0.002%-0.005% concentration with suitable synergists is sufficient to protect fats for all practical purposes (2). Therefore, the anticipated demand is not of great volume. Raw material and facilities for production are ample to take care of the demand.

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The Diffraction of X-Rays by Stearates of Calcium, Barium and Magnesium*

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THE commercial interest of calcium, barium, and magnesium soaps lies in their use in lubricating greases, as dusting powders, water-proofing agents, lubricants for rubber and plastic moulding, etc. The growing use of these compounds renders their analysis by x-ray diffraction of interest. The x-ray method also permits the investigation of reactions between the metallic stearates and the other constituents with which they may be mixed in commercial preparations. The present paper describes methods of preparation and of purification of some metallic stearates, reports the x-ray powder diffraction data by means of which qualitative analysis can be conducted, and investigates some reactions of commercial importance in the manufacture of lubricating greases.

Materials

The samples of magnesium chloride ($MgCl_2 \cdot 6H_2O$), calcium hydroxide [$Ca(OH)_2$], barium acetate monohydrate, and calcium acetate monohydrate which were used in this work were all Baker's C. P. Analysed Reagents. The barium hydroxide [$Ba(OH)_2 \cdot 8H_2O$] was Baker's Purified Reagent. Baker and Adamson Reagent Grade of calcium chloride ($CaCl_2 \cdot 2H_2O$) barium chloride ($BaCl_2 \cdot 2H_2O$) and glacial acetic acid were employed. By x-raying a sample taken directly from the reagent bottle, the calcium acetate monohydrate was found to be predominantly the anhydrous form mixed with the monohydrate.

Eastman Kodak stearic acid was used for the preparation of the samples by direct reaction. This acid had been recrystallized twice from acetone and had a neutralization value 197 mg. KOH/g. of acid (theory = 197.3).

The potassium stearate used for metathetical reactions with the metal chlorides was prepared in methyl alcohol. Equivalent amounts of alcoholic carbonate-free potassium hydroxide solution and Eastman Kodak stearic acid (neutralization value 198) were reacted and the soap formed was washed free of the alcohol, using acetone. The soap was dried to constant weight over phosphorus pentoxide.

Methods

Preparation of soaps by metathesis—The preparation of calcium stearate by metathesis between 0.7 g. of $CaCl_2 \cdot 2H_2O$ (a slight excess) and 3.0 g. of potassium stearate, each dissolved in 250 cc. of boiled-out distilled water, was carried out by slowly adding the potassium stearate solution to the calcium chloride solution at 60°C. During the addition of the soap solution the precipitation mixture was vigorously stirred, using a Medco Easy-Mix Blendor. The calcium soap was separated by filtration and washed with distilled water until the addition of silver nitrate solution to the filtrate produced no turbidity. The soap was then dispersed in acetone and filtered to extract free fatty acid and water, and washed with acetone until the filtrate was free from dissolved material. This soap was dried in air until light and powdery. Then it was dried to constant weight over phosphorus pentoxide in an evacuated desiccator.

Barium stearate was prepared by the same procedure using 1.2 g. of $BaCl_2 \cdot 2H_2O$ and 3.0 g. of potassium stearate, conducting the precipitation at 60°C.

A sample of magnesium stearate was prepared from 2.2 g. of $MgCl_2 \cdot 6H_2O$ and 3.0 g. of potassium stearate, in the manner described above, but the precipitation was conducted at 25°C. The lower precipitation temperature is necessary since aqueous magnesium chloride solution hydrolyzes on heating, yielding hydrochloric acid and eventually magnesium oxide.

Preparation of soaps by direct reaction—The direct reaction of 0.4 g. of calcium hydroxide with 4.0 g. of melted Eastman Kodak stearic acid (recrystallized from acetone) was used to prepare samples of calcium stearate. The mixture was heated until foaming had ceased, which indicated that most of the water of reaction had been driven from the batch. Then the soap was quenched under acetone and the hard soap mass ground while still in the acetone. It was filtered and the residue washed with fresh portions of acetone until the filtrate was free from dissolved material. The soap was dried in air and then dried to constant weight over phosphorus pentoxide.

Barium stearate samples were prepared in the same manner using barium hydrate and Eastman Kodak stearic acid.

Treatment of the metallic stearates with acetic acid—Portions of the calcium, barium, and magnesium stearates prepared by metathesis were each dispersed in acetone and an equivalent amount of glacial acetic acid added to each. They were warmed to about 40°C. while stirring and then filtered. The residue was washed with acetone until the filtrate contained no dissolved material. The salts were dried in air, powdered, and then redried to constant weight over phosphorus pentoxide.

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The use of acetone as dispersing medium for these soaps was prompted by its ability to wet the soaps and also act as a solvent for the acetic acid and the stearic acid freed by reaction.

X-ray measurements—The source of x-rays was a General Electric beryllium window tube with a copper target and nickel filter. The x-ray unit was the General Electric XRD-2. The identification of inorganic salts by means of the powder diffraction diagram was effected by comparison with the data published by Hanawalt, Rinn, and Frevel (1). The specimens were powdered, packed into a brass washer, and photographed "naked," using a flat cassette.

Results

Calcium soaps—Calcium stearate formed by metathesis was easily freed from water-soluble salts and excess fatty acid, and is, therefore, a purer product than that formed by direct reaction, as in the latter process excess calcium hydroxide cannot all be removed readily. For the purpose of establishing a standard x-ray pattern the soap formed by the reaction of two mols. of potassium stearate with one mol. of calcium chloride was purified and x-rayed. The powder lines and their intensities, visually estimated, are given in Table I. These data were used for establishing the presence of calcium stearate.

TABLE I.
Powder Diffraction Data for Normal Calcium, Barium, and Magnesium Stearates.

Calcium stearate		Barium stearate		Magnesium stearate	
d/n	Intensity	d/n	Intensity	d/n	Intensity
24.6	s	23.6	s	25.5	vs
16.3	vs	15.5	s	17.5	vs
12.4	w	11.9	m	10.3	vw
9.97	s	9.50	m	8.85	vw
7.14	m	7.98	w	7.54	vw
5.75	vw	6.77	m	7.06	vvw
5.46	halo	5.95	vvw	6.55	w
4.35	m	5.30	vvw	6.05	w
4.02	vs	4.54	s	5.73	vvw
3.92	vw	3.84	m	5.27	vvw
3.61	m	3.69	m	4.94	vw
3.37	w	3.32	m	4.46	vs
2.90	vw	......	......	4.15	m
2.46	w	......	......	3.91	vw
......	......	......	......	3.75	vs
......	......	......	......	3.27	vvw
......	......	......	......	3.15	vvw
......	......	......	......	2.99	m
......	......	......	......	2.42	m
......	......	......	......	2.27	w
......	......	......	......	2.20	m
......	......	......	......	2.08	w
Long spacing—Å					
49.5		47.4		51.0	

Reaction of two mols. of stearic acid with one mol. of calcium hydroxide, at 60°C., produced a mixture, identified by x-rays as calcium stearate and calcium hydroxide.

The standard sample of calcium stearate was submitted to an attempt at further dehydration by heating in vacuum at 110°C. for 24 hours in the presence of phosphorus pentoxide. It was then transferred to a vacuum x-ray camera. The pattern that resulted was in no way different from the undried sample, confirming that the soap as normally prepared was essentially anhydrous.

A chemical analysis of this calcium stearate was performed by decomposing the soap with 6N hydrochloric acid, removing and weighing the dried fatty acid:

% stearic acid observed	94.0
% stearic acid calculated on the basis of calcium di-stearate[1]	94.2

An attempt was made to prepare basic calcium stearate, analogous to the basic barium stearate, prepared by directions given in U. S. Patents Nos. 2,033,148 and 2,154,383. An equimolar mixture of calcium hydroxide and stearic acid was heated to 170-200° C. (340-390° F.). At that temperature the mixture darkened, indicating decomposition. The resulting x-ray picture showed the presence of neither calcium stearate nor calcium hydroxide, and the lines which appeared could not be identified. Chemical evidence, i.e., the lack of titratable hydroxide and the increase of acidity with continued heating, prevents our interpreting this pattern as resulting from basic calcium stearate.

To preclude possible decomposition of the mixture, other experiments with equimolar quantities of the reactants were conducted where the temperature was not raised above 110-120°C. (230-250°F.). In these cases, the product consisted of only calcium stearate and calcium hydroxide.

The reaction between calcium stearate and calcium hydroxide at 150-170° C. (320-340° F.) was investigated in vacuum to prevent darkening from oxidation. The resulting mixtures were examined by x-rays. They showed the presence of unreacted calcium stearate, unreacted calcium hydroxide, calcium carbonate, and an unidentified long-chain organic compound with a long spacing of about 40Å. This is probably stearone, as kindly pointed out by the referee on the basis of the similarity in long spacing values of the higher n-paraffins and corresponding ketones (6, 7). Calcium stearate treated in the same way in the absence of calcium hydroxide showed no apparent change when examined with x-rays.

Barium soaps—The standard x-ray pattern for barium stearate was established in the same way as for the calcium stearate. The spacings and their intensities were included in Table I. As with the calcium soap, the x-ray diffraction indicated that the same product is obtained both by metathesis and by direct neutralization of the hydrate by stearic acid.

Further experiments with barium soaps corresponding to those already described for calcium soaps produced inconclusive results because the barium compounds absorb copper Kα radiation to such a degree that satisfactory exposures were not obtained.

A chemical analysis of the barium stearate which was produced by metathesis was carried out in the same manner as that described for calcium stearate.

% stearic acid observed	81.4
% stearic acid calculated on the basis of barium stearate[2]	81.2

Magnesium stearate—The standard x-ray pattern for magnesium stearate was obtained from a sample prepared by the metathetical reaction,

$$MgCl_2 + 2KSt \longrightarrow MgSt_2 + 2KCl$$

The data are reported in Table I.

A chemical analysis of the magnesium stearate yielded the following results:

% stearic acid observed	96.0
% stearic acid calculated on the basis of magnesium di-stearate[3]	96.6

Commercial soap samples—Commercial samples of Mallinckrodt's calcium stearate and Harshaw's ba-

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[1] Based on the titration value of the actual stearic acid used.

[2] Based on the titration value of the actual stearic acid used.

[3] Based on the titration value of the actual stearic acid used.

rium stearate and magnesium stearate gave patterns which were essentially the same as those reported in Table I. In those commercial samples the long spacings were 2-3Å shorter than those recorded here for the pure stearates. The presence of palmitate and possibly laurate is thereby indicated.

Discussion

Mixed acid soaps—The x-ray examination of calcium, barium, and magnesium stearates after treatment with an equivalent amount of acetic acid shows that for the calcium soap a mixture of the original soap and anhydrous calcium di-acetate was obtained. The reaction taking place, therefore, was replacement of a weaker acid by a stronger one. No x-ray evidence of any reaction was found for the barium and magnesium stearates although a residue left from drying the filtrate showed that some reaction had occurred.

The introduction of the concept of a basic soap in U. S. Patent No. 2,033,148 has influenced some engaged in industry to postulate a neutralization reaction between the basic soap and organic acids resulting in mixed acid soaps. Such mixed acid soaps have, *prima facie,* the same improbability of existence as have basic soaps. No published evidence of the preparation or properties of such compounds could be discovered from a search of the literature. The present investigation also failed to produce mixed acid soaps when the anions used were stearate and acetate.

Basic soaps—The concept of a basic soap, Ba(OH)R, has been introduced in U. S. Patent No. 2,033,148. Nevertheless, an attempt to produce basic barium stearate and basic calcium stearate by reaction between two equivalents of hydroxide and one of stearic acid at a temperature of 230°F. resulted only in a mixture of normal distearate and unreacted hydroxide, as revealed by x-ray analysis.

U. S. Patents Nos. 2,033,148 and 2,154,383 state that mixtures of hydroxide and normal soap, when heated to between 340°F. and 375°F. will react together exothermally until "substantially all of the free barium hydroxide has reacted or is reduced to less than about 0.5%." The formation of basic barium soap of the type Ba(OH)R is assumed to take place at this higher temperature as follows:

$$BaR_2 + Ba(OH)_2 \longrightarrow 2Ba(OH)R + \Delta H \quad (1)$$

This experiment was repeated in the present investigation using pure $BaSt_2$ and an equivalent amount of $Ba(OH)_2 \cdot 8H_2O$ mixed in lubricating oil (SAE 30), and heating the mixture to 350-370°F. until there was no longer any free hydroxide indicated by phenolphthalein. This confirms the factual statements in the patents but simultaneously reduces the probability of the presence of a basic soap of the type Ba(OH)R as such a compound would be expected to show a basic reaction in solution.

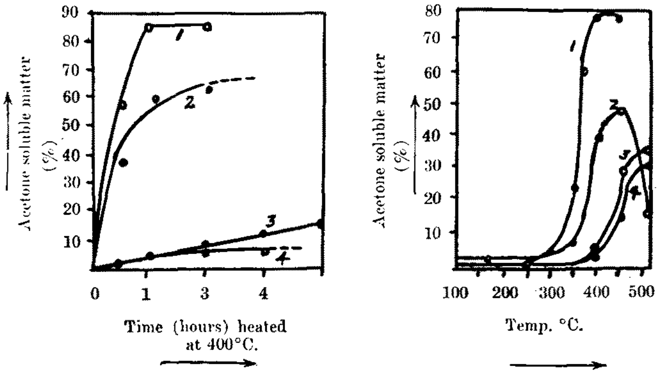
A more probable course of reactions at this temperature would be,

$$Ba[OOC \cdot (CH_2)_{16}CH_3]_2 \longrightarrow BaCO_3 + CH_3(CH_2)_{16} \cdot CO \cdot (CH_2)_{16}CH_3 \quad (2)$$

It is also possible that further reactions occur, as for example, an "aldol condensation" of the ketone in the presence of barium hydroxide to form an unsaturated, branched ketone (2). The darkening of the mixture during the operation at elevated temperatures is an indication of decomposition. Oxidation of ketones, resulting in acids, accounts for the loss of the free hydroxide. Equation 2 has been extensively studied both with the barium and calcium soaps; it is, in fact, the basis of the chemical method for the preparation of high molecular weight ketones and the acids resulting from the oxidation of these ketones (3) (Krafft, 1882).

The decomposition of calcium stearate according to equation 2, however, is profoundly influenced by the presence of catalysts (4), e.g., iron filings and other reduced metals, and such conditions as temperature and pressure. Heating $CaSt_2$ alone, for 18 hours at 150 to 170°C. (320-340°F.), even *in vacuum* where the reaction is favored, did not produce enough calcium carbonate to be detected by x-ray analysis. The probable formation of carbonate was established by a fading end-point observed during a hot titration of the free base in a portion of the final mixture, whereas the original mixture, before heating, had a sharp end-point. The presence of calcium carbonate in this final mixture is incontrovertible evidence of the decomposition of the calcium stearate, since the reaction was conducted in the absence of air. During this heat treatment (in vacuum, where no oxidation of the ketone can occur) the change in amount of calcium hydroxide as determined by titration was negligible.

These facts are very significant since the thermal decomposition of calcium stearate to form stearone was found by Krafft (4) to result in very small yields. Furthermore, a study of the rate and extent of this decomposition by Sato and Ito (5) showed that for calcium stearate less than 1% of ketone was obtained below 350°C. (662°F.) and that a temperature above 420°C. (788°F.) was necessary to yield more than 10%. Thus their results check those reported in the present study. Furthermore, Figure 1, reproduced from the abstract of the paper by Sato and Ito, reveals that heating of calcium stearate at 400°C. (752°F.) for from two to four hours would have been necessary to yield enough ketone for detection by x-ray powder diffraction.



Thus it is evident from the preceding discussion that the presence of the free calcium hydroxide had the remarkable effect of catalyzing the thermal decomposition of the calcium stearate at 170°C. (338°F.) or even lower. This temperature has been used successfully in the manufacture of lubricating greases, and it is evident that the use of an excess of the base, in the process described by the patents for barium grease, cited above, could act in the same way.

These experiments go far toward the elucidation of the reactions taking place at elevated temperatures in the production of greases such as those described by the patents quoted.

Summary

1. Pure calcium, barium, and magnesium stearates have been prepared.
2. X-ray diffraction powder diagrams of these metallic soaps have been obtained as standard references for analysis.
3. The probability of the non-existence of basic alkaline earth and mixed acid soaps were shown.
4. The probable course of reactions taking place during the production of greases at high temperatures involving the presence of excess base is outlined.

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Report of Soap Analysis Committee[*]

AOCS—ASTM Committee D-12, 1945

DURING the last few years the soap companies were called upon to furnish the armed services with special types of soaps for use in soft, hard, and sea water. The composition of these products differed from normal soaps in that they contained in addition to soda soap, synthetic detergents and inorganic salts, the latter consisting essentially of sodium sulfate and sodium chloride, which are normal constituents of the synthetic detergents. Because of the presence of the synthetic detergents and inorganic salts the official analytical methods commonly used for normal soaps were found, for the most part, to be inapplicable to these products. Accordingly, a set of special analytical methods had been developed by the Soap Analysis Committee in cooperation with the laboratories of the Army and Navy departments. During 1944 the committee made a comprehensive study(1) on three cooperative samples of soap containing synthetic detergents using these methods, and at its annual meeting in 1944 the committee voted the tentative adoption of these methods. Some slight revisions had been made in these methods, and it was the consensus to analyze additional samples of soap in 1945, following strictly the revised procedures as tentatively adopted.

Since the work in 1944 did not include a study of the starch determination in these types of soaps, it was agreed to analyze a sample of soap of the synthetic detergent type containing this ingredient. Therefore two samples of these special soaps representing commercial production were used in these studies by 13 collaborating laboratories. The compilation of results submitted by the various laboratories is shown in Tables I and II.

Sample No. 45-1 represented a bar containing moisture, anhydrous soap, active synthetic detergent, and neutral inorganic salts. Sample No. 45-2 was a similar type except that it contained approximately 20% starch. Some of the members of the committee questioned the factor of 0.9 which is used in the official soap methods in converting the dextrose by the Munson-Walker method to starch. To check on this point a sample of starch representing the same material used in the manufacture of Sample No. 45-2 was submitted to the members of the committee with a request that they determine the actual factor thereon. In Table II under column "Starch" Result A represents figures obtained using the official factor 0.9 whereas Result B represents figures obtained using the actual factor determined on the sample of starch used in the preparation of Sample No. 45-2. The actual starch factor obtained by the individual laboratories is shown in the last column of this table. A detailed method for determining starch in the sample of soap was submitted to the participants in this work and is included as a part of this report.

In examining the results shown in Tables I and II, it will be noted that the figures for the most part can be considered in fairly close agreement. Although there appears to be some divergence in results in some of the determinations, it was the consensus that the methods are quite satisfactory for these types of soaps and that with more experience with these procedures operators should be able to obtain more accurate and uniform results.

Recommendations

I. SOAPS CONTAINING SYNTHETIC DETERGENTS

The committee voted the official adoption of the methods for analyzing soaps containing synthetic detergents with the stipulation that the following revisions be made thereto:

a. *Anhydrous Soap.* Instead of weighing the fatty acids in the anhydrous soap determination the fatty acids are to be titrated with alkali in the presence of alcohol, evaporated to dryness, and weighed as anhydrous soap. Because of the hygroscopic nature of this soap a caution is to be included in the method to cool in a desiccator before weighing.

b. *Fatty Matter.* The present tentative method calls for evaporating the petroleum ether on the steam bath and dry the residue (fatty matter) in an oven at 100 to 105° C. to constant weight. This will be changed to read as follows: "Evaporate on a steam bath until the odor of petroleum ether is no longer perceptible and then dry for one-half hour in an oven at 105° ± 2° C."

c. *Starch Factor.* The committee voted to change the present factor of 0.9, which is used in converting dextrose to starch, to 0.93.

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[*] Presented at fall meeting of the American Oil Chemists' Society, Nov. 7-9, 1945, Chicago.