# The Phase Behavior of Soaps in Organic Solvents and Its Relation to Lubricating Greases

GEROULD H. SMITH*
Stanford University, California

## Introduction

THE first lubricating greases are said to have been simple mixtures of calcium soaps in oils for use on axles of wagons and carts. However, the calcium soap greases of commerce are estimated (1) to contain 500 to 1000 distinct chemical compounds. In addition, as little as 5% by weight of calcium soap will thicken mineral oil when the calcium grease is properly stabilized. In view of these considerations the calcium greases are in reality neither simple nor mixtures. Such is the case with all other greases of commerce which may contain many different types of fatty materials as soap stocks (2), different metals as bases, and oils of varied types from different sources.

In view of the complexity of lubricating greases, contributed both by their nature and by practice, it is not surprising that their manufacture and use is attended by many instances of apparently anomalous behavior. The occurrence of syneresis, formation of hard, gelled lumps of soap, liquefaction of greases in service, and unpredictable changes in texture either in service or during manufacture, all have been troublesome. The alleviation of these troubles has depended on empirical trial and error.

Only a few systematic phase studies (3, 4, 5, 6, 7, 8) of soaps in non-aqueous solvents have been reported. The data reported in one of these (7), together with important effects of water and other additives are related to the structure of lubricating greases in this communication.

## Materials

The sodium stearate, prepared from sodium ethylate and Eastman Kodak Company stearic acid (white label) No. 402, was identified as the $\gamma$-form by x-ray analysis (9, 10). It was neutral to phenolphthalein in boiled-out 95% ethyl alcohol.

The toluene, cyclohexane, lauric acid and nitrobenzene were the best products obtainable from the Eastman Kodak Company. The methyl alcohol was a product of the Carbide and Carbon Chemicals Company, and the glycerine was Merck's U.S.P. grade. The solvents and additives were all dried over Drierite (anhydrous calcium sulfate). The refractive indices of the dried solvents agreed with those in International Critical Tables.

## Experimental Techniques

Samples of soap and solvent were sealed in pyrex glass tubes as described by Smith and McBain (7). These samples were visually studied, using polarized light, while they were heated and cooled in thermostatically controlled air or liquid baths. Changes in opacity, birefringence, viscosity, syneresis, and volume were used to follow the phase behavior of the systems. Microscopic examinations and photomicrography, both with polarized light, supplemented the visual studies.

Temperatures, designated by $T_I$, were those at which, on cooling, anisotropic material began to separate from the single phase isotropic systems.

All thermometers and thermocouples were carefully calibrated.

## Terminology

The ordinary terminology of the physical chemists is based on changes of state among large well-defined crystals, true liquids, and bases. This terminology is inadequate to describe the changes associated with colloidal behavior such as transformations without phase change from sol to jelly, or from thixotropic to dilatant systems of the same composition, and other equally important, well marked transformations which may or may not involve phase changes. Since sodium stearate and hydrocarbons form such colloidal systems, it is necessary to enumerate and define the chief characteristic forms in which these are found to occur:

*Gels* are two-phase systems involving a crystalline soap phase, more or less disintegrated or comminuted, and a second phase which may be liquid-crystalline, a jelly or a sol. Varieties of gels differ in appearance according to whether the crystalline soap is compacted or dispersed, coherent or non-coherent, together with all intermediate stages. Gels are usually white and opaque but may be translucent and, in rare cases, with a suitable combination of refractive indices, the two-phase gel can appear transparent. Some gels, like Pears soap (11), are transparent because the crystalline phase is ultramicroscopically fine. The crystalline phase can usually be recognized by x-ray examination. Gels made of the same materials may not be equally stable for this depends on such factors as degree of crystallinity of the solid and its state of subdivision and solvation.

*A liquid crystalline solution* is a single phase which is birefringent and anisotropic, ranging from transparent to semi-opaque, depending upon orientation and concentration. Usually it is plastic and only slightly elastic and does not flow in small samples under the influence of gravity. X-ray examination shows one- or two-dimensional, not three-dimensional orientation, giving a pattern quite different from that of the crystalline solid.

*Sol or jelly* is a single phase system, identical for sol and jelly, in which there is a gradual change from complete fluidity to the rheology of a typical jelly, depending upon concentration and temperature. Such a system is isotropic, elastic, thixotropic, and transparent.

The Gibbs Phase Rule is found to apply to true reversible equilibria among these phases. Owing to the defective fluidity of the liquid-crystalline phases, other phases with which they are in equilibrium, such as sol, jelly, crystals or other liquid crystals, quite frequently cannot separate or segregate. Many writers include all such systems under the name "gels," not reserving it, as has been done here, for the systems involving the solid, crystalline phase.

---

* Present address: Union Oil Company of California, Oleum, Calif.

## Experimental Observations and Data

Anhydrous systems of sodium stearate in a pure hydrocarbon are shown to exist as a gel, one of two liquid-crystalline phases, a jelly or a sol, depending on temperature, concentration, and history of the sample (7). The transformations among these forms occur at about the same temperature for corresponding samples in all of the pure anhydrous hydrocarbon solvents tested. The phase diagrams are based upon several hundred observations of upwards of one hundred samples with the twelve hydrocarbons (7). The behavior of the pure, dried sodium stearate in dried hydrocarbon solvents is illustrated by solid lines in the generalized temperature-composition phase diagram in Figure 1. However, the use of undried soap, impure solvents or the deliberate addition of water, fatty acids or alcohols cause remarkable deviations from the behavior of the anhydrous pure systems.

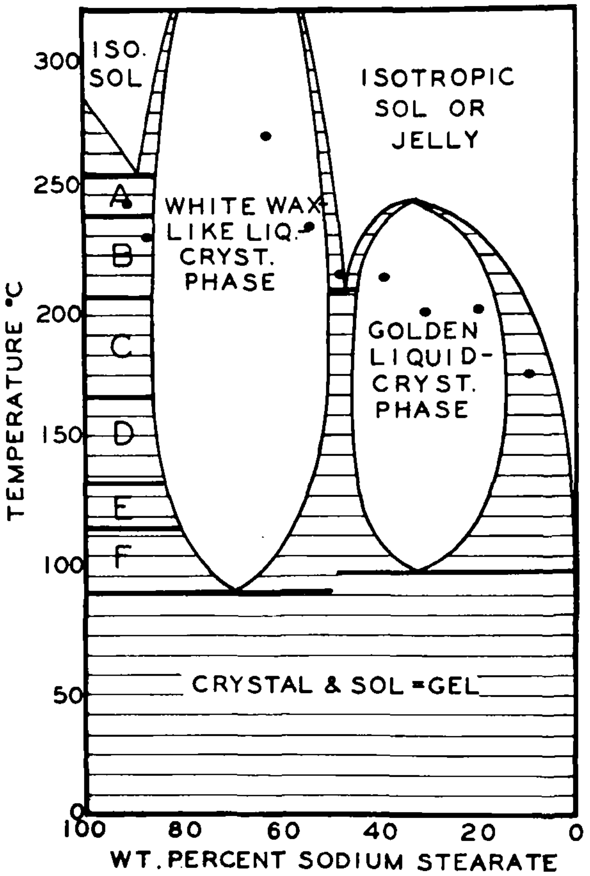

FIG. 1. Phase diagram of sodium stearate in dried toluene. Lines represent values obtained with dried soap and black dots represent values with undried soap. A, neat soap and liquid-crystalline phase; B, subneat soap and liquid-crystalline phase; C, superwaxy soap and liquid-crystalline phase; D, waxy soap and liquid-crystalline phase; E, subwaxy soap and liquid-crystalline phase; F, supercurd soap and liquid-crystalline phase.

The more marked effects of these additives were a lowering of the temperature of transformation to the isotropic phase, and acceleration of the transformation from the liquid-crystalline state to the gel form. Very small amounts of moisture were so effective in causing both of the above modifications that either could be used as a measure of the dryness of the system. Corresponding data for systems of toluene containing dried and undried sodium stearate, respectively, the latter with 0.75% of water by weight, are summarized in Table I. The $T_i$ values of those samples prepared with undried soap are represented as black spots in Figure 1, illustrating the marked decrease of the $T_i$ values caused by the presence of moisture therein. Water appears to cause a much greater lowering of the $T_i$ values in the white, wax-like, liquid-crystalline phase than in the golden, liquid-crystalline phase. Comparative data may be found in Table II.

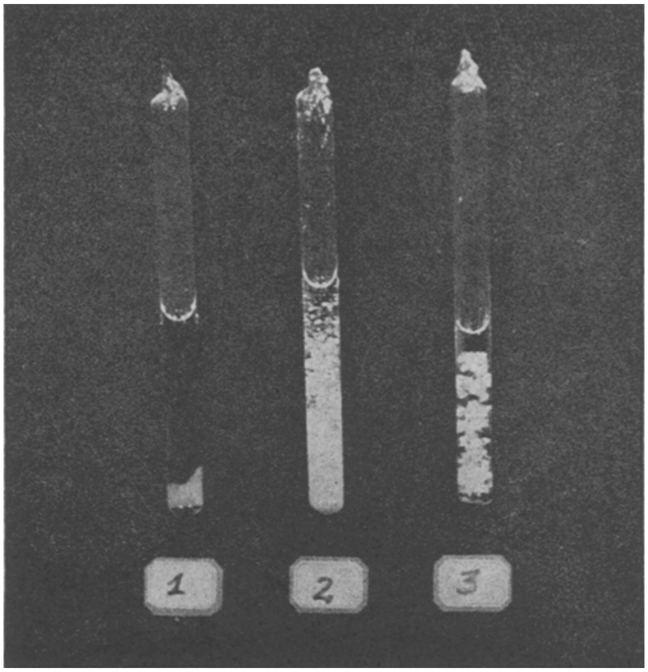

FIG. 2. Unheated samples of sodium stearate in cyclohexane, containing additives. (These samples stored one year at room temperature.) Legend:

| No. | Additive | % Additive | % Soap |
|---|---|---|---|
| 1 | Nitrobenzene | 9.72 | 2.84 |
| 2 | Lauric acid | 2.41 | 3.74 |
| 3 | Methyl alcohol | 2.4 | 3.1 |

Samples of sodium stearate in cyclohexane were prepared with water, nitrobenzene, lauric acid, and methyl alcohol as modifiers. Those modified with water or nitrobenzene, when stored and examined before heating, exhibited the same behavior as the anhydrous systems; that is, the stearate does not swell. However, under the same conditions, those containing methyl alcohol and lauric acid swell five- to ten-fold, as shown in Figure 2. The individual, white, opaque particles are each surrounded by a shell of clear, isotropic jelly. Both methyl alcohol and lauric acid depress the $T_i$ values by as much as 60 or 100° C.

Lauric acid or water causes the system to become very hard and white on cooling while samples containing methyl alcohol cool to a soft, white, silky system that becomes semi-fluid on shaking.

A microscopic examination of a sample containing lauric acid showed that the white appearance is the result of a myriad of small, round clusters of needle-like crystals, shown in Figure 3. The white appearance of the samples modified with methyl alcohol is caused by the felt-like structure in Figure 4. This felt is composed of oriented aggregations of very small, needle-like crystallites less densely packed. The dry nitrobenzene had no observed effect and, like the

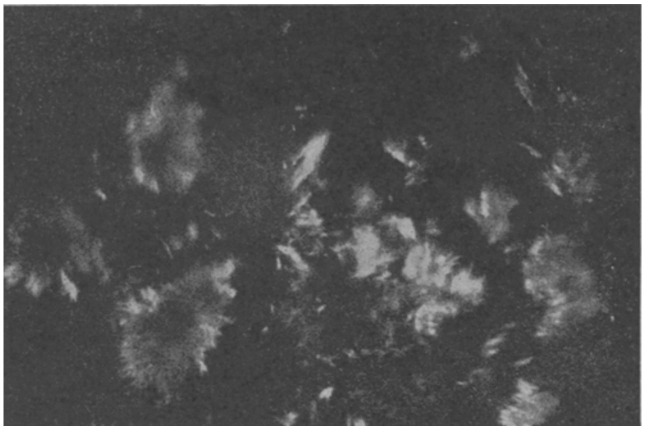

Fig. 3. Photomicrograph of gel of sodium stearate in cyclohexane, with lauric acid as an additive. (Cooled from isotropic solution; magnification 60 ×; polarized light.)

anhydrous uncontaminated sample, resulted in a syneretic plug of gel (Figure 5) which may be compared with Figures 3, 4, and 6). The addition of nitrobenzene to systems of aluminum dilaurate in hydrocarbons causes a marked lowering of the temperature of transformation to the jelly phase (12).

Table III summarizes data pertinent to the modified samples of sodium stearate in cyclohexane.

## Discussion

The complicated and confusing behavior of lubricating greases can be explained largely by correlation with the properties of those various phases and modifications. Furthermore, these properties, phases, and forms are not peculiar to systems of sodium soaps in hydrocarbons. Similar behavior is reported for the various aluminum disoaps in hydrocarbons (6), soaps in water (13), rubber in hydrocarbons (14, 15), gelatin in water (16, 17), and silver soaps in hydrocarbons (18).

## Anhydrous Systems of Sodium Stearate in Hydrocarbons at Room Temperature

The anhydrous sodium stearate does not noticeably swell in the pure, dried hydrocarbons until heated but remains as opaque, white dispersible particles (7). When heated, the systems pass to one of the two liquid crystalline phases and then to an isotropic jelly or sol with further heating. Thus, the soap must

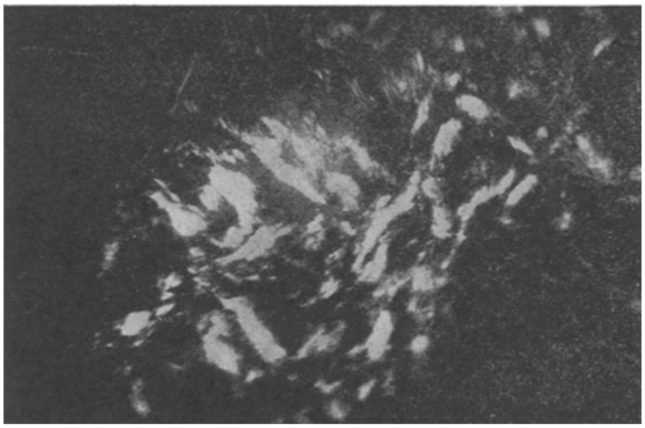

FIG. 4. Photomicrograph of gel of sodium stearate in cyclohexane, with methyl alcohol as an additive. (Cooled from isotropic solution; magnification 24 ×; polarized light.)

TABLE I.

Systems Containing Anhydrous Sodium Stearate, or Undried Sodium Stearate in Dried Toluene.
(Critical Temperature of Toluene = 320.6° C.)

| Soap | | Water | | $T_1$,°C. | Description of Cooled Systems | |
|---|---|---|---|---|---|---|
| Wt.% | Mol % | Wt.% | Mol % | | Immediately | After Storage |
| 0.93 | 0.3 | .... | .... | (133)* | Very slightly opalescent gel in clear liquid | Very slightly opalescent gel particles in clear liquid |
| 9.1 | 3.14 | .... | .... | (165) | Clear gel in clear liquid (opalescent overnight) | Very slightly opalescent gel plug in clear liquid |
| 18.9 | 6.5 | .... | .... | 225 | Opalescent gel; syneretic | Slightly opalescent plug; syneretic |
| 36.0 | 15.5 | .... | .... | 244 | Faintly cloudy; no syneresis | Partly cloudy; slightly syneretic |
| 45.4 | 21.2 | .... | .... | 235 | Slightly opalescent; no syneresis | Opalescent plug; slightly syneretic |
| 55.9 | 29.0 | .... | .... | 287 | Semi-translucent gel with clear liquid | Opalescent plug; slightly syneretic |
| 60.3 | 33.0 | .... | .... | 331 | Opaque in semi-translucent gel | Opaque in semi-translucent gel; slightly syneretic |
| 77.9 | 53.3 | .... | .... | 335 | Opaque in semi-translucent gel | Opaque in semi-translucent gel; slightly syneretic |
| 89.8 | 74.1 | .... | .... | 257 | White, opaque | Opaque in semi-translucent gel; slightly syneretic |
| 94.6 | 85.0 | .... | .... | 264 | Hard white, opaque | Opaque in semi-translucent gel; slightly syneretic |
| 8.9 | 3.0 | 0.07 | 0.4 | (175-180) | Badly strained; syneretic; opalescent gel | No change |
| 20.0 | 7.4 | 0.15 | 0.9 | 202 | Opaque; white; not syneretic | Like semi-cold paraffin wax; not syneretic; semi-translucent; white |
| 31.3 | 12.8 | 0.24 | 1.5 | 201 | White; opaque; slightly syneretic | White; opaque; slightly syneretic |
| 38.8 | 19.3 | 0.29 | 2.4 | 215 | White; semi-translucent; syneretic | White; semi-translucent; slightly syneretic; contracted |
| 48.0 | 22.6 | 0.36 | 2.7 | 216 | White; opalescent; not syneretic | White; opalescent; milky; contracted; not syneretic |
| 54.2 | 27.0 | 0.41 | 3.3 | 235 | Semi-translucent; white gel | Semi-translucent; white; slightly syneretic |
| 63.0 | 34.4 | 0.48 | 4.2 | 271 | White layer; semi-translucent; not syneretic | White, opaque kernels in translucent; not syneretic |
| 87.2 | 64.8 | 0.66 | 7.6 | 231 | White; semi-opaque; not syneretic | White, opaque kernels in translucent; not syneretic |
| 91.5 | 72.4 | 0.69 | 8.6 | 245 | White; semi-opaque; slightly syneretic | White; semi-opaque; not syneretic |

* Temperatures in parentheses are approximate; because on heating, the dispersion could not be made quite uniform; and on cooling, the systems undercool as isotropic jellies.

TABLE II.
Effect of Varying Moisture Content on Samples of Sodium Stearate in Toluene.

| % Soap | % Water | $T_1$,°C. | Description of cooled system |
|---|---|---|---|
| 60.3 | none | 331 | Opaque in semi-translucent gel; slightly syneretic |
| 63.0 | 0.48 | 271 | White opaque kernels in translucent; not syneretic |
| 59.7 | 4.0 | 221 | Opaque, white, contracted; not syneretic |
| 45.4 | none | 235 | Opalescent plug; slightly syneretic |
| 48.0 | 0.36 | 216 | White, opalescent, silky contracted; not syneretic |
| 45.0 | 9.3 | 124 | Opaque, white curd fibers, silky |

be heated to disperse it thoroughly. The systems undergo a sharp reversal passing from the isotropic phase to liquid crystal when cooling. The lower change to gel form is hardly ever sharp and may require months or years to become complete. Because of this, lubricating greases are useful even though they actually may be metastable systems.

## Sodium Stearate in Glycerine

The mode of the recrystallization of the jelly and liquid-crystalline phases to the gel form, was observed with systems of sodium stearate in glycerine. Samples of glycerine, containing 8 and 35% of sodium stearate, were heated to clear, isotropic sols. These sols became rigid when cooled and the system containing 8% of soap remained clear and isotropic as a jelly for two weeks while the more concentrated system became opaque and white on cooling. The 8% jelly became cloudy with the simultaneous appearance of syneretic drops on the surface after two weeks. A microscopic examination of thin slices of each sample (magnification 20) showed that the white appearance or milkiness resulted from needle-like segments of crystals that exhibited a white, sharp birefringence when viewed with polarized light.

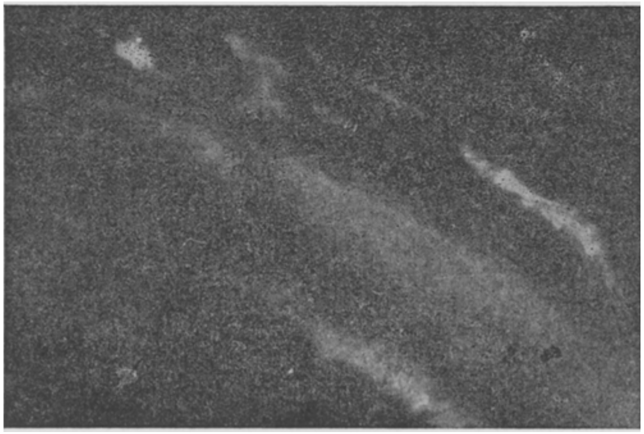

FIG. 5. Photomicrograph of gel of sodium stearate in cyclohexane, with nitrobenzene as an additive. (Cooled from isotropic solution; magnification 24 ×; polarized light.)

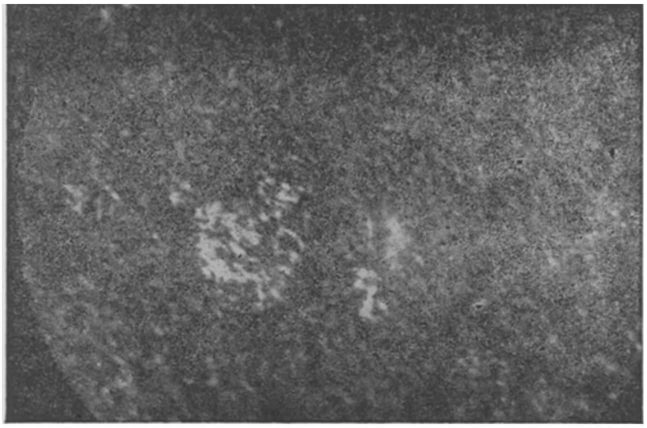

FIG. 6. Photomicrograph of sodium stearate recrystallizing from an isotropic, glycerine jelly. (Magnification 230 ×; photographed using polarized light.)

When the gel was squeezed between a coverglass and slide, these crystals were transported by a micromatrix, in which they were embedded, that was self-supporting and elastic. The crystalline particles were not responsible for the structural behavior characteristic of the thickened hydrocarbon system. The slide of the 8% gel was re-examined, using a magnification of 860 diameters. The crystalline particles observed at the low magnification were found to be aggregates of smaller birefringent particles and a fine, three-dimensional, partially birefringent netting was visible as a woven matrix. It was composed of extremely small centers of birefringent material, and when ruptured exhibited an uneven and ragged edge.

A microphotograph, Figure 6, shows the structure of the system magnified 230 times. The small, birefringent particles cluster to form more compact crystal groups and the network does not consist entirely of the clearly resolvable gel crystallite, suggesting still smaller, unresolvable crystallites aggregated to form the fine structure exhibited here.

Since the soap is so insoluble at room temperature it was probable that these slowly crystallizing systems are similar in structure to the inorganic gels prepared by P. P. von Weimarn (19). Gelatinous precipitates of barium sulfate in water were rigid

TABLE III.
Selected Data on Systems of Sodium Stearate in Cyclohexane, Containing Additives.

| % Soap | | Additive | | | $T_1$,°C. | Description of cooled system | |
|---|---|---|---|---|---|---|---|
| By wt. | Mol % | Name | Wt. % | Mol % | | Immediately after cooling | After storage |
| 11.5 | 3.8 | None | ...... | .... | 192 | Slightly opalescent plug in clear liquid | Opalescent chunks in clear liquid |
| 12.3 | 3.9 | Water | 0.17 | 0.9 | (150+) | Part curdy, part semi-translucent | All white, curdy syneretic |
| 8.9 | 2.7 | Water | 1.19 | 5.7 | 125 | All white, opaque curd | All white, opaque curd, syneretic |
| 2.84 | 0.9 | Nitrobenzene | 9.72 | 7.9 | 160-180 | Slightly opalescent, syneretic gel chunks in clear liquid | All white, opaque curd, syneretic |
| 3.74 | 1.1 | Lauric acid | 2.41 | 1.0 | 100 | White, not syneretic, opaque, rigid. Broke up on vigorous shaking | Centers of crystallization growing in system, perhaps slightly syneretic |
| 3.1 | 0.9 | Methyl alcohol | 2.4 | 6.2 | 93 | White, flowing, silky, opaque gel | Centers of crystallization growing in system, perhaps slightly syneretic |

but unstable, with the growth of large particles proceeding rapidly at the expense of the primary particles, with simultaneous freeing of water. The primary particles were so fine that they could not be resolved by either the microscope or the ultramicroscope.

Other studies, where a close relationship was found to exist between the growth of crystalline particles and reversible jelly or liquid-crystalline formation, have been reported by Thomas and Sibi (20) for soaps and organic compounds, P. P. von Weimarn (21) for sodium oleate in aromatic hydrocarbons, Laing and McBain (13), and McBain and McBain (22) for aqueous soap systems.

### Additives and Their Effects

All systems of soap and hydrocarbons are changed in texture, appearance or other characteristics by the addition of certain substances such as water, fatty acids, alcohols, glycerine and glycol type solvents, phenols, rosin, etc. (5, 6, 23, 24, 25). The net result in many cases is the formation of a jelly or colloidal sol from systems which were more or less unthickened gels without additives. The main result of the modification of the systems of sodium stearate and hydrocarbons has been the lowering of the temperature for phase transformations. In addition, the soap is recrystallized to form fibers or crystalline clusters. This demonstrates that the action of these additives is both to lessen the extreme insolubility of the soap and to combine with it, facilitating crystallization. Sodium stearate forms hydrated curd fibers with water. In fact, the bundles of curd fibers are visible to the naked eye in samples containing about 10 to 20% of water. A similar action may occur with other additives.

A microscopic examination of a cooled sample containing lauric acid as an additive shows that the white, opaque appearance was caused by innumerable circular clusters of needle-like crystallites (Figure 3). Since the system recrystallized at 98°, crystals of the lauric acid (m.p. 48°) could not have initiated crystallization. Sodium stearate was placed in solutions of lauric acid in cyclohexane and the change of concentration of the fatty acid in the supernatant liquid measured. The decrease in the concentration of the lauric acid indicated that the additive associated itself with the soap, reacting to form acid soap (NaStr.HL) or some other type of complex with the soap.

Slater (26) concluded that "peptization" involved sorption of the additive by the dispersed phase through primary or secondary valence forces, one part of the "peptizer" molecule uniting with a part of the colloid molecule. Palit (27) has shown that mixed solvents of a hydroxylated solvent-hydrocarbon type dissolve sodium soaps when none of the constituents of the mixture alone will dissolve any appreciable amount of soap. Solution was attributed to the solvation of different parts of the soap by van der Waals' forces and hydrogen bonding.

These previously published conclusions are in accord with the observations of the current study. Systems of sodium stearate in p-cymene and n-butylbenzene exhibited lower temperatures of transformation than the other purer hydrocarbon solvents (7). The p-cymene probably contained terpenes. The use of terpenes was shown by Markowicz (28) to form lower melting gels or jellies with the aluminum dipalmitate than with other hydrocarbons.

### The Thickening of Hydrocarbons by Soap

A hydrocarbon may be thickened by soap in a gel form, in a liquid-crystalline form, or in the jelly form. The thickening occurring with soap in a gel form is often the result of compaction of swollen lumps, which may or may not have swelled to a limit. That occurring with soap in the jelly phase is caused by homogeneous, associated, colloidal dispersion of the soap in so random a manner that the resulting system is isotropic. The jelly will exhibit unlimited swelling and thus, when in equilibrium, no free solvent will be present. The gel, on the other hand, exhibits only limited swelling and can exist in equilibrium with an excess of free solvent. Likewise, at least some liquid-crystalline forms can exist in equilibrium with an excess of solvent even though these are more efficient than the gel form for thickening the hydrocarbon. The jelly form is the most efficient thickener but, in practice, probably co-exists with the other forms as a result of undercooling and incomplete initial dispersion of the soap.

The familiar behavior of aluminum and lithium stearate during commercial grease production is a practical example of the greater thickening efficiency of the jelly form. When these soaps are dispersed in cold oil, they remain suspended as opaque, crystalline material without becoming thick and grease-like. They are gels. However, on heating, the slurries develop a heavier, stringy body. Oil containing aluminum stearate exhibits this behavior at about 40-50° C. (110-120° F.) and that containing lithium stearate at about 200° C. (390-400° F.). This change corresponds to the change to the jelly state for the aluminum stearate (7) and the same would be expected to be true for the lithium stearate.

### The Texture of Lubricating Greases

Each type of grease is commonly associated *a priori* with a definite type of texture or structural appearance. However, in view of this phase study, similar work with other soaps (3, 6), and with practical experiments during the actual manufacture of greases, this does not appear to be justified. The various phases and forms observed for the systems of soap and hydrocarbons exhibit different structures or textures which are characteristic of the forms. Furthermore, the use of additives produces marked changes in the appearance and texture of greases. Thus grease texture can be changed by a suitable readjustment of the conditions of temperature, composition, and pressure or by the use of selected additives which shift the temperature of transformation between phases or modify the rate of recrystallization or orientation on cooling.

As an example, consider the case of sodium greases which may vary from a soft, clear, buttery, sticky texture to a coarser fiber grease containing fibers which may be macroscopic in some dimensions. Both extremes may contain the same amount of soap and be prepared from the same oil. They may contain the same amount of crystalline soap, differing only in degree of comminution. Water, glycerine and other polar compounds promote fiber-growth by facilitating the recrystallization to the gel form while the free fatty acid can smooth the grease by lowering the temperature of transformation to the jelly form. The fibers result from the orientation or alignment of hydrated crystals of curd soap, when water is used as an additive. Gallay and Puddington (29, 30) have studied the curd fiber effect of glycerine in the formation of a phenomenon known to occur by grease manufacturers when tallow is used as a soap stock. Mechanical orientation occurs with kettle working if it takes place below the temperature of transformation to the gel form. Thus an extended mild working of any sodium base grease in the kettle, regardless of its modification may develop a fibrous structure below 80-90° C.

Thus, the texture of greases should be attributed to the nature of the form in which the system exists, regardless of the base.

### The Structural Stability of Lubricating Greases

The consideration of the stability of lubricating greases is confused by the lack of a clear idea concerning its relation to the phase transitions and the role of additives. Studies have been conducted to show that soaps cannot thicken oils without a third component or stabilizer (31, 32). On the other hand, it has been claimed that soaps can thicken mineral oils in the absence of stabilizers (33). All such studies may well have been affected by the inadvertent presence of impurities in either the soap or the oil.

The desired structural stability for lubricating greases is one which does not exhibit syneresis, liquefaction in service, or the formation of hard lumps. All of these undesirable occurrences are the direct result of the reversion of the jelly or liquid-crystalline states to a gel form. In all cases where this reversion has been observed to occur, the system acquires a milky, turbid or opalescent appearance in the system with the simultaneous occurrence of free, isotropic solvent. This then ultimately progresses to gelled chunks of soap in supernatant solvent or oil. X-ray diffraction shows these gelled soap chunks to be completely recrystallized to the original dimensions of the dry soap (12).

The phenomenon of syneresis is simply the accumulation of solvent which was engaged in the stable forms containing randomly distributed soap. It becomes freed when the soap recrystallizes, thus robbing the system of the basic thickening units and reorienting them in a more compact form which has little if any affinity for the solvent. Therefore, contrary to a popular belief, the thickening agent in a stable grease is not so much the fibers as the colloidal jelly or liquid crystal structures.

Often the soap remains in a metastable condition as a liquid-crystalline phase or jelly when the thickened system is under-cooled below the temperature of crystallization. A majority of buttery, clear greases are examples of this. A slow rearrangement may occur since the soap molecules realign themselves with difficulty having too little kinetic energy. Accordingly, some systems revert more rapidly if heated.

No phase changes are observed to occur at temperatures above the transformation where the jelly is formed; the only observed change is a gradual decrease in viscosity as the temperature increases. Thus, as long as the systems are kept in the jelly state, they are stable and homogeneous. Certain additives depress the temperature of the transformation to the jelly phase and if this is depressed below the lowest temperature to which the system will be exposed, then the system should be indefinitely stable, barring chemical changes or complete destruction.

In some cases, however, the successful use of a soap as a thickener in practice depends on extreme undercooling. A striking example of this is lithium stearate grease which forms a colloidal jelly or sol at 200 to 210° C. (400° F.) even when as little as 3% of soap is used. This jelly must be properly cooled or the product will become semifluid, syneretic, and opaque. The cooled grease can be milled to result in a soft, clear, buttery, sticky grease.

Another mechanism which may account for the loss of structural stability is metathesis between soap and additive. This probably precedes crystallization in cases where it is a significant factor. The fact that metathesis can occur in hydrocarbon solvents was shown by Smith, Rogers, and Mysels (25). It can occur between soaps and free fatty acid or other organic acids and seems to approach an equilibrium among the compounds involved in such reaction. It is likely that such a reaction occurs during storage in greases prepared with several types of soap stocks, and if so, then it could be expected to lead to instability by initiating recrystallization. Systems of aluminum dilaurate in hydrocarbons are more stable toward reversion than corresponding systems containing aluminum distearate (12). If there is such a variation in stability among soaps of different fatty acids used for greases, then such metathesis would be of greater importance to the stability of greases than might be realized.

Hence, the resolution of the problems of structural stability depends on a knowledge of the phases which may be encountered, their characteristics, and the ability to obtain the desired properties by modifying the systems with suitable additives.

### Summary

1. The addition of water, methyl alcohol, and lauric acid all greatly lower the temperature at which anisotropic material separates on cooling from an isotropic solution of sodium stearate in hydrocarbon. Crystallization then appears in these cooled samples. No effect was observed when dry nitrobenzene was used as an additive.

2. The thickening of hydrocarbons by soaps has been shown to be possible either by compaction of gelled lumps exhibiting only limited swelling or by a much more efficient, homogeneous dispersion of the soap in colloidal micelles and secondary colloidal aggregation thereof, forming the jelly phase.

3. The texture of lubricating greases can be attributed to the condition and state of dispersion of the soap and it is influenced markedly by the stability of the system. The formation of fibers is the result of recrystallization of the soap and they are indicative of a previously unstable or metastable system. They are of relatively little permanent value in thickening hydrocarbons as compared with jelly or liquid-crystalline states.

4. The conditions which define a stable, homogeneous, phase area occupied by the jelly also define to a large extent the conditions under which lubricating greases exhibit structural stability. The reversion of a jelly or liquid-crystalline phase to a gel is always accompanied by syneresis. Metathesis of soaps in hydrocarbons can be another contributing factor in unstable greases exhibiting syneresis.

**Acknowledgment**

The author wishes to acknowledge the interest and encouragement offered by Prof. James W. McBain during the preparation of this paper and guidance during the experimentation.

REFERENCES

1. Klemgard, E. N., "Lubricating Greases; Their Use and Manufacture," Reinhold Publishing Co., 1937.
2. Georgi, C. W., and Stucker, J. B., J. Am. Oil Chem. Soc., *24*, 15 (1947).
3. Vold, R. D., Leggett, C. W., and McBain, J. W., J. Phys. Chem., *44*, 1056 (1940); *46*, 429 (1942).
4. Doscher, T. M., and Vold, R. D., J. Colloid Sci. *1*, 299 (1946).
5. Vold, R. D., and Phillipson, J. M., J. Phys. Chem., *50*, 39 (1946).
6. McBain, J. W., Mysels, K. J., and Smith, G. H., Trans, Farad, Soc., *in press.*
7. Smith, G. H., and McBain, J. W., J. Phys. & Coll. Chem. *51*, 1189 (1947).
8. Prasad, M., Hattiangdi, G. S., *et al.*, Proc. Ind. Acad. Sci., *21*, 1, 56, 90 (1945); *22*, 320 (1945); *24*, 287, 295 (1946); J. Univ. Bombay *14*, 23 (1945); Curr. Sci., *11*, 300 (1945); J. Soc. Ind. Res. (India), *1946*, 489.
9. de Bretteville, A., Jr., and McBain, J. W., J. Chem. Phys., *11*, 426 (1943).
10. McBain, J. W., de Bretteville, A., Jr., and Ross, S., J. Chem. Phys., *11*, 179 (1943).
11. McBain, J. W., and Ross, S., Oil and Soap *21*, 97 (1944).
12. Smith, G. H., Doctor's Dissertation, Stanford University (1946).
13. Laing, M. E., and McBain, J. W., J. Chem. Soc., *117*, 1507 (1920).
14. Midgely, T., Jr., and Henne, A. L., J. Phys. Chem., *36*, 3880 (1932).
15. White, L. M., Ebers, E. S., Shriver, G. E., and Brock, S., Ind. Eng. Chem., *37*, 770 (1945).
16. Davis, C. E., and Oakes, E. T. J. Amer. Chem. Soc., *44*, 466 (1922).
17. Lloyd, D. J., Biochem. J., *14*, 584 (1920).
18. Whitby, G. S., Colloid Symposium Monographs, Vol. IV, 213 (1926).
19. von Weimarn, P. P., "Zur Lehre von de Zustanden du Materiae," Bd. I, Text; Bd. II 1913; "Die Allgemeinheit des kolloiden Zustanden," Theodor Steinkopf, Dresden (1925).
20. Thomas, P., and Sibi, M., Compt. rend., *189*, 292 (1929).
21. vonWeimarn, P. P., "Die Allgemeinheit des Kolloidzustandes," Vol. I, 2nd ed., Theodor Steinkopf, Dresden, p. 351 (1926).
22. McBain, M. E. L., and McBain, J. W., Nature, January 25, 1930.
23. Lawrence, A. S. C., Trans. Farad. Soc., *35*, 702 (1939).
24. Weichkerz, J., Naturwissenschaften *16*, 654 (1928).
25. Smith, G. H., Rogers, L. B., and Mysels, K. J., J. Amer. Chem. Soc. (communicated).
26. Slater, A. V., J. Soc. Chem. Ind., *T44*, 499 (1925).
27. Palit, S. R., J. Ind. Chem. Soc., *19*, 271 (1942).
28. Markowicz, E., Farben-Ztg., *34*, 326, 414, 503 (1928).
29. Gallay, W., and Puddington, T. E., and Tapp, J. S., Can. J. Research, *22B*, 66 (1944).
30. Gallay, W., and Puddington, T. E., Can. J. Research, *22B*, 90, 103 (1944).
31. Velikovskii, D. S., and Vorentson, V. P., Neftyanal Khoz., *1936*, No. 10, 73.
32. Velikovskii, D. S., and Shekhoyan, L. S., Neftyanal Khoz., *1938*, No. 8, 41.
33. Levant, G. E., Colloid J. (USSR) *3*, 143 (1937).

# Determination of Nitrogen in Vegetable Oils[1]

**T. A. McGUIRE, F. R. EARLE, and H. J. DUTTON**
**Northern Regional Research Laboratory[2]**
**Peoria, Illinois**

THE quality of edible oils has improved steadily during recent years. In seeking further improvement, new means of measuring and testing oil are needed in order to evaluate the effect of laboratory and plant processing procedures. It has been recognized for some time that nitrogen compounds occur in nature along with glycerides and accompany the oil as it is separated and processed for use. The removal of these nitrogen compounds and other nonglyceride materials is a major purpose of present-day refining practice. Free acids in oils can be determined, even in very small amounts, with relative ease and accuracy and this determination is now in use to control refining operations. It would be of material assistance if a similar satisfactory method for measuring the nitrogen content of vegetable oils could be found.

The difficulty of determining nitrogen in vegetable oil results from the exceedingly small amounts of nitrogen present. The efficiency of present refining methods is so high that the amount of nitrogen left in oil after treatment is of the order of 1 to 10 mg. of nitrogen per kg. of oil, or 1 to 10 p.p.m. In attempting to use the conventional Kjeldahl procedure for measuring such small quantities of nitrogen, the well known difficulty of measuring small differences between large numbers is encountered. Thus, with the A.O.C.S. Official Method Aa-5-38, using 25 ml. of concentrated sulfuric acid and appropriate quantities of other reagents, about 0.1 mg. of nitrogen is found in the blank even though the best commercial A.C.S. grade reagents are used. Since 25 ml. of acid will decompose properly only about 1.0 gram of oil, the nitrogen present in the sample will be from 0.001 to 0.01 mg. while about 0.1 mg. of nitrogen will be present from the reagents used. Modifications of the Kjeldahl method, such as increasing the weight of the oil sample, using very dilute acid and alkali, or adopting micro-Kjeldahl techniques, cannot change the unfavorable ratio between the nitrogen content of the reagent blank and the amount of nitrogen to be determined.

The Nessler reagent provides a means of determining, with somewhat limited accuracy, extremely small amounts of nitrogen in the form of ammonia. Here again, however, the conversion of nitrogen compounds in the oil to ammonia by the usual Kjeldahl procedure would introduce so much extraneous nitrogen that Nesslerization would not be successful.

This paper describes the development and application of a method for concentrating and separating the nitrogenous compounds, and gives in detail the precautions required. Since most of the nitrogen compounds expected to be present would be basic in character, conditions of acid hydrolysis were sought under which the nitrogen compounds present in a large amount of oil could be converted to products soluble in a relatively concentrated aqueous phase while at the same time the major portion of the glycerides would remain insoluble.

---

[1] Presented by Dr. R. T. Milner of the Northern Regional Research Laboratory at the Spring Meeting of the American Oil Chemists' Society at New Orleans, Louisiana, May 20-22, 1947.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.