

## CHEMMOTOLOGY

### STRUCTURE AND PROPERTIES OF NATURAL SURFACTANT BASED OLEOGREASES

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*The results of study of the structure and properties of high-temperature oleogreases containing thickener components that can be derived from renewable natural materials are presented. The constitution of the primary structures of the oleogreases prepared by using calcium soaps of fatty acids of poultry fat and palm oil as the organic component of the thickener is established. It is proved that the distinctive properties of the oleogreases are ensured by the thickener system based on a dispersion of calcium carbonate and a natural surfactant. In bulk-mechanical, antioxidative, tribological, and protective properties, the obtained oleogreases are not inferior to commercial superalkaline sulfonate lubricant.*

**Keywords:** oleogreases, renewable material, calcium carbonate, calcite, vaterite, palm oil.

In recent times there has been a steady move in lubricating compositions to replace components produced from petrochemical raw material by renewable materials. The increased interest in agricultural raw material and in oils and fats, in particular, is a response to the instability of the petroleum market and the ecological problems associated with the poor biodegradation of petroleum products.

Among greases produced by the domestic industry hydrated calcium greases (solidols), produced by thickening an oil base (hydrocarbon or vegetable oil) with the soaps of fatty acids in animal fats or vegetable

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oils, are of sufficiently high ecological grade. The widespread use of solidols is favored by their low cost, a series of good characteristics, and the relatively low manufacturing temperatures. However, the working temperatures of these greases are no higher than 60-80°C, which is clearly not sufficient for present day needs.

In the authors' opinion an pressing task of potential scientific interest is the development of a new generation of multifunctional high-temperature greases with the essential degree of biodegradation and ecological safety. Researches are being conducted on the creation of a technology for a new generation of greases in which the thickeners are nanodispersions of calcium carbonate stabilized by the calcium soaps of carboxylic acids. These greases have been named "oleogreases." The present work presents the results of investigations into the constitution of the structural framework and the properties of oleogreases in which the thickening agents are calcium salts of the fatty acids of poultry fat (subsequently referred to as poultry fat grease, PFG) and palm oil grease (POG). This renewable raw material was chosen on the basis of the fatty acid composition of the triglycerides and also its availability on the world market.

The manufacturing technology of oleogreases includes the following stages:

- saponification of fatty material in oil and a hydrocarbon solvent;
- solubilization of calculated amounts of calcium hydroxide and promoter in oil—soap dispersion;
- carbonatization with formation of the superalkaline component of the grease;
- removal of hydrocarbon solvent and promoter from suspension of the highly alkaline component of the grease in oil;
- thermomechanical treatment of the grease.

The greases were prepared with hydrocarbon oil corresponding to group II of the API classification. The oil contained 72 wt. % of paraffin–naphthene hydrocarbons, 21.6 wt. % of "light" and 4.7 wt. % of "medium" aromatic hydrocarbons, and 1.7 wt. % of resins. The fatty acid composition of the triglycerides in poultry fat and palm oil, determined by adsorption chromatography, is presented in Table 1.

Like sulfonate greases, the oleogreases belong to the superalkaline group of greases. This term is generally used to denote dispersions containing an excess of a metal hydroxide in order to neutralize the dispersing agent.

It is known [1] that the specific characteristics of superalkaline greases are determined by the presence of ultradispersed calcium carbonate, formed during the carbonatization process, in their structure. So far, however, a unified theory about the occurrence of this process in complex emulsions and the formation of the structure of superalkaline greases has not been developed. In the opinion of some researchers [2] the elementary particles in the structural framework of sulfonate greases are micelles that in the simplest case consist of

Table 1

Fatty acids	Content, %	
	in palm oil	in poultry fat
Myristic	1.5	1.0
Palmitic	48.5	25.0
Stearic	7.0	7.0
Oleic	35.0	41.0
Linoleic	3.0	21.0
Others	5.0	5.0

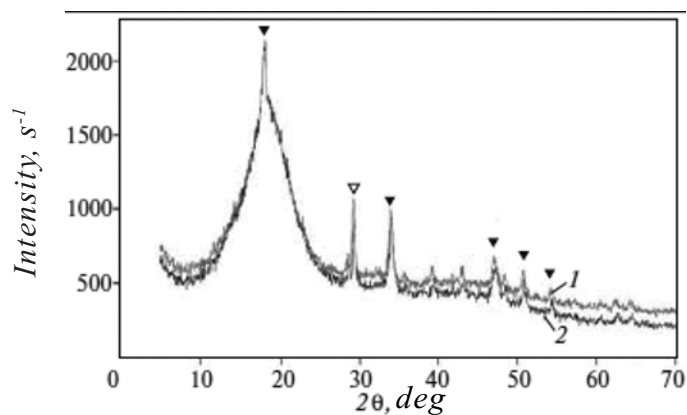


Fig. 1. X-Ray diffraction spectra of oleogreases POG (1) and PFG (2): ▼ –  $\text{Ca}(\text{OH})_2$ ; ▽ –  $\text{CaCO}_3$  (calcite).

calcium carbonate (the inorganic component) and sulfonate (the organic component). However, the mechanism of formation of the macrostructure in the framework of the thickener and the role of the ultradispersed particles in this process have not been explained.

Four modifications of calcium carbonate are known (amorphous calcium carbonate and the three crystalline modifications calcite, vaterite, and aragonite). Vaterite is the least stable polymorph of calcium carbonate and is very rarely encountered in nature. However, cases where the vaterite modification of calcium carbonate is present in superalkaline greases are known [3]. In sulfonate and salicylate greases the calcium carbonate is present in the calcite form.

X-Ray phase analysis was used to determine the form in which the calcium carbonate exists in the oleogreases. The diffractograms were obtained on an automatic DRON-3M diffractometer with a copper anode and a nickel filter in reflected beams of Bragg–Brentano geometry with focused x-ray beams. The diffractograms of the PFG and POG oleogreases hardly differ at all (Fig. 1). The dominant reflection of the calcite crystalline form of  $\text{CaCO}_3$  is a peak at  $29.13^\circ$ . The other diffraction peaks belong to  $\text{Ca}(\text{OH})_2$ . The  $\text{CaCO}_3/\text{Ca}(\text{OH})_2$  ratio by weight, calculated by means of Match! V.1.9a software, is 54/46 for PFG and 58/42 for POG. The reason for the appearance of the broad diffraction halo at  $2\theta = 9\text{--}26^\circ$  is the dispersion medium (hydrocarbon oil). Reflections characteristic of vaterite and aragonite were not detected.

Thus, the results of x-ray phase analysis show conclusively that there are only two crystalline phases (calcite and calcium hydroxide) in the oleogreases. Because of this it can be supposed that the inorganic phase of the thickener represents a composite of the core–shell type. The core is  $\text{Ca}(\text{OH})_2$ , and the shell is calcium carbonate in the calcite form.

It is known [4, 5] that the pH of the medium and the carbonatization temperature play a key role in the formation of one or the other polymorph of calcium carbonate. In a medium with high alkalinity ( $\text{pH} > 12$ ) and at a low process temperature calcite is the dominant product. The formation of vaterite is favored at pH 8.5–10 and at temperatures up to  $40^\circ\text{C}$ . Crystals of predominantly aragonite are formed above this temperature. Eventually, however, all the polymorphs are transformed into calcite as the most stable polymorph at any temperature and any pH value.

During carbonatization calcium carbonate in the vaterite or calcite form is formed in the alcohol–water phase depending on the concentration of  $\text{Ca}(\text{OH})_2$ . Since carbonatization takes place at temperatures below  $40^\circ\text{C}$  the formation of aragonite is unlikely. A compensating layer of hydroxide ions is

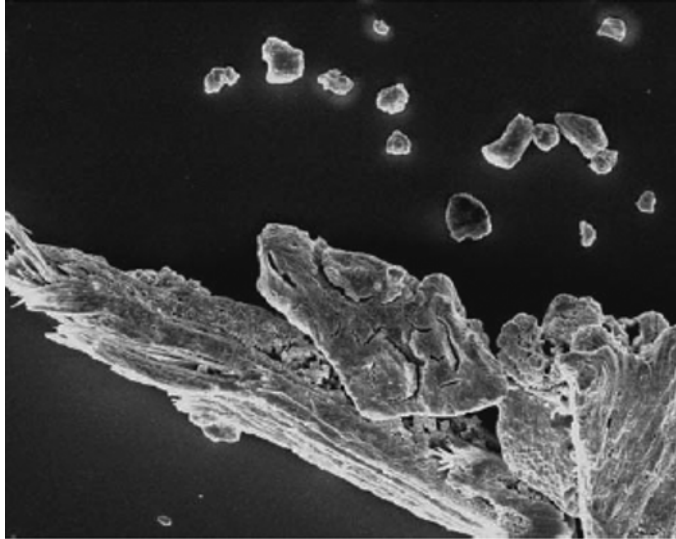
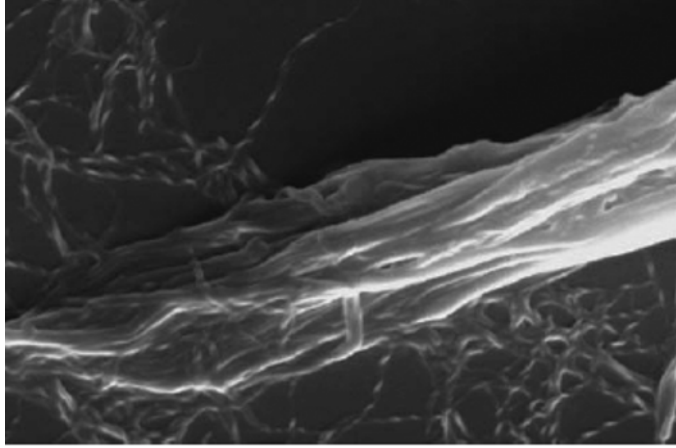


Fig. 2. Microstructure of the dispersed phases of PFG oleogreases (a) and hydrated calcium grease based on soap of technical (inedible) fat (b).

formed on the surface of the positively charged carbonate core. As the temperature increases and the solvent, promoter, and water are removed from the system the calcium carbonate crystals change into the calcite form, and the hydroxide ions are substituted by the oleophilic surfactants (fatty acid soaps). Their concentration on the surface of the calcite is low on account of its low adsorption capacity. However, at high concentrations, like greases with inorganic fillers, the calcite cores are capable of forming supermicellar structures (elements of the structural framework of the grease).

The external form and the spatial structure of the framework in the oleogreases were studied by scanning electron microscopy. With a Camscan microscope it was possible to obtain clear three-dimensional images of the disperse phase of the greases (Fig. 2). Since the calcite polymorphous modification is characterized by low adsorption capacity the presence of disperse phase elements of various shapes and sizes in the structure of the oleogreases (Fig. 2) is explained by the tendency of the colloidal particles to form aggregates. These aggregate formations are involved in the formation of the thickener structure.

The structure of the oleogreases based on natural fats includes various types of fibers the external appearance of which is characteristic of hydrated calcium greases (fatty solidols) [6]. The degree of dispersion of the crystals of the calcium soaps is increased as a result of the presence of solidols of a wide range of saturated and unsaturated fatty acids in the composition of the thickener. Concurrent enlargement of the

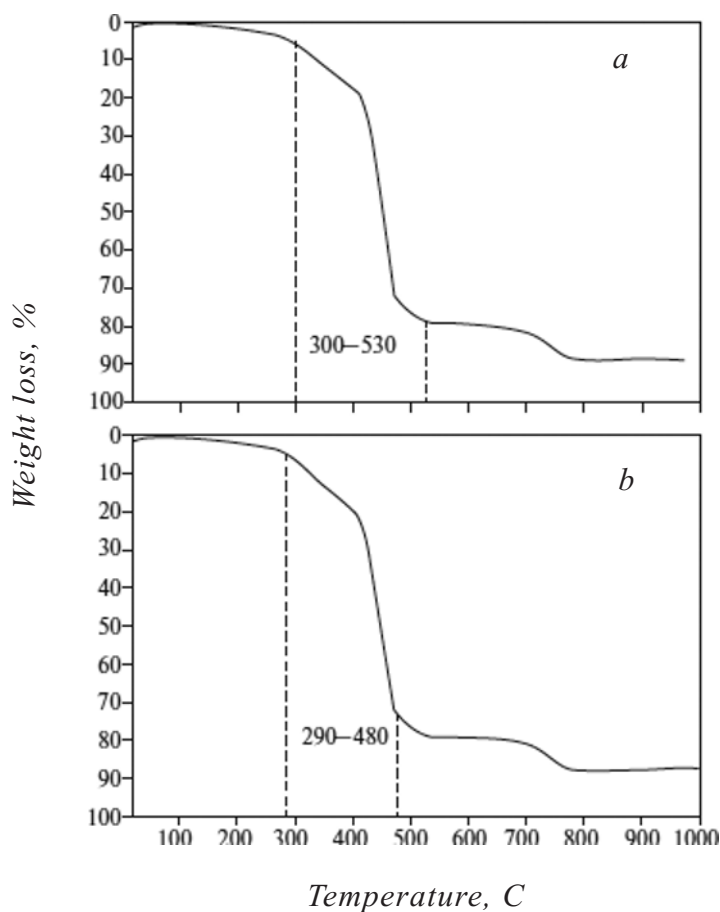


Fig. 3. Thermogravimetric analysis curves of POG (a) and PFG (b).

Table 2

Indices	PFG	POG	Commercial sulfonate grease	Testing methods
Dropping point, °C	305	290	>250	GOST 6793
Penetration at 25°C with agitation, mm/10	287	274	305	GOST 5346, method C
Colloidal stability, % released oil	1.8	1.4	1.5	GOST 7142
Effective viscosity (Pa·s) at temperature –20°C and average gradient of deformation rate 10 s <sup>-1</sup>	1828	1432	1962	GOST 7163
Shear strength at 20°C, Pa	500	560	230	GOST 7143, method B
Antioxidant stability from increase of acid number at 150°C, 10 h, mg KOH/g	3.1	3.36	1.12	GOST 5734
Mechanical stability: change of shear stress at 20°C in Shell roll test, failure index, %	8	0	1	ASTM D 1831
Water washout at 79°C for 1 h, %	1	1	1	ASTM D 1264
Lubricating properties on four-ball machine at (20±5)°C: weld load, N	3685	3479	4136	GOST 9490
Diameter of wear spot at 110°C, mm	0.46	0.49	0.42	ASTM D 2266
Coefficient of friction at 110°C	0.045	0.024	0.033	ASTM D 2266

particles of soaps of various acids leads to the appearance of a large number of crystallization centers and, by preventing the free formation of crystals of the individual soap molecules, gives rise to the formation of a highly developed structural network containing a large number of contacts in unit volume.

Thus, the structure of the disperse phase in the oleogreases contains aggregated calcium carbonate formations and fibers of calcium soaps of fatty acids with various structures.

Since the oleogreases are intended for use at high temperatures their upper working temperature limit was determined by thermogravimetric analysis (TGA). On the curve for the temperature dependence of the weight loss (Fig. 3) the initial horizontal section indicates that the oleogreases are relatively stable up to 300°C. The vertical drop on the curve beginning at 400°C indicates strong chemical decomposition of the greases when this temperature is reached. The form of the curves indicates that the two oleogreases behave almost identically as the temperature rises. In this case the nature of the components of the thickener does not play a significant role.

During the investigations it was found that preparation of samples for greases with penetration characteristics corresponding to class 2 of the NLGI scale requires a different amount of thickener based on fat and vegetable material, i.e., the thickening capacity of the investigated oils varies and depends on the fat/oil composition, the manufacturing conditions, the degree of purification, and so forth.

The results of the investigations are presented in Table 2. As seen, the oleogreases are characterized by high colloidal stability and dropping points and good low-temperature characteristics. Tests were also done on the operating characteristics of the oleogreases: resistance to oxidation, mechanical stability, antiscuffing characteristics (weld load), and water washout (Table 2). The characteristics of commercial superalkaline sulfonate grease are given for comparison.

The antiwear and antifriction characteristics of the oleogreases were determined according to ASTM D 2266 on a Falex FB Wear Test Machine. The antiwear characteristic of the greases was the mean value of the diameter of steel ball wear spots. The average coefficient of friction, determined in the last 10 min of the four-ball friction test, was determined as a measure of the antifriction characteristics. The test conditions, corresponding to the ASTM D 2266 procedures, reduce the likelihood of a liquid (hydrodynamic) friction regime and favor a boundary friction regime and also mechanochemical wear of the friction surfaces.

As follows from the test results (Table 2), the antiwear characteristics of the oleogreases are high, while the coefficient of friction is fairly low. Altogether, the properties of the oleogreases correspond to high-grade antifriction greases. It should be noted that complex sulfonate greases usually include a parcel of antiwear, antioxidant, and anticorrosion additives. These additives are not present in the oleogreases. However, the oleogreases do show good tribological performance without these additives.

Since the oleogreases were prepared from the same base oil and do not contain functional additives all their distinguishing features are produced by the thickener system. While effectively thickening the base oil and keeping it within its framework the thickener in addition confers good performance characteristics onto the grease.

As shown by the results of the investigations, the oleogreases compare well in mechanical, antioxidant, and tribological characteristics with the commercial superalkaline sulfonate grease containing parcels of additives. Moreover, the oleogreases are environmentally safer since they are made with available renewable raw material components in the thickener. This is demonstrated by the high level of biodegradation (>50%) of the oleogreases.

Thus, to summarize the results of the investigations it is possible to make the following conclusions:

- Simple but not complex superalkaline oleogreases with balanced mechanical, antioxidant, tribological, and protective characteristics were synthesized, and they compared well with or even surpassed commercial superalkaline sulfonate grease in performance;
- The constitution of the primary structures for the oleogrease thickeners was established, and the ultradispersed substances formed in the carbonatization process were identified; the inorganic component of the thickener in the oleogreases is a composite of the core-shell type, and the shell is represented exclusively by the calcite modification of calcium carbonate;
- It was shown that all the distinguishing characteristics of the oleogreases are secured by a thickener system based on a dispersion of calcium carbonate and a surfactant of natural origin.

## REFERENCES

1. R. J. Muir, *NLGI Spokesman*, 52, No. 4, 140-146 (1988).
2. O. Makedonsky, E. Kobylansky, Y. Ishchuk, *Eurogrease*, 4, 5-23 (2003).
3. R. Zhang, *Eurogrease*, 4, 15-24 (2009).
4. C. Y. Tai, F. B. Chen, *AIChE Journal*, 44, No. 8, 1790-1798 (1998).
5. K. Sawada, *Pure and Applied Chemistry*, 69, No. 5, 921-928 (1997).
6. Yu. L. Ishchuk, *Composition, Structure, and Properties of Plastic Greases* [in Russian], Naukova Dumka, Kiev (1996), p. 512.