NEW VIEWS ON THE COLLOIDAL STRUCTURE OF LUBRICATING GREASES

By

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Introduction

Our knowledge on the structure of lubricating greases is incomplete although many scientists tried to clear up these questions [2, 3, 6, 9]. Their investigations yielded partial results confined to a few types of greases in a narrow range of conditions. Difficulties arose from the fact that most of these investigations aimed at practical purposes and were conducted by technologists, application research groups, or even mechanical engineers.

Considering the macroscopic texture and rheological properties of lubricating greases, it may be assumed that they have, to some extent, a colloidal structure and therefore information on their structure may be obtained from methods of colloidal chemistry. As a matter, of fact there exist some publications according to which lubricating greases are considered to be colloidal systems of the type of the jellies, in which solid structure is given by a soap or some similar substance, while the liquid phase consists of oil. Dimensions, morphology and interrelations of the particles are, however, not very well known.

The colloidal structure of lubricating greases

For further consideration, let us assume in accordance with literature [2, 4, 5, 6, 8, 9, 12] that lubricating greases are colloidal systems. At a closer view, this statement is seen not to hold for every case.

According to a definition of GRAHAM, colloidal systems are, as against crystalline systems, of amorphous character [1, 6, 8, 15]. Recent investigations, evidenced, however, the crystalline structure of soap particles in lubricating greases. X-ray diffraction investigations show a fully crystalline, and not a mesomorphic structure.

According to the definition of BUZÁGH [1], colloids are systems of submicroscopic discontinuities with particle sizes ranging from 1 to 500 μm. According to this definition many types of lubricating greases cannot be regarded as fully colloidal, because the soap fribrils are greater than this and can easily be detected even by optical microscopy. They are often much longer than 1 μm [3] so that according to this assumption, lubricating greases have to be classified as rough disperse systems.

Fuks [7] describes lubricating greases as jellies without going into particulars, but with the remark that some lubricating greases have a sol structure.

Thus, views on lubricating greases are rather divergent.

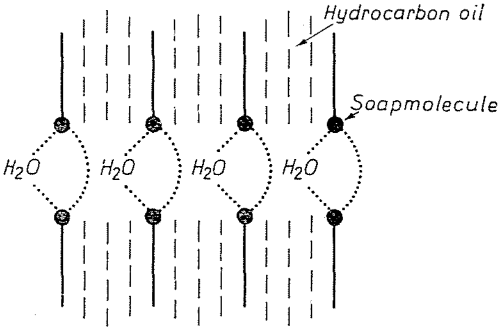

Fig. 1. Structure of soap fibrils in lubricating greases according to Trapesnikow

Fig. 2. Scheme of complex soap structure in lubricating greases

It seems to be more adequate to classify lubricating greases as complex colloids [1, 8]. In this case the term "complex" is used exclusively to denote morphology and not in the way usual in lubricating grease technology, in which complex lubricating greases are considered, to contain structure modifiers.

The structure of soap base lubricating greases is likely to be the following: lubricating greases are phase colloids in which, at first approximation, two phases are present, the continuous liquid phase and the usually roughly dispersed or deformed solid phase. At a closer look, however, this structure is seen to contain in the liquid phase colloidally dispersed and even molecularly dissolved soap particles i. e. the liquid phase may be shown to be submicroheterogenous. It can be argued that even in the solid phase colloidally or molecularly dispersed particles of the components of the liquid phase are present [9, 10]. Trapesnikow described this system according to Fig. 1. Fig. 2 is a schematic design of the above described complex structure according to our views.

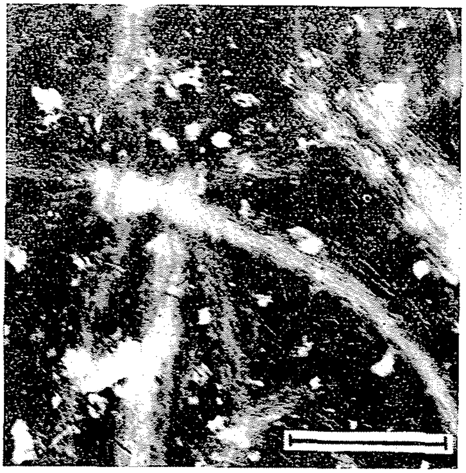

Fig. 3. Electrone micrograph of the soap structure of a barium base lubricating grease

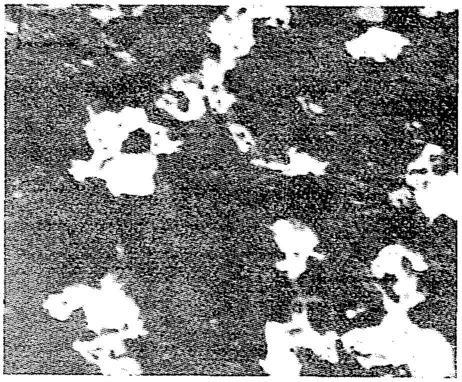

Fig. 4. Foam structure of a calcium-oleate-acetate base complex lubricating grease, giving basic reaction

In order to get some idea on the formation of this colloidal structure, it will be now assumed, in accordance with Lawrence [11], that metal salts of high molecular weight fatty acids are dissolved in hydrocarbon oils above a temperature of 200 °C in a molecular dispersion. On cooling, soap molecules will get associated and these associated particles of the solid phase grow to colloidal dimensions, at temperature T_1 accompanied by a considerable increase of the system viscosity so that soap-oleosol is formed. On further cooling, particles of the solid phase associating at temperature T_2 attain the dimensions of roughly dispersed particles, at the same time the quasi-viscous sol changes gradually to a pseudoplastic jelly.

These phenomena show that at any temperature a part of the soap (although decreasing with decreasing temperature) is in a molecularly dissolved state. At temperature T_1 the following equilibria may be assumed:

$$C_M \rightleftharpoons C_K \quad (C_{M+K} = \text{const.}), \tag{1}$$

where C_M concentration of the molecularly dissolved soap;
and C_K concentration of soap present in colloidal associates at temperature T_1
With decreasing temperature, the equilibrium is shifted to the right.

Similarly, at temperature T_2 not only roughly dispersed particles are present in the system, but there also remain some soap particles both in molecular solution and in colloidal dispersion. For this case the following equation will hold:

$$C_D \rightleftharpoons C_{K'} \rightleftharpoons C_{M'}$$

$$(C_D + C_{K'} + C_{M'} = C_M + C_K = \text{const.}), \tag{2}$$

where C_D concentration of roughly dispersed particles;

$C_{K'}$ $C_{M'}$ concentrations of colloidal and molecularly dispersed soap particles, respectively, at temperature T_2.

Other symbols being used in the same sense as in Eq. (1).

The above assumption may be verified by means of electronmicroscopic photographs. Fig. 3 shows the soap structure of a barium base soap-salt complex grease. Roughly dispersed fibrils and colloidally dispersed soap particles are clearly seen in the photo, while of course no molecularly dispersed particles are seen at the given magnification.

Considering these facts and the theory by Lawrence on the formation of lubricating greases, our previous definition may be completed by the statement that soap base lubricating greases are usually polydisperse oleogels.

It has to be pointed out, however, that the mechanism of formation of lubricating grease jellies differs in certain cases from that described by Lawrence. Different mechanisms have to be assumed, some with fibrillar, others with foam structures. In these cases the soap base has a difformed structure and this is swollen by the addition of oil. Such is the case with certain calcium-complex greases, the soap complex of which cannot be dissolved completely in oil at any temperature.

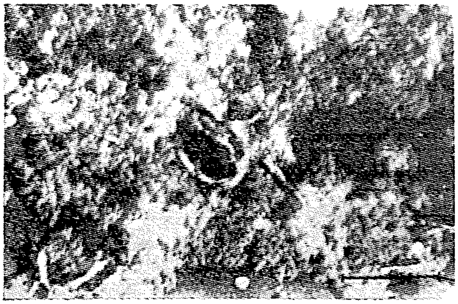

Fig. 5. Foam structure of an aluminium-stearate base lubricating grease

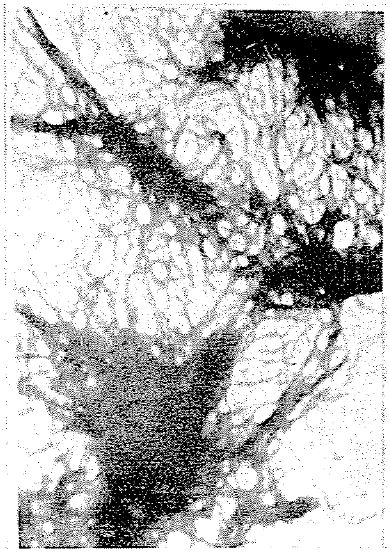

Fig. 6. Continuous soap network of a lithium-ricinoleate base grease

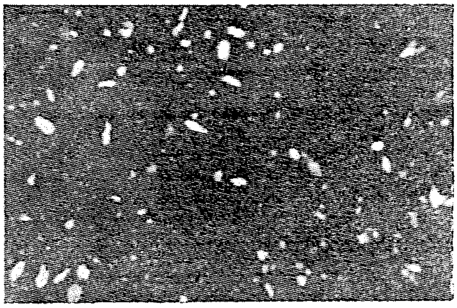

Fig. 7. Soap structure of a bentonite grease

It is known that jellies may be either reversible or irreversible. Most of the lubricating greases may be considered as reversible jellies because, if the liquid phase is eliminated and then remixed with the coagulated solid phase, the jelly will be reformed again. Hence, lubricating greases may be classified as reversible lyophilic jellies. It may be mentioned here that the term *reversibility* has a different meaning in colloidal chemistry than in lubricating grease technology. In colloidal chemistry it denotes the above described phenomena, while in lubricating grease technology it denotes the ability of the lubricating grease to form a homogeneous jelly on cooling after having gone to molecular solution at high temperature. It has to be pointed out that the terminology of colloidal chemistry is often in contradiction to the terminology of lubricating grease technology.

Most concepts on the structure of lubricating greases are based on the view that lubricating greases contain a dispersed phase of soap fibrils. According to one theory (by DUNKEN), fibrils seen in electronmicrographs are unreal and the true structure of any lubricating grease is foamlike, fibrils being formed by secondary deterioration of foam particles in the electronmicroscope upon electrone impact. As to our experience, both statements are confined to the types examined by the given author. As a matter of fact, we found that greases of both types are common, and there are even types which escape classification by any system published up to now. In many lubricating greases the solid phase is a difformed phase and not a dispersed one. In these greases neither of the phases is dispersed, both of them are difformed. Such systems may be classified according to BUZÁGH [1] as transition types. These structures are characteristic of lithium ricinolate, aluminium distearate, and some calcium-complex base greases, the soap structure of which is either of the foam type or it forms a continuous network. On the other hand, bentonite and silica gel greases have a structure approaching that of concentrated sols and suspensoids, rather than to that of jellies. Fig. 4, 5, 6, 7 show the electronmicrographs of such systems.

Changes of the gel structure under mechanical-dynamic stresses

Lubricating greases in use are usually exposed to heavy mechanical stresses, their structure changes under such conditions with serious practical consequences. One of the main questions is, how the solid phases change during mechanical operation. Changes of this structure will cause changes in the rheological behaviour, on which one of the authors of this paper has published his views recently, therefore rheological structure will only be alluded to here.

According to PAVLOV and VINOGRADOV [4, 5, 12], the apparent viscosity of lubricating greases changes with the shear stress as shown in Fig. 8. Changes have been followed by these authors in the range of six orders of magnitude of shear stress values. If these statements are compared with our own electronmicrographs [17, 18, 21], it can be assumed that the figure given by Pavlov and Vinogradov holds only for a part of soap base greases. According to them, the increase of viscosity at low shear stresses can be explained by the fact that at the points of contact of soap fibrils the oil layer is so thin that van der Waals forces may act even through this layer. Therefore, at the starting of deformation of soap structure, first of all these forces must be overcome. These views may certainly hold for greases with a fibrillar structure pattern but not for greases with a deformed continuous soap structure.

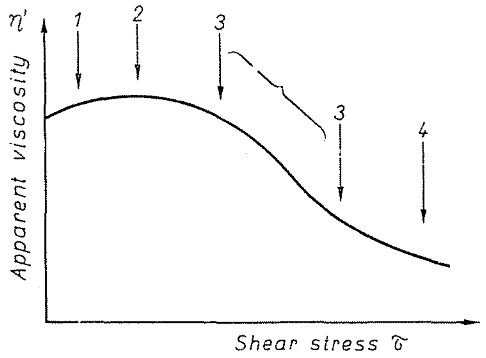

Fig. 8. Change of apparent viscosity of a grease with increasing mechanical stress

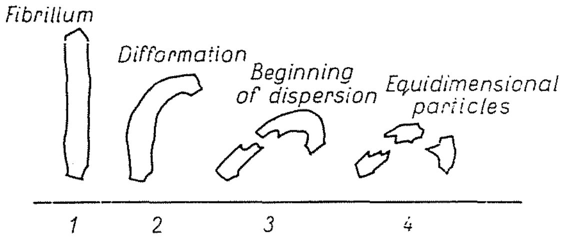

Fig. 9. Differming and dispersion of fibrillar soap particles during mechanical working

Even the changes of apparent viscosity in fibrillar, dispersed type greases may be interpreted more correctly if results of electronmicrographs are taken into account. According to us, fibrils in a lubricating grease of fibrillar soap structure, will be bent by shearing forces in the direction of flow and afterwards, with increasing shear force they will be torn or broken to pieces. This phenomenon schematically shown in Fig. 9 occurs already at relatively low shear stresses.

Fig. 10. Fibrils of a calcium-hydrate base grease at rest

Fig. 11. Calcium-hydrate base grease after 100,000 strokes in the ASTM worker

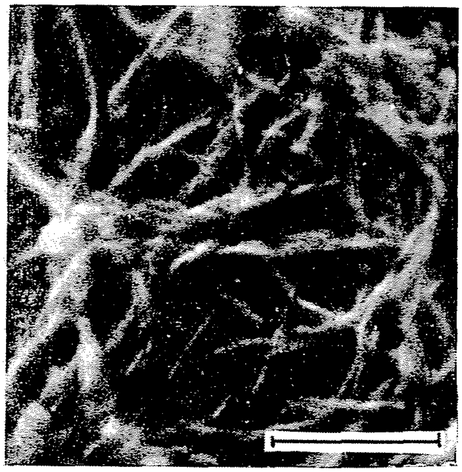

Fig. 12. Fibrils of a lithium-calcium mixed-base grease at rest

Fig. 13. Lithium-calcium base grease after 100,000 strokes

The pattern No. 1 in the figure shows the approximate form of the fibril at rest. If deformed, the grease will develop elastic resistance forces (in state No 2.) to react deformation forces, therefore the apparent viscosity will increase. The higher the elasticity of the fibrils, the higher the increase of viscosity. In state No. 3 and 4, fibrils are torn or broken to pieces, whereby viscosity will be reduced, mostly irreversibly. Processes of breakage of rigid calcium-stearate fibrils could be proved by electronmicrography. Fig. 10 and 11 show the fibrillar structure of a grease at rest and after 100 000 double strokes in the mechanical grease worker, respectively [19, 20].

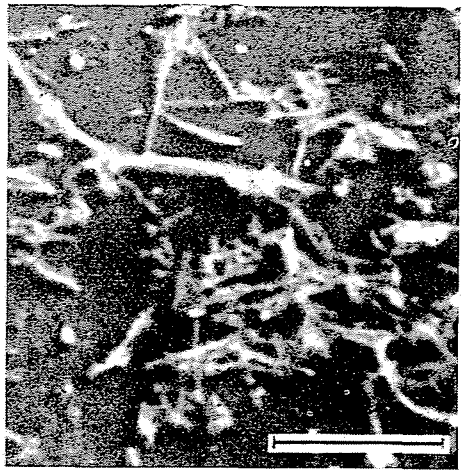

Fig. 14. Fibrils of the lithium-calcium mixed-base grease worked in the roller bearings of the SKF test rig

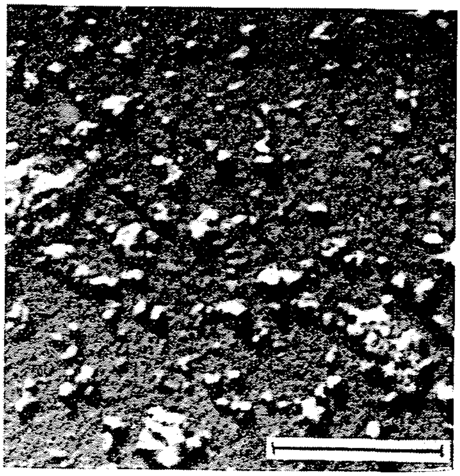

Fig. 15. Fibrils of the lithium-calcium base grease after working in the ball bearings of the SKF test rig

The more elastic lithium or lithium-calcium mixed base soaps behave differently. Changes of their morphology depend on the type of the mechanical stress applied to them. Fig. 12 shows the fibrils of a lithium-calcium mixed base lubricating grease at rest. Fig. 13 shows the same grease, exposed to 100 000 double strokes in the ASTM mechanical worker, to keep the form of the fibrils, yet with reduced lengths. Fig. 14 shows the structure of the same grease after heavy milling in a roller bearing and Fig. 15 shows the dispersing effect of a ball bearing under heavy load and speed [11, 18, 19]. At very high loads the final result is practically the same with all greases. Fibrillar systems are dispersed to small equidimensional colloidal particles and therefore grease structures exposed to long-term high mechanical stresses will finally be more like concentrated sol structures than like fibrillar jellies. In ball bearings, however, this state of the lubricating grease will be reached only in the lubricating layer, while the bulk of the grease, acting as sealer or in reserve, will but slightly change in fibrillar structure.

In conclusion, viscosity changes of lubricating greases in service may be explained partially by the change of colloidal structure. These changes occur in three main steps:

1. reversible, elastic difformation;
2. reversible orientation;
3. irreversible dispersion.

Orientation phenomena have to be assumed but cannot be proved at present by the described electronmicroscopy methods.

As a consequence of these mechanisms, most lubricating greases will be rheopectic at extremely low shear stresses, they may be more or less thixotropic at medium stresses and will be rheodestructive at high stresses. With sodium-based greases with highly elastic fibrils, rheopectic behaviour may be met even at medium stresses. It is a well-known phenomenon that penetration of many sodium-based greases decreases after testing in the ASTM grease worker.

It may be considered as of general validity, that at very high stresses the fibrillar structure is perfectly destroyed and the viscosity of the grease is decreased to a minimum. This low, and during further use practically constant viscosity is called the base viscosity of the grease. As in this state the structure is not deformed but entirely destroyed, after the decrease to the base viscosity no isothermal regeneration of the gel structure can be expected. In lubrication practice it may happen, however, that a machine will run hot in consequence of the low viscosity so that the lubricating grease is heated thereby. At this higher temperature thermal regeneration of jelly structure may occur (Thermorückfederung).

Summary

Lubricating greases may be classified generally as phase colloids. They are complex colloidal systems, in which soap forms the dispersed part, while oil is the dispersion medium. Some structures, however, differ from these types. Most lubricating greases are reversible lyophilic gels. The solid phase contains usually aggregates of associated molecules. During use, lubricating greases are subjected to shear changing the structure of the grease. At high stresses the particles of the soap skeleton are difformed and dispersed. The latter process is usually irreversible.

References

1. Buzágh, A.: Kolloidika (Colloidal Science). Budapest, 1946.
2. Boner, C. J.: Manufacture and Application of Lubricating Greases. McGraw Hill Publ. Co. NY. 1954.
3. Guba, F.—Vámos, E.—Fehérvári, A.: Acta Chim. Acad. Sci. Hung. **31**, 101 (1962).
4. Pavlov, V. P.—Vinogradov, G. V.—Sinitsin, V. V.—Deinega, J. F.: Rheologica Acta **1**, 470 (1961).
5. Vinogradov, G. V.—Pavlov, V. P.: Rheologica Acta **1**, 455 (1961).
6. Lipatow, S. M.: Physiko-Chemie der Kolloide (Physical Chemistry of Colloids). Verlag Chemie, Berlin (1950).
7. Fuks, G. I.: Viscosity and Plasticity of Petroleum Products. Moscow 1951.
8. Kuhn, A.: Kolloidchemisches Taschenbuch (Pocket-Book of Colloidal Chemistry). Leipzig, 1960.
9. Trapesnikow, A. A.—Shlosberg, E. M.: Colloidni Shurnal **8**, 421 (1946).
10. Vámos, E.: Freiberger Forschungshefte, **A 196**, 429 (1962).
11. Lawrence, A. S. C.: J. Inst. Petr. **24**, 207 (1938).
12. Vámos, E.—Fehérvári, A.: Freiberger Forschungshefte, in print.

13. Pavlov, V. P.—Vinogradov, G. V.: Lubr. Engr. **21**, 479 (1956).
14. Vámos, E.—Fehérvári, A.: MÁFKI Közl. (Publ. of the MÁFKI) **3**, 122 (1962).
15. Houwink, R.: Elastizität, Plastizität und Struktur der Materie (Elasticity, Plasticity and Structure of Substances). Springer Verlag, Wien 1950.
16. Göttner, G. H.: Stahl und Eisen, Sonderberichte, Vol. 3, 1963.
17. Vámos, E.—Guba, F.: Schmiertechnik **10**, 5, 275 (1963).
18. Guba, F.—Vámos, E.: Chem. and Ind. Apr. 14, 694 (1962).
19. Vámos, E.—Mózes, Gy.—Fehérvári, A.: M. K. L. (J. of the Hung. Chem. Soc.) **22**, 8, 435 (1967).
20. Liebl, X.—Vámos, E.: Schmierstoffe und Schmierungstechnik **23**, 14 (1967).
21. Vámos, E.—Guba, F.: Freiberger Forschungshefte **A 296** (1963).
22. Liebl, X.—Vámos, E.: Schmiertechnik und Tribologie **15**, 5, 217 (1968).
23. Vámos, E.—Liebl, X.: M. K. L. (J. of the Hung. Chem. Soc.) **12**, 694 (1968).

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