A Study of Some of the Properties of Silver Soaps

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ONLY a relatively small amount of literature exists concerning the properties of silver soaps. A thorough knowledge of their physical properties still appears to be lacking. The commercial interest in aluminum, barium, calcium, and similar soaps should render of interest the analysis of another group of compounds in this family.

The possibility of using silver soaps in red and green linseed oil paints has been studied (5). Silver resinate has been used to some extent in ceramic work for achieving brilliant color effects (6). Due to economic reasons as well as lack of confidence in potential value, silver soaps have never been thoroughly considered. These soaps can be made but are not normally available because of the high price silver commands and the lack of demand. Several investigators have included some material or mention silver soaps in published work (1, 4); others have gone into the subject more deeply (2, 3).

Data and information is presented here on composition, physical properties, and gelling characteristics of several silver soaps prepared from different fatty acids. The soaps investigated were made with commercially available acids and should indicate the type of products that could be offered industrially if a demand for these soaps were established. Properties reported are for compounds made in an aqueous media since this would offer the most economical manner of manufacture.

Experimental

Silver soaps were prepared by the reaction of sodium soaps of fatty acids with c.p. silver nitrate in an aqueous media at 80°C. The products were then filtered and washed with distilled water.

Commercial grades of fatty acids were used for making sodium soaps for precipitation of the silver compounds. Composition of the fatty acids used are shown in Table I as given in the specifications for each by the manufacturers.

TABLE I

Characteristics of Fatty Acids Used and Oxide Values for Silver Soaps

Soap Made	Composition of Fatty Acids				Analysis of Soap % Ag_2O	
	Stearic	Oleic	Palmitic	Other	Theoretical	Found
1. Silver caproate	......	......	......	100.0	52.0	49.2
2. Silver laurate	......	......	......	90.0	37.6	36.9
3. Silver palmitate	6.0	4.0	90.0	......	31.7	29.3
4. Silver stearate	55.0	......	45.0	......	30.8	30.3
5. Silver stearate	97.0	......	3.0	......	29.9	27.1
6. Silver stearate	90.0	4.0	6.0	......	29.7	29.3
7. Silver-hydroxystearate	10.0	2.0	......	88.0[a]	27.2	28.7

[a] 85.5% 12-hydroxystearic, 2.5% ricinoleic.

Characteristics. The physical constants given in Tables I and II were determined by conventional procedures. Maximum deviation between calculated and determined oxide values was 2.8%. Water and acetone soluble matter for each of the soaps was found to be less than 1.0% of the sample tested with the exception of the silver-hydroxystearate. Acetone soluble material for silver-hydroxystearate was 1.6%. The water soluble material represents those salts present in the ashed sample which are soluble in boiling water. Acetone soluble material is the free fatty acid content or unreacted acid in the soap.

Reaction to temperature rise was studied in the work presented here by use of capillary tubes. The temperature, T, shown in Table II, are ranges at which thermal contraction was observed. From observations made it can be said that this may be considered a softening point where the sample goes from a crystal stage to one of semi-plasticity or soft crystalline. This was also noted by Lawrence (3) for silver stearate, where at 130°C. the soap was observed to become a hard crystalline solid when cooling the sample from a plastic state. Melting points previously reported in literature for silver soaps ranged from 205 to 213°C. (2), melting with decomposition.

TABLE II

Properties of Soaps Determined

Soap	% Water Soluble Matter	Acetone Soluble Matter (F.F.A.)	T°C.	Soap Color
1	0.3	0.1	155-56	Light tan
2	0.2	0.5	153-55	Tan-gray
3	0.1	0.7	142-43	Light tan
4	0.7	0.2	132-35	Tan
5	0.6	0.4	130-33	Light tan
6	0.5	0.7	133-35	Light tan
7	0.2	1.6	130-33	Brown

Appearance. The colors of the soaps made were for the most part light tan, almost white powders. On standing over the period of a week the soaps assumed a slightly darker color tint than when originally made, but the color became stable after this. This indicates that the compounds are photosensitive. Boner (1) states that the soap used in his experiments was a white powder. Color of each of the soaps made are shown in Table II.

Gelling Properties. Five per cent concentrations of each of the soaps was made up in xylene. This mixture was then heated to 100°C. with stirring. Gel stability and characteristics after 24 hours as well as gelling temperatures are shown in Table III.

TABLE III

Gelling Characteristics

Soap	Gel Temperature °C.	Gel Color	Gel Character After 24 Hours
1	None	Light tan solution	No gel, soap separated
2	73-74	Olive green	Heavy brittle
3	82-85	Dark brown	Heavy brittle
4	71	Dark brown	Heavy brittle
5	80	Brown	Heavy brittle
6	88-90	Brown	Heavy brittle
7	None	Dark brown	No gel, soap separated

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It was found that temperatures at which gellation begins ranged from 70 to 90°C. The introduction of an –OH group to the silver stearate soap prevented gelling altogether as silver-hydroxystearate did not gel. Silver caproate also did not gel in xylene. Other soaps made gave heavy gels with generally good stability.

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Summary

1. Silver soaps of several commercially available fatty acids, with varying percentages of different component acids, have been prepared.

2. Properties: oxide, water soluble matter, acetone soluble matter and thermal contraction or softening points. Appearance of these silver cups is reported.

3. Gelling characteristics of each of the soaps in xylene are reported.

REFERENCES

1. Boner, C. J., Ind. Eng. Chem., *29*, 58 (1937).
2. Jacobson, C. A., Holmes, A., J. Biol. Chem., *25*, 29 (1916).
3. Lawrence, A. S. C., Trans. Faraday Soc., *34*, 665 (1938).
4. McBain, J. W., McClatchie, W. L., J. Phys. Chem., *36*, 2567, 2570 (1932).
5. National Paint, Varnish, Lacquer Asso. Sci. Circ. No. 589, 1940.
6. Stubbs, E., Chem. Age, *37*, 429 (1937).

ABSTRACTS . . . . Don Whyte, Editor

• Oils and Fats

R. A. Reiners, Abstractor

Collaborative analysis of tung fruit by the whole fruit and component procedures. R. S. McKinney (U. S. Tung Oil Lab., Bogalusa, La.). *Proc. Am. Tung Oil Assoc.* **15**, Pt. 2, 25-30 (1949). Collaborative studies on 6 logs of tung fruit varying widely in content of moisture, hull, and oil have shown good agreement for the oil content when analyzed by either the whole fruit procedure or by the component procedure adopted as a tentative method for the analysis of tung fruit by the American Oil Chemists' Society. The highly significant differences observed in the results reported for the moisture content have indicated that serious errors may be encountered by calculating the oil content of tung fruit to a moisture-free basis. (*Chem. Abs.* **45**, 3173)

Investigation on the preparation of superior copra. I, II. Th. Morel (Centraal Inst. Tech. Onderzoekingen, Jakarta, Java). *Chem. Weekblad* **46**, 719-24, 733-9(1950). Superior copra is defined as a product of light color and good odor, taste, and keeping qualities, containing less than 5% water; the oil expressed from it has an acid no. of less than 0.3. Using a tunnel drier the fat acid content of the oil was 0.025-0.04% for a drying temperature of 75-105° and 0.045-0.8% for a drying temperature of 60°. Discoloration took place at 75-105°. Best results were obtained at 70° or lower with washed strips 0.5 cm. wide. (*Chem. Abs.* **45**, 3173)

The component acids of a hippopotamus fat. C. Barker and T. P. Hilditch (Univ., Liverpool). *J. Chem. Soc.* **1950**, 3141. The chief component acids of the fat of a hippopotamus were found to be myristic 2.3, palmitic 27.1 stearic 22.2, arachidic 1.1, hexadecenoic 2.2, oleic 39.3, linoleic 1.6, and linolenic 1.5% by weight.

Margarine manufacture. A dairy industry. A. J. C. Anderson. *Dairy Ind.* **15**, 611-16, 618(1950). Chemistry, physics, bacteriology and nutrition of margarine and its processing are discussed in comparison with butter. (*Biol. Abs.* **25G**(2), 43)

The component acids and glycerides of a badger fat. S. Gupta, T. P. Hilditch and M. L. Meara (Univ. Liverpool). *J. Chem. Soc.* **1950**, 3145. The chief component acids of badger body fat are myristic 5.7, palmitic 21.2, stearic 8.2, tetradecenoic 6.2, oleic 30.9, octadecadienoic 8.4, octadecatrienoic 3.9, and unsaturated C_{20} (mean unsaturation —5.1 H) 14.6% by weight. The triglyceride composition follows the principal of even distribution.

Flow rates through soybean flakes. D. Cornell and D. L. Katz (Univ. Michigan, Ann Arbor). *Ind. Eng. Chem.* **43**, 992(1951). The flow rate of hexane miscella percolating at flooding or higher rates through soybean flakes can be predicted providing that the miscella viscosity and density, bulk density of the bed, and the average diameter of the flakes are known. These data can be correlated by the procedure similar to that developed for porous beds. Predicted flow rates average 20% lower than observed values.

The fats: 1900-1950. An essay in historical chemistry. T. P. Hilditch (Univ., Liverpool). *Chem. Ind.* **1951**, 153). An historical review.

A rapid method for the determination of oil in potato chips. K. T. Williams and E. A. McComb (Western Reg. Res. Lab., Albany, Calif.). *Potato Chipper* 10(9), 5(1951). Coarsely ground potato chips are extracted 3 times with hot CCl_4 in a sintered glass crucible. The chips are then finely ground and extracted 3 more times with CCl_4. The oil is recovered from the extract and weighed. The precision is ± 0.5%.

Effect of heat on some constants of ghee. R. Chand and H. Ahmad. *Indian J. Med. Research* 38, 235-9(1950). On heating buffalo butter fat, the refractive index increases, there is a loss of volatile fatty acids and a decrease in unsaturation. The extent of these changes is dependent on the temperature and period of heating. (*Chem. Abs.* **45**, 2597)

A study of the effect of nordihydroguaiaretic acid on the oxygen absorption of the phospholipid fraction of milk. I. The effect of concentration of antioxidant. J. W. Stull, E. O. Herreid and P. H. Tracy (Illinois Agricultural Exp. Station, Urbana). *J. Dairy Sci.* 34, 181(1951). The optimum concentration of N.D.G.A. for the most effective antioxygenic action at 50° was 0.001 to 0.01% based on the phospholipid present.

II. Effect of synergists, metallic catalysts and pH. *Ibid.*, **187.** Methionine, ascorbic and citric acids were found to be very effective synergists with N.D.G.A. The order of greatest catalytic effect was copper, nickel, iron and cobalt, but the differences were slight. When the system was buffered at pH 6.5 the antioxidant effect of N.D.G.A. was greatest.

Bromination of methyl linoleate with n-bromosuccinimide. S. Bergstrom and G. Hansson (Univ., Lund, Sweden). *Acta Chem. Scand.* 4, 435-43(1950). Methyl linoleate and N-bromosuccinimide were refluxed in dry CCl_4 in ultraviolet light and the reaction mechanism studied by means of absorption spectra. The author suggests that bromination under the conditions used is a free-radical reaction. (*Chem. Abs.* **45**, 2397)

The determination of the position of the double bond in monoethenoid fatty acids. P. H. Bergemann, J. G. Keppler and H. A. Boekenoogen (Unilever Lab., Zwijndrecht, Holland). *Rec. trav. chim.* **69**, 439-56(1950). The dibasic acids obtained by oxidation of mono-ethenoid fatty acids with either permanganate or ozone were separated by chromatography using a silica gel column pretreated with aqueous alcohol. Dehydrated dihydroricinoleic acid was shown to be a mixture of 11- and 12-octadecenoic acids. Vaccenic acid from butter fat proved to be 11-octadecenoic acid. The same acid from tung oil contained considerable 13-(probably), 12-, 10-, and 9-, as well as only 25-30% 11-octadecenoic acids. (*Chem. Abs.* **45**, 2397)

Viscosity data of organic liquids. J. W. M. Boelhouwer, G. W. Nederbragt and G. Verberg (Koninkl. Shell-Lab., Amsterdam).