EFFECT OF HEAVY METAL SOAPS ON THE PROPERTIES OF Ca-COMPLEX GREASES

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Introduction

One of the most important tendencies in the development of lubricants is that of complex-soap base greases. Up to now three types have been succeeded, among the great number of possibilities studied, such as the sodium-stearate-furane-carboxilate, the barium-stearate-acetate and the calcium-stearate-acetate type complex greases. Of them, the calcium-stearate-acetate greases proved to be utmostly efficient for high temperature lubrication. Such greases are also commercially produced in Hungary [1—4].

One of the disadvantages of Ca-complex greases is, however, their relative hardness. All products belong to NLGI consistency groups 0, 1 and 2, useful in hand lubricated systems but not in those of central lubrication.

Several authors attempted to modify their structure and consistency by adding other metal soaps, such as sodium, aluminium and lead soap in order to improve consistency, i.e. penetration. Up to now, however, no systematized data on the effect of such components have been published [5, 6].

Components of the greases studied

The properties of the ingredients used for the greases investigated have been compiled in Table 1.

Pb-stearate was prepared from stearic acid by saponification with analytical grade NaOH, and precipitation of the lead soap by adding Pb-acetate to the sodium soap solution. The greases were prepared by conventional methods usual for the production of Ca-complex greases [4, 5].

After boiling, the greases were subjected to milling in a three-cylinder homogenizer and deareated by panning for 48 hours.

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Table 1

Ingredients of the test greases

	Stearic acid	Zn-stearate	Acetic acid	Calcium hydroxide	Pb-acetate*	Lubricating oil, GT-50
Molecular weight	280	623	60	74	379.3	—
Saponification value, mg KOH/g	210	—	—	—	—	—
Iodine number, g I/100 g	0.8	—	—	—	—	—
Pour point, °C	51	—	13.6	—	—	−18
Ash content, % by wt	0.018	—	—	—	—	0.005
Free mineral acid	none	none	—	—	none	none
Zn content, % by wt	—	14.5	—	—	—	—
Pb content, % by wt	—	0.001	0.0001	0.05	54.6	—
Alkali and earth metal content, % by wt	—	1.0	—	—	0.048	—
Cl′ content, % by wt	—	—	0.001	—	0.0005	—
SO_4'' content, % by wt	—	—	0.002	0.32	—	—
Fe content, % by wt	—	—	0.0001	0.17	0.0010	—
Mg and alkali content (in MgO), % by wt	—	—	—	0.95	—	—
Cu content, % by wt	—	—	—	—	0.0010	—
Viscosity, cSt at 50°C	—	—	—	—	—	46.9
Flash point, Marcusson, °C	—	—	—	—	—	218

* Pb-acetate content 99.94% by wt

Beside conventional testing methods, mechanized working and electron microscopy were applied for evaluating the products. Resistance to mechanical stresses was calculated by means of the stability index [7]:

$$S,I._n^{60} = \frac{P_{60}}{P_n} \cdot 100$$

where $S.I._n^{60}$ the stability index

P_{60} the penetration of the grease at 25°C in 0.1 mm, after a working of 60 double strokes

n the number of double strokes applied in the mechanical worker (usually 10,000 or 100,000)

P_n the penetration of the grease after being exposed to n (usually 10,000 or 100,000) double strokes

Experimental results

Table 2 shows the properties of a conventional Ca-stearate-acetate base complex grease, corresponding in structure and behaviour to the so-called normal complexes, with a Ca-stearate to Ca-acetate mole ratio of about 1 : 4 [8]. The values are given for the sake of comparison. Such greases are seen to exhibit very good thermal and colloidal stability, and fairly good shear resistance, but are relatively hard.

Table 2

Properties of reference Ca-complex grease

	Grease No. 1
Ca-stearate, % by wt	10
Ca-acetate, % by wt	10
Penetration, unworked, mm/10 at 25 °C	150
after 60 double strokes	185
,, 10,000 ,, ,,	210
,, 100,000 ,, ,,	240
Drop point, unworked, Ubb. °C	230
after 100,000 doubles strokes	230
Syneresis, unworked, at 100 °C, % by vol.	0.0
after 100,000 double strokes	0.0
Stability index $S.I._{10^4}^{60}$	88
$S.I._{10^5}^{60}$	77

Three sets of complex greases were prepared, containing, beside Ca-salts, also heavy metal derivatives. As commercial greases contain usually 20% of gelling components (i.e. soap + structure modifier), an overall concentration of 20% gelling agent was chosen to 80% oil, and composition and ratio of the components of the gelling agent was varied, keeping constant the overall concentration.

In the first set, part of Ca-stearate and/or of Ca-acetate was substituted by Zn-stearate (Table 3). Consistency is seen to be reduced (i.e. penetration increased) by adding Zn-stearate to the mixture.

This impaired, however, the thermal and mechanical stability (see worked penetration values, stability index values and drop points). Only grease 2 shows equal or better values in every respect, compared to the pure Ca-stearate-acetate complex grease.

In a second set of experiments, Pb-stearate was substituted for Zn-stearate. Table 4 shows the unworked penetration to be substantially reduced, at a loss, however, of thermal and mechanical stability. In addition, the colloid stability decreased, i.e. syneresis of the product increased to an inadmissible degree. Only grease No. 7 shows acceptable characteristics, approaching those of some commercial products of foreign make, examined in our laboratory.

In a third set of experiments, replacing Pb-acetate for Ca-acetate as complexing or structure modifying agent was attempted. The properties of these products are shown in Table 5. This method yields very unstable products. At low Pb-concentrations the penetration values are favourable, but thermal stability and colloid stability are reduced (i.e. syneresis is high). For medium and high Pb-concentrations, both thermal and colloid stability are fairly good, but stability to shear is reduced.

Electron micrographs

To get an insight into the structure of the above mentioned greases, electron micrographs were made, shown in Figs 1 through 7.

For each grease two micrographs were taken, after 60 and after 100,000 double strokes, respectively, i.e. the first in a homogenized but practically unworked state, the other after a heavy mechanical stress.

Electron micrographs were made by the well-known method, described earlier in detail [9—12].

Table 3

Properties of Zn—Ca complex greases

	Grease		
	No. 2	No. 3	No. 4
Zn-stearate, % by wt	5	3	3
Ca-stearate, % by wt	5	5	3
Ca-acetate, % by wt	10	12	14
Penetration, mm/10 at 25 °C			
unworked	239	288	250
after 60 double strokes	245	310	273
,, 10,000 ,, ,,	250	398	355
,, 100,000 ,, ,,	268	417	389
Drop point, Ubb. °C			
unworked	250	150	136
after 100,000 double strokes	250	141	130
Syneresis at 100°C, % by Vol.			
unworked	0.0	8.9	9.3
after 100,000 double strokes	0.0	10.6	10.8
Stability index			
$S.I.^{60}_{10^4}$	96	77	76
$S.I.^{60}_{10^5}$	90	74	70

Table 4

Properties of Pb—Ca complex greases

	Grease		
	No. 5	No. 6	No. 7
Pb-stearate, % by wt	5	3	3
Ca-stearate, % by wt	5	5	3
Ca-acetate, % by wt	10	12	14
Penetration, mm/10 at 25 °C			
unworked	237	278	284
after 60 double strokes	282	300	300
,, 10,000 ,, ,,	402	440	350
,, 100,000 ,, ,,	liquid	liquid	380
Drop point, Ubb. °C			
unworked	175	171	250
after 100,000 double strokes	120	168	229
Syneresis at 100 °C, % by Vol.			
unworked	13.6	7.5	8.9
after 100,000 double strokes	19.0	17.9	16.0
Stability index			
$S.I._{10^4}^{60}$	72	68	86
$S.I._{10^5}^{60}$	unmeasurable		79

The structure of the reference grease No. 1, typical of Ca-stearate-acetate complex greases, is shown in Fig. 1.

Figs 2(a, b) show the structure of the grease No. 2 before and after heavy mechanical working. The structure is seen to be little affected by the addition of Zn-stearate. After working some destruction of fibrils is shown.

The structure of grease No. 3 is seen in Figs 3(a, b) to be substantially altered as compared with No. 1 the fibrillar structure being less compact, and more intensively destroyed by mechanical forces.

Figs 4(a, b) show the structure of grease No. 4, where fibrils have been displaced by a foam-like structure and after working, an absolutely indefinite structure came about, accompanied by mechanical breakdown of the grease.

Figs 5(a, b) show the structure of grease No. 5, to entirely differ from the fibrils of any complex grease, very similar, in turn, to the soap particles of conventional non-complex lead greases, known from literature [10, 13]. This structure is seen to have a fairly good shear resistance and to change little after 100,000 double strokes.

Figs 6(a, b) show the structure of grease No. 6 in which Pb-stearate fibrils are less prevailing than before. This grease has a very low shear resistance, as shown by the completely destructed fibrils in Fig. 6b.

Table 5

Properties of Ca—Pb base greases

	Grease No. 8	Grease No. 9	Grease No. 10
Ca-stearate, % by wt	15	12	10
Pb-acetate, % by wt	5	8	10
Penetration, mm/10 at 25 °C			
unworked	214	177	185
after 60 double strokes	220	202	193
,, 10,000 ,, ,,	254	260	264
,, 100,000 ,, ,,	283	398	397
Drop point, °C			
unworked	174	250	250
after 100,000 double strokes	170	171	175
Syneresis at 100°C % by Vol.			
unworked	2.0	0.1	0.0
after 100,000 double strokes	3.7	0.3	0.0
Stability index			
$S.I.^{60}_{10^4}$	86	78	73
$S.I.^{60}_{10^5}$	77	50	48

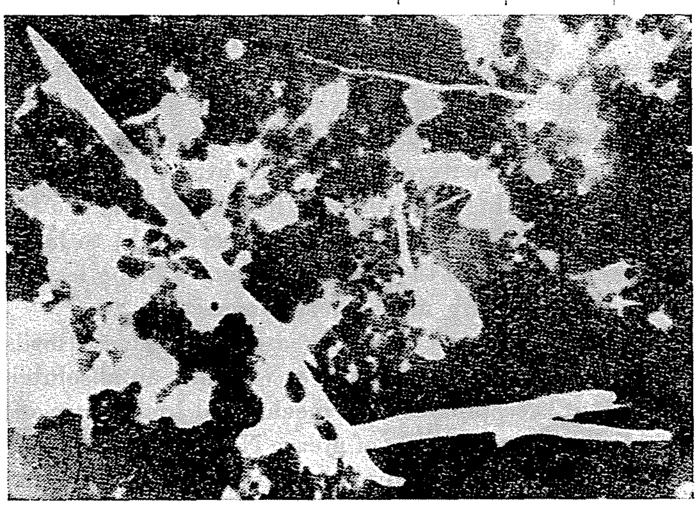

Fig. 1

Figs 7(a, b) show Ca-acetate crystals to prevail at high Ca-acetate concentration and to be inaffected by shearing.

The greases containing Pb-acetate as structure modifier (complexing agent) are different is structure from Ca-complex greases as seen from pictures

Fig. 2a

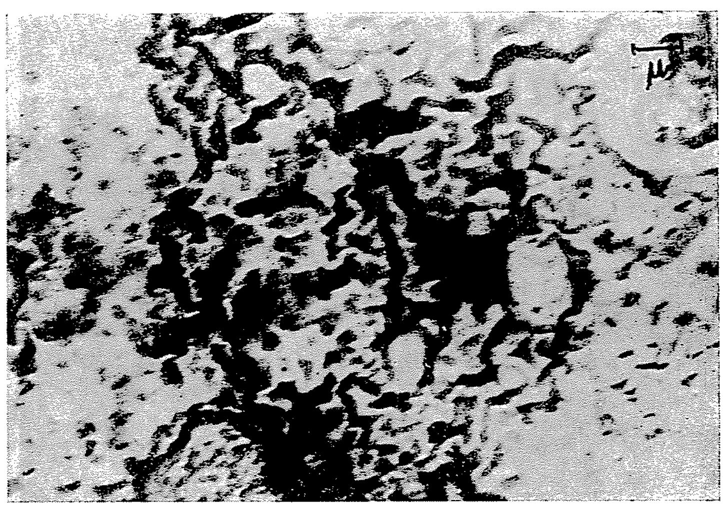

Fig. 2b

Fig. 3a

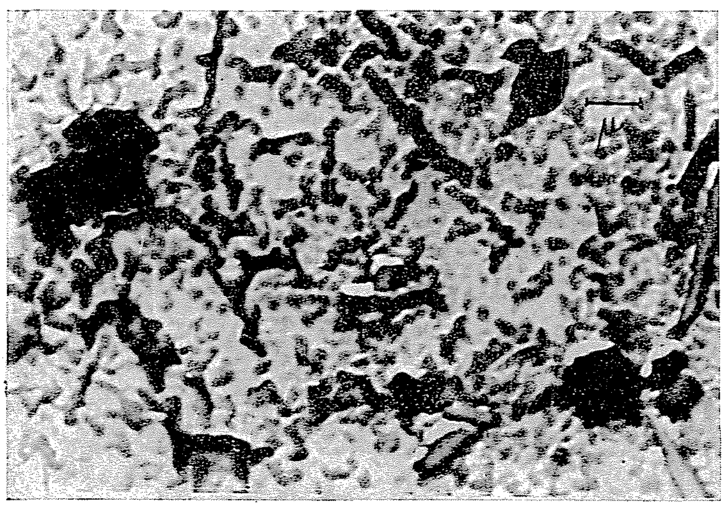

Fig. 3b

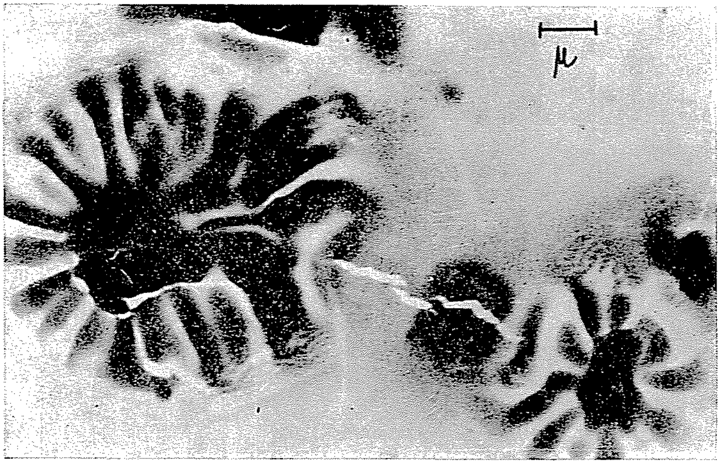

Fig. 4a

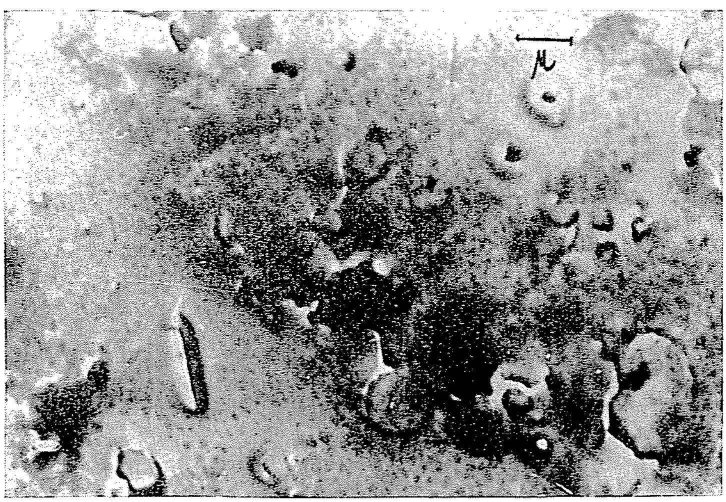

Fig. 4b

Fig. 5a

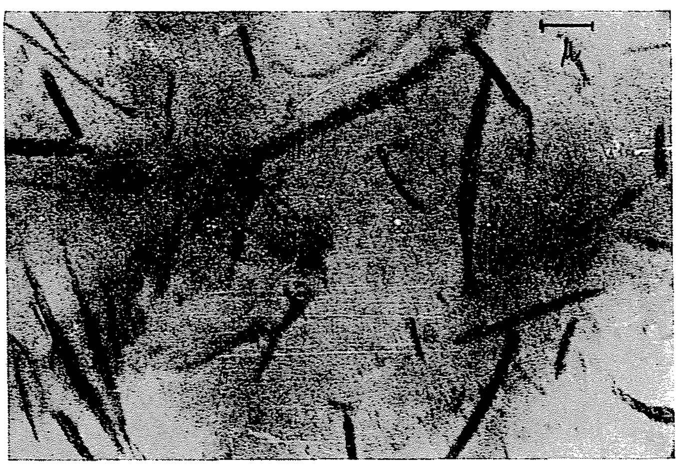

Fig. 5b

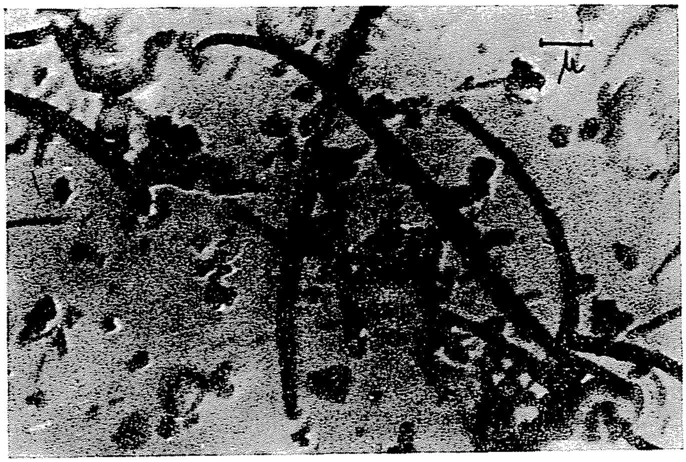

Fig. 6a

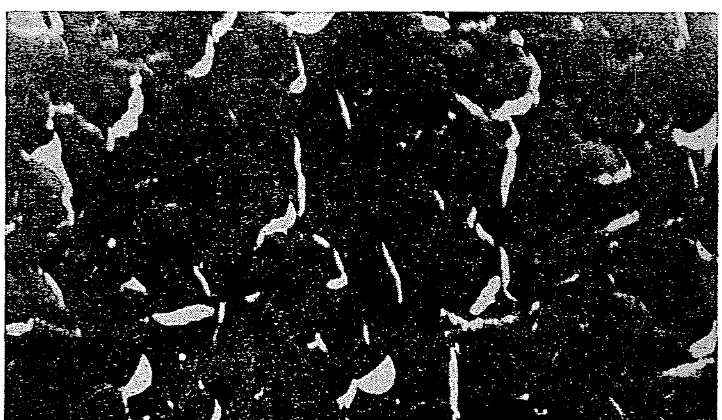

Fig. 6b

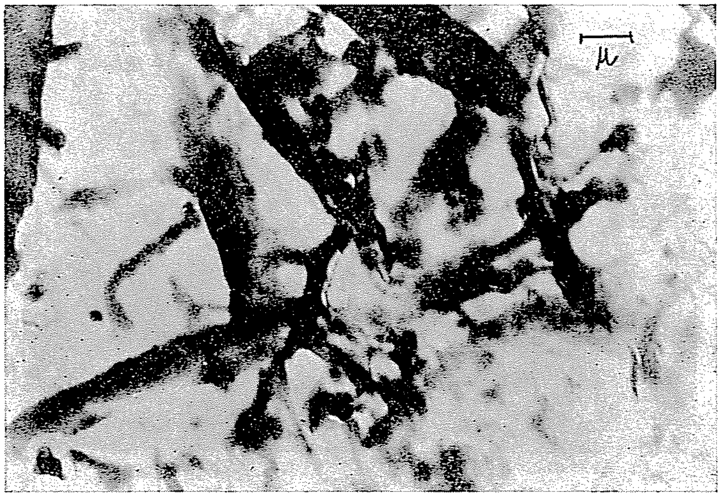

Fig. 7a

Fig. 7b

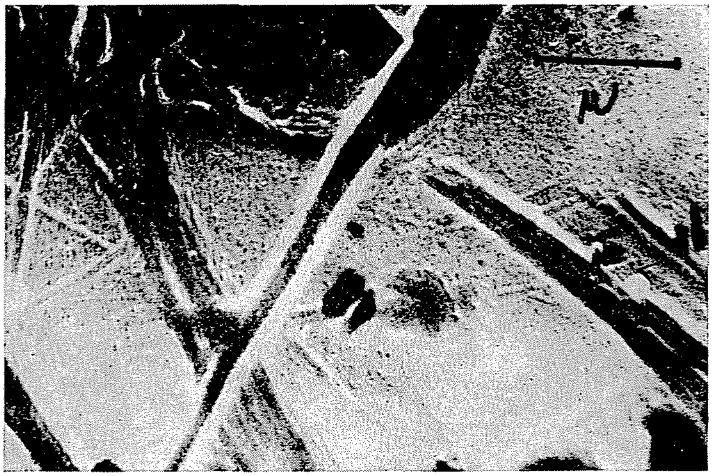

Fig. 8a

Fig. 8b

Fig. 9a

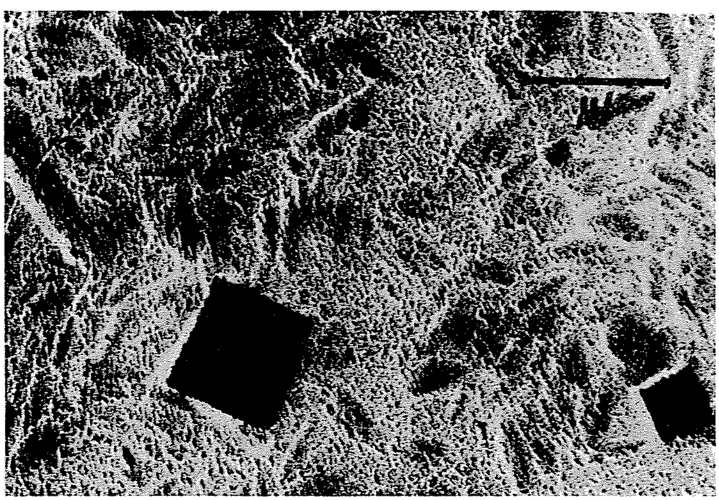

Fig. 9b

of grease No. 9 in Figs 8(a, b). The coarse fibrils are seen, to be entirely destructed by shearing, the destruction being responsible for the thixotropy or rheodestructive behaviour of these greases.

Figs 9(a, b) representing the structure of grease No. 10 are similar as above, the very coarse fibrillar structure, being similar in type to that of sodium base greases, and so is the bleeding tendency (syneresis).

Summary

The effect of the addition of heavy metal soaps and salts on the properties, structure and behaviour of Ca-complex greases has been studied. A desirable reduction of consistency (increase of penetration) was seen to be possible in any case. This improvement however is often accompanied by loss of thermal, mechanical and colloid stability. The reduced mechanical resistance was shown to result from the liability of the fibrillar lattice of the soap structure to destruction.

At some favourable concentrations, however, products with the desired soft consistency could be prepared, keeping their good or fairly good mechanical, thermal and colloid stabilities.

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