	no	passing	no	passing

In binary mixtures containing the low dropping grease Zs-90, the dropping point is near to the lower value. Syneresis of binary mixtures is higher than that of unmixed greases, the latter being 0 throughout the set of experiments. Some of the syneresis values are detrimental if long life lubrication of bearings is wanted. Characteristic for damages caused by mixing is the case

Fig. 5. Fibrillar structure of grease mixture 1 : 1 of Zs-90 + Zs-175 (after 60 strokes)

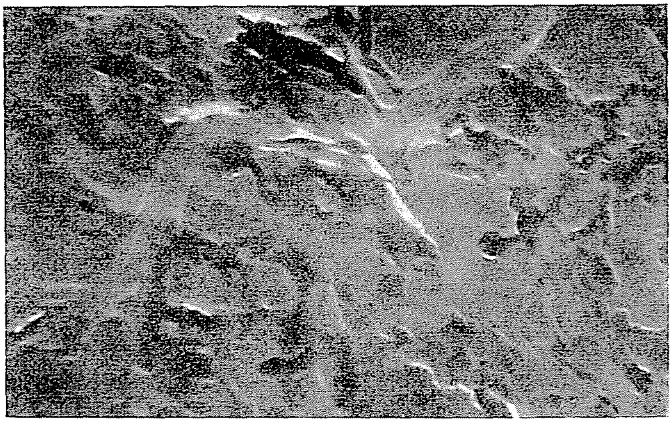

Fig. 6. Mixture of Zs-90 + Zs-175 (after 100 000 strokes)

of lubricant failure in back-axle bearings of motor-cars, which in Hungary are usually lubricated with the high-dropping-point sodium base greases Zs-130, or Zs-160. If at servicing, normal lime-base ball bearing grease Zs-90 is applied at this point, the running hot of the bearing is due to syneresis.

Stability values show inconsequent changes; some of the grease mixtures are "passing", others "non passing".

Comparing these results with electron micrographs we first may consider Figs 5 and 6 showing the grease mixture Zs-90 + Zs-175 after 60 and

100,000 double strokes. Fig. 5 shows a mixed structure of long and large sodium-soap fibrils and slightly distorted twisted lime-hydrate soap structures. After 100,000 double strokes a non-fibrillous texture results, which seems scarcely to be able to form stable gels. Syneresis values (see Table 2) are therefore high and stability test is "non passing".

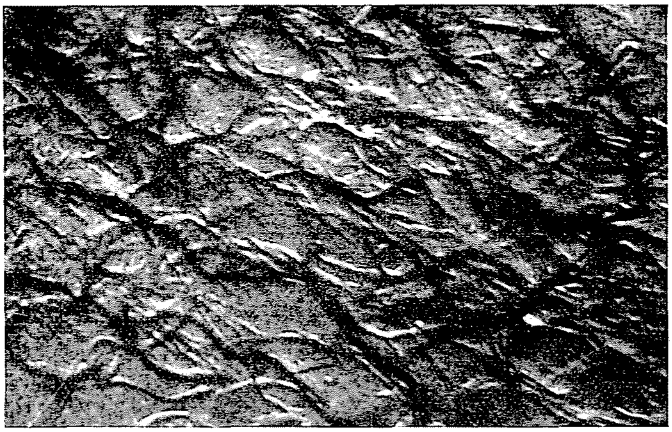

Fig. 7. Fibrillar structure of grease mixture 1 : 1 of Zs-90 + Li-C-12/2 (after 60 strokes)

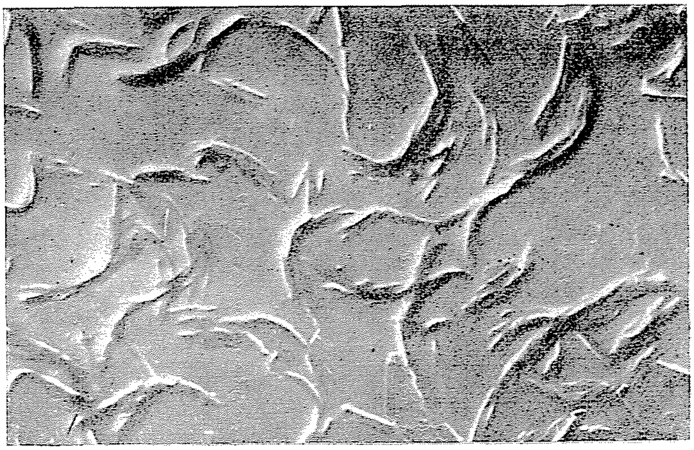

Fig. 8. Mixture of Zs-90 + Li-C-12/2 after 100,000 strokes

It is interesting to see in Figs 7 and 8 no strict correlation to exist between soap structure and physical properties. A good, tight fibril structure, differing from those of both lime-hydrate and lithium soaps characterizes the 60 times worked mixture of Zs-90 and Liton-C-12/2, while after 100,000 strokes, although the structure is loose, distinct lithium-soap-like fibrils can be observed in the electron micrograph. Yet syneresis tendency is rather high, the droping point is low and the stability is poor.

A better correlation can be found in cases of the mixture Zs-90 + CaK. The mixture worked 60 times contains undistinct and small, twisted lime-hydrate soap elements mixed with larger, non-characteristic fibrils. After 100,000 strokes a slightly fibrillic unstable network results, corresponding to low dropping points (Table 2), high syneresis and poor stability.

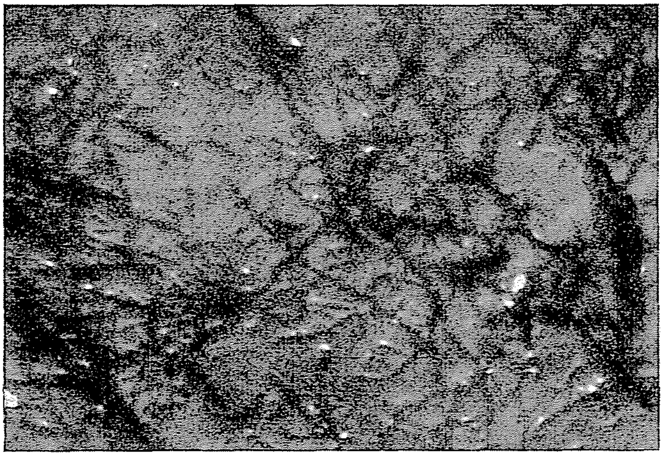

Fig. 9. Fibrillar structure of grease mixture 1 : 1 Zs-90 + CaK (after 60 strokes)

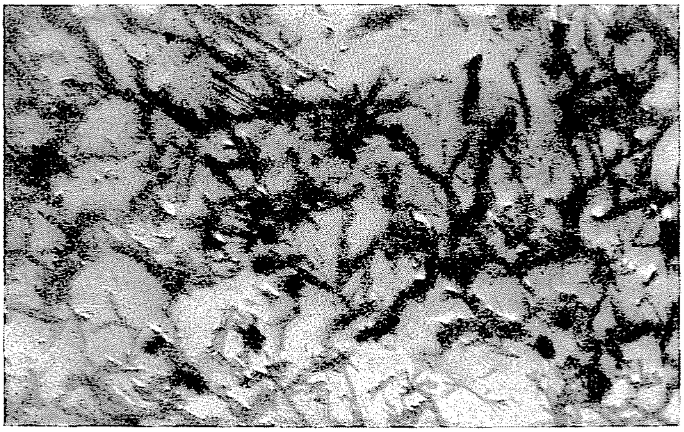

Fig. 10. Mixture of Zs-90 + CaK (after 100,000 strokes)

Good correlation exists between physical constants and electron micrographs in the case of the mixture Zs-175 + Li-C-12/2. The particles have the typical shape of those of lithium soap. The fibrils are uniform, and evenly distributed. This mixture is the only one, which is in no respect inferior to the properties of the components. Good dropping point, low syneresis and good stability characterize the mixture.

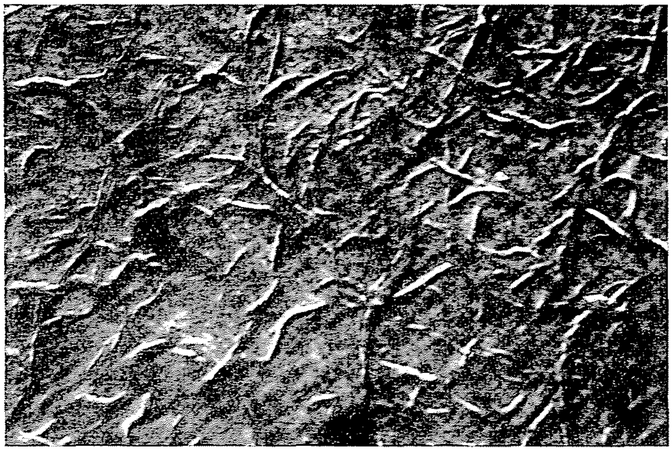

Fig. 11. Fibrillar structure of grease mixture 1 : 1 Zs-175 + Li-C-12/2 (after 60 strokes)

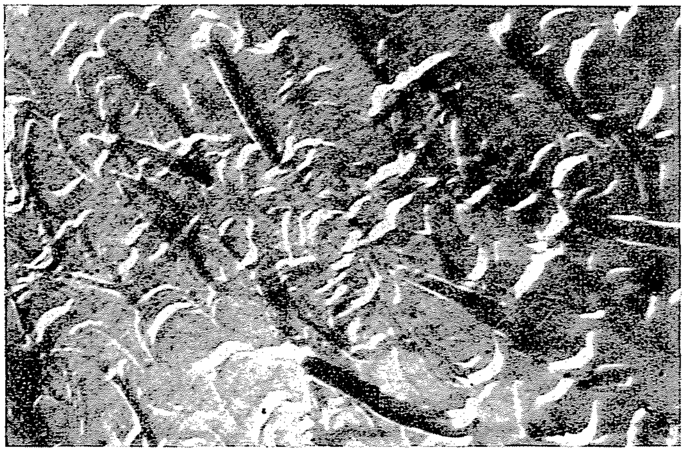

Fig. 12. Mixture of Zs-175 + Li-C-12/2 (after 100,000 strokes)

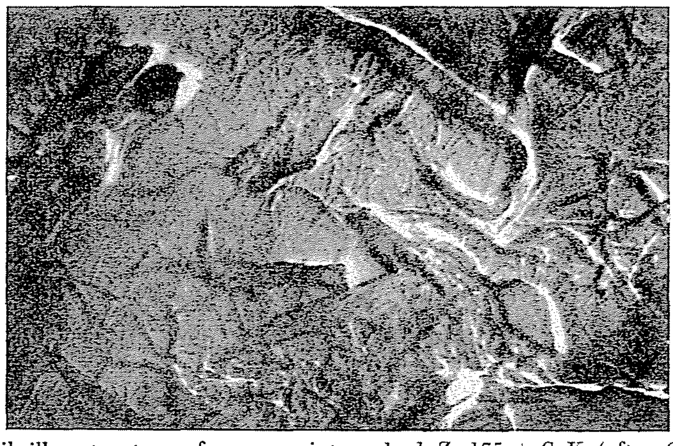

Fig. 13. Fibrillar structure of grease mixture 1 : 1 Zs-175 + CaK (after 60 strokes)

Fig. 14. Mixture of Zs-175 + CaK (after 100,000 strokes)

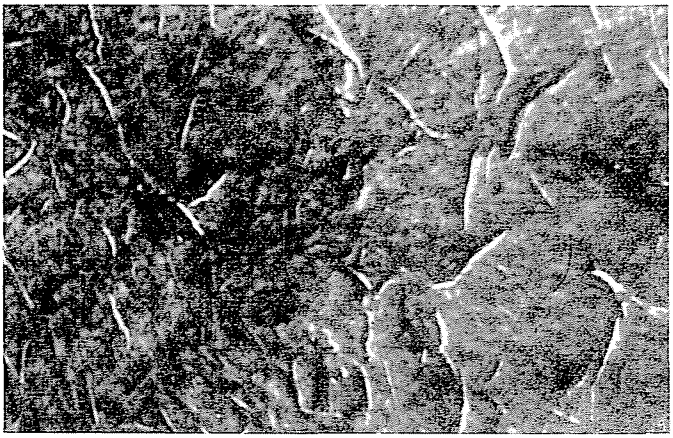

Fig. 15. Fibrillar structure of grease mixture 1 : 1 Li-C-12/2 + CaK

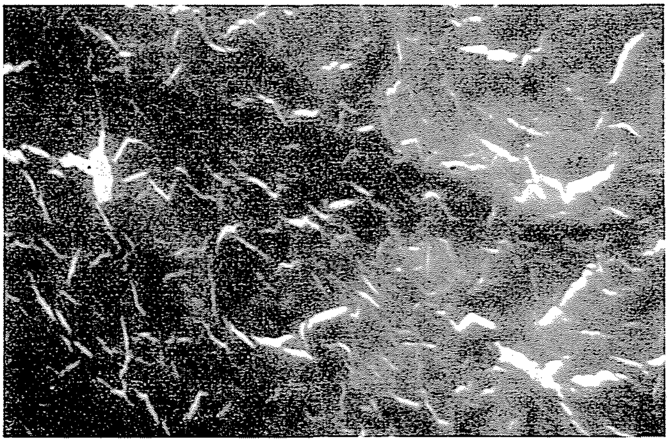

Fig. 16. Mixture Li-C-12/2 + CaK (after 100,000 strokes)

The electron microscopic photographs of the mixture Zs-175 + CaK show that in the mixture worked by 60 strokes, the large particles of the sodium-base grease prevail, and practically no calcium-complex soap particles are seen, while after 100,000 strokes loose structure of small particles results. The grease has a lower dropping point than any of its components, it has some syneresis tendency and a poor stability.

Finally, the mixture Li-C-12/2 + CaK shows structures both in mildly and in heavily worked state, which are rather similar to lithium soap particles, although finer and smaller. The structure is distinctly fibrillar before and after working. It is of importance that the particle size is but slightly affected by working. Therefore the grease mixture has a good shear stability (high W.I.), almost no syneresis, and a good stability. However, the dropping point of the mixture, although it remains fairly high, is still lower than the value of either component.

Summary

Investigations on four different-base, characteristic Hungarian lubricating greases have shown that both structure and physical properties of these products are affected by mixing. In many cases dropping points tend to be almost as low as that of the less valuable components, and in several cases they are even lower. Mixtures have often a higher syneresis tendency than their components and their stability is poorer. A single exception was found, that of the mixture of sodium-base grease with lithium-calcium mixed base product (Zs- 175 + + Li-C-12/2). In all other cases, at least one of the properties of the mixture was worse than that of one or both components. Electron micrographs show that often a change of grease texture results as a consequence of mixing, and that usually the fibrils are not only simply mixed by the process, but mutually change their structure, often resulting in loose, undefined and unstable soap networks.

It is shown that the old practice of lubrication engineering, according to which "greases are miscible" does not hold any longer, and it is advisable to insist on the same lubricant for a given bearing.

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