Summary

A polarographic method for the determination of peroxides has been applied to fats and related esters. The data presented show that at least three different peroxide structures are present in early stages of oxidation and persist during extensive autoxidation. The peroxides of lard, methyl oleate, and methyl linoleate cannot be distinguished by the polarographic method used in this investigation. Autoxidation of lard at 100°C. is shown to give reduction curves which are much different than those obtained when lard is autoxidized at 45°C. Preliminary work has indicated that the chromatographic technique of Dugan *et al.* does not separate the peroxide structures which are determined polarographically.

REFERENCES

1. Dugan, LeRoy, Henick, Albert S., and Beadle, B. W., Jour. A. O. C. S., *25*, 153 (1948).

2. Farmer, E. H., Trans. Faraday Soc., *38*, 340 (1942).

3. Farmer, E. H., and Sutton, D. A., J. Chem. Soc. *1943*, 119.

4. Lewis, W. R., Quackenbush, F. W., and DeVries, T., Anal. Chem. (In press.)

5. Lingane, James J., and Laitinen, H. A., Ind. Eng. Chem., Anal. Ed. *11*, 504 (1939).

6. Markley, Klare S., Fatty Acids, Their Chemistry and Physical Properties. (1947) Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y.

7. Staudinger, H., Ber. *58B*, 1075 (1925).

8. Swift, C. E., Dollear, F. G., and O'Connor, R. T., Oil and Soap, *23*, 355 (1946).

9. Wheeler, D. H., Oil and Soap, *9*, 89 (1932).

10. Wheeler, D. H., and Riemenschneider, R. W., Oil and Soap, *16*, 207 (1939).

Sodium Palmitate in Organic Liquids as Studied by X-Ray Diffraction[1]

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SOAPS in organic liquids have been studied by a number of investigators using various physical-chemical methods.[2] A visual study of the phase behavior of sodium palmitate in various organic liquids was made several years ago in this laboratory (1, 2). This is now followed by an examination of some of the same systems by x-ray diffraction. It is found that at room temperature these systems consist of: 1. the organic liquid; 2. soap curd fibers of one of several types of gamma sodium palmitate; and 3. usually a second crystalline component of unknown composition.

Experimental Methods

The materials used were the original systems prepared for the previous study (1, 2). These sealed tubes had remained undisturbed for several years and so are presumed to be at equilibrium. Samples were removed from them, packed in thin-walled Pyrex capillaries, and mounted in the x-ray beam by a method previously described (3). Care was taken to avoid loss of organic liquid during the loading of the capillary.

The source of x-radiation was a General Electric XRD-1 unit having a tube with copper target and beryllium windows. The radiation was filtered through nickel foil and collimated through guarded pinholes 0.010 inches in diameter and placed 12.5 cm. apart. For the side spacings, a sample to film distance of 50 mm. was used, but for the long spacings this distance was increased to 100 mm. These distances were checked by the 2.814 Å line of sodium chloride.

Results

The x-ray diffraction photographs of these systems are similar to the usual powder photographs produced by solid soaps. They consist of circles or lines corresponding to several orders of a "long spacing" (or spacings, if more than one phase is present) together with lines corresponding to "side spacings." Superimposed on the latter are several haloes due to the organic liquid component of the systems; these haloes tend to obscure some of the side spacings in several of the photographs, in particular those of samples containing the least amount of soap.

Since x-ray powder photographs of heterogeneous mixtures consist of a superposition of the patterns of the individual components, the evaluation of the photographs of the systems studied consisted of comparing the various lines or circles with those of known crystalline substances that might be present. On this basis a few generalizations can be made on all of the systems other than those in cetyl alcohol or palmitic acid as the other organic compound.

In all cases the longer spacings can be ascribed to the various orders of either one or two long Bragg spacings. By far the strongest is that due to the "major" crystalline component present in all photographs (40.5 ± 0.5 Å) which does not change with either the second organic compound present or the concentration of the soap. The weaker long spacing, due to a "minor crystalline component," varies with both concentration and organic liquid and so is not due to a specific chemical substance. It is not present in the photographs of all systems, particularly those containing only a small amount of soap. This may be due to either insufficient material to produce a pattern or else to its complete absence.

For all systems there is one strong "side spacing" which remains constant at 4.71 Å. The other side spacings apparently vary somewhat with the organic liquid but not with concentration. However, these side spacings can be placed in three different groups, as can be seen by a comparison of the data in Tables I, II, and III. The systems more dilute in soap lack the weaker lines, which is to be expected.

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[1] This investigation was conducted partially under contract with the Office of Naval Research under the supervision of Prof. J. W. McBain.

[2] For a recent review of this subject see M. Prasad, G. S. Hattiangdi, and B. K. Wagle, J. Coll. Sci., *2*, 467 (1947).

TABLE I

X-Ray Diffraction of Sodium Palmitate in Alcohols

Grouped in long spacings for crystalline sodium palmitate, long spacings for a minor crystalline component, and side spacings.

Order	Ethyl Alcohol		Isopropyl Alcohol		*n*-Heptyl Alcohol		*n*-Cetyl Alcohol
	3.5%	56%	21%	79.5%	24.5%	75%	14%
	d/n, A; Int.	d/n, A; Int.	d/n, A; Int.	d/n, A; Int.	d/n, A; Int.	d/n, A; Int.	d/n, A; Int.
Sodium Palmitate							
1	41 m	39 vs	38 vs	38 vs	39 s	38 vs	38 vs
2		20.4 m	20.3 w	20.4 m	20.4 w	20.4 m	
3	13 vw	13.3 s	13.4 m	13.43 s	13.4 m	13.4 s	13.3 m
4		10.1 vvw		10.1 vw		10.1 vvw	
5		8.06 w	8.06 w	8.06 m	8.1 vw	8.06 m	8.1 vw
7				5.8 vvw			
c sin β	40 ± 1	40.4 ± 0.2[1]	40.4 ± 0.2[1]	40.5 ± 0.2[1]	40.5 ± 0.3[1]	40.5 ± 0.2[1]	40.2 ± 0.3[1]
Minor Crystalline Component							
1		50 m	50 m	50 m	52 w	50 m	(45 vs)[3]
2		25.7 w	26.0 w	25.7 w	27.6 vw	25.7 w	(22.7 vw)
3							(15.3 m)
c sin β		51 ± 0.5	51 ± 1	51 ± 0.5	53 ± 1.5	51 ± 0.5	45 ± 0.3[1]
Side Spacings							
				7.8 vvw		7.8 vvw	
		7.1 vvw		7.1 vvw			(5.1 w)
	4.7 vw	4.71 vs	4.71 m	4.71 vs	4.71 m	4.71 vs	4.70 m
				4.48 vvw			
				4.29 vvw			(4.25 vs)
		4.02 s	4.02 w	4.02 s	4.06 w	4.06 s	4.05 m
		3.70 vw		3.70 w		3.77 vw	(3.73 s)
							(3.90 vw)
		2.9 vvw		2.92 w		2.92 w	
							(2.51 w)
				2.35 vvw			
				2.25 vvw			

Order	Glycerol			Diethylene Glycol		
	18%	32.2%	64.3%	2.78%	19.9%	60.0%
	d/n, A; Int.	d/n, A; Int.	d/n, A; Int.	d/n, A; Int.	d/n, A; Int.	d/n, A; Int.
Sodium Palmitate						
1	40 s	38 vs	38 vs	40 m	38 s	38 s
2		20.4 w	20.1 s			20.4 w
3	13.3 vvw	13.4 s	13.4 vs	13.6 w	13.5 w	13.4 m
4		10.1 vvw	10.1 vw			
5		8.06 w	8.01 m			8.1 vw
7			5.8 w			
c sin β	40	40.5 ± 0.2[1]	40.2 ± 0.2[1]	40.4 ± 0.4	40.5[1]	40.5 ± 0.3[1]
Minor Crystalline Component						
1			46 w			
2		26[2]	26.5 w			
3			16 vw			
c sin β		52	49 ± 4			
Side Spacings						
			7.8 vvw			
		5.0 vvw	7.1 vvw			
	4.71 w	4.71 s	4.71 vs			
		4.17 vw		4.7 vw	4.7 w	4.71 w
		4.05 m	4.06 vs			
			3.65 w			4.06 vw
		2.9 vvw	2.92 m			
			2.65 vvw			
			2.22 vvw			
			2.35 vvw			

[1] The first orders of these patterns were not used in the averaging for the Bragg spacing because they were too intense for accurate measuring. The mean average deviation is also given.

[2] These first orders were present, but could not be measured accurately. The c sin β is calculated on the basis of what is believed to be the second order.

[3] Spacings for the cetyl alcohol are included in parentheses.

The pattern from cetyl alcohol systems consists of the pattern of the "major crystalline component" superimposed on that of cetyl alcohol. No lines due to any other crystalline component are present, for reasons described above.

Unfortunately, only one concentration of sodium palmitate in palmitic acid was available. The lines from its pattern could be ascribed to the major crystalline component found in other systems and to another component whose lines are given in Table III.

Discussion

Since all of these systems were x-rayed at room temperature (26° ± 2°), subsequent to their having been heated, this is a study of the "descendent phases" of sodium palmitate in these organic liquids, somewhat like the the work of Buerger *et al.* (4, 5), on the "descendent phases" of the previously heated

TABLE III

84% Sodium Palmitate in Palmitic Acid

Bragg Spacings Due to			
Sodium Palmitate		Acid Sodium Palmitate	
Order	d/n, A; Int.	Order	d/n, A; Int.
1	38 vs	1	46 s
2	20.2 m	2	23.9 vw
3	13.3 s	3	15.3 w
5	8.1 m		
c sin β	40.3 ± 0.2[1]	*c sin β*	46.2 ± 0.4
	4.71 m		4.15 m
	4.02 w		3.72 w
	2.9 vw		

[1] The first orders of these patterns were not used in the averaging for the Bragg spacing because they were too intense for accurate measuring. The mean average deviation is also given.

systems of sodium soaps in water, but with time allowed for final changes to occur. These authors found seven different descendent soap phases in their systems. Of particular interest to the present study, they found three different descendent soap phases in the system sodium palmitate: water.

All the systems of sodium palmitate in organic liquids had been heated during the course of the previous investigation until they were isotropic; since that time they have been standing at room temperature between 20 and 30°C. All of the tubes used in the original investigation were not available. Because of these two factors neither the range of temperatures nor the range of concentrations covered in Buerger's work could be covered here.

From the experimental results several hypotheses can be made. Since the strong long spacing and strong side spacing (4.71 Å) are present in the photographs of all samples, they are probably due to the same crystalline phase. In all of the photographs there is a second relatively strong side spacing; the intensity is proportionate to that of the 4.71 Å spacing, but its magnitude varies with the organic liquid present. By an inspection of Tables I, II, and III, it can be seen that the various systems fall into three groups within each of which this second side spacing is practically constant:

1. At 4.02 Å in ethyl alcohol and isopropyl alcohol.
2. At 4.06 Å in *n*-heptyl alcohol, cetyl alcohol, glycerol, diethylene glycol, *n*-cetane, and Nujol.
3. At 4.17 Å in *o*-cresol and *m*-cresol.

Because of the aforementioned variation in intensity it is believed that this spacing is also due to the "major crystalline component." On this basis the experimental results lead to several possibilities:

1. Solid solution, similar to that found by Ferguson *et al.* (6) for β-sodium palmitate in water. Only a few values of the second side spacing have been observed, rather than a continuum, which makes this hypothesis unlikely.

2. A series or group of pure soap phases in which some of the parameters of the unit cell are constant for the series and some vary; those that vary would, however, be constant for a given phase. For the general case the unit cell would be triclinic, although it would be possible for it to be monoclinic if the angles α and γ are equal to 90° for one of the phases. For the following discussion one assumption need be made: that the angle between the *ac* and the *bc* planes of the unit cell be a right angle. The two constant Bragg spacings can then be arbitrarily assigned as follows: $c \cdot sin\ \beta = 40.5$ Å and $a \cdot sin\ \beta = 4.71$ Å (or integral fractions thereof). By this assignment *a, c,* and β (i.e. the molecular arrangement in the *ac* plane) are fixed, and *b*, α, and γ can vary. The several different phases might be formed by finite shifting of sheets of soap molecules lying in the *ac* plane of the so-called carbon-carbon zigzag. For all three phases the soap molecules would remain fixed with respect to each other within this plane, but for each phase they would have different and distinct positions relative to molecules in adjacent sheets.

The above is a tentative hypothesis which explains the known experimental facts. Unfortunately, the x-ray scattering of the liquids in the system makes accurate measurement of the other weaker side spacings difficult. Because of this, they are of little value in elucidating the picture.

The observed Bragg spacings do not agree with any in the literature, but are close to those published by Ferguson *et al.* (7) for their omega sodium palmitate. This form had been previously observed in this laboratory and was designated the gamma form. Ferguson's values for this form are included in Table II for comparison. DeBretteville (private communication) states that the side spacing 4.7 Å is most promi-

TABLE II

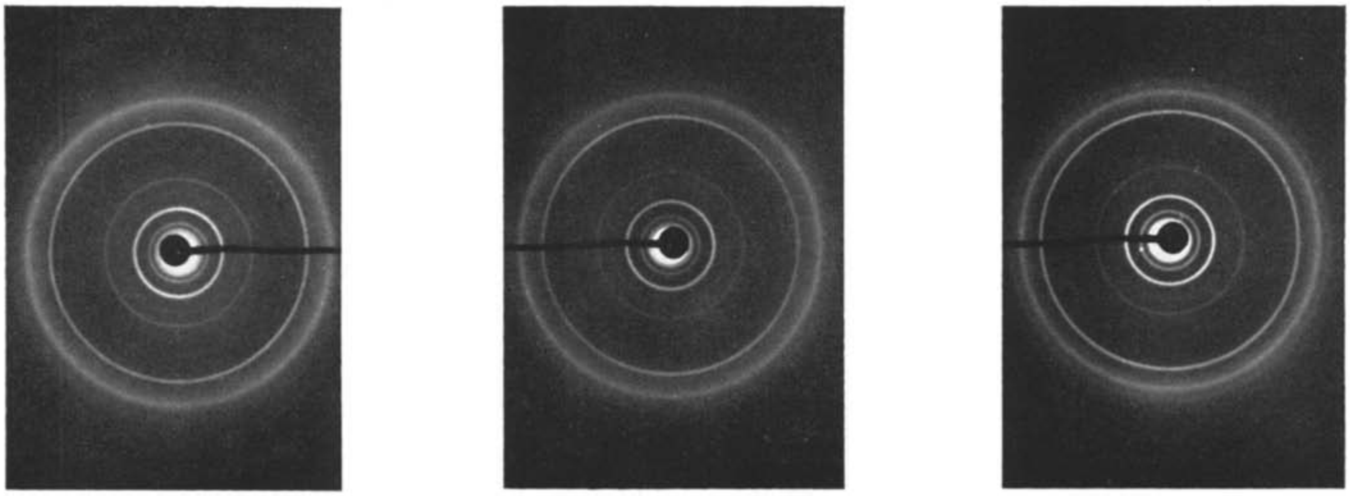
X-Ray Diffraction of Sodium Palmitate in Cresols ond Hydrocarbons

Grouped in long spacings for crystalline sodium palmitate, long spacings for a minor crystalline component, and side spacings. Bragg spacings fof Ferguson's omega sodium palmitate are included for comparison.

Order	*o*-Cresol				*m*-Cresol				*n*-Cetane				Nujol		Omega Na Palmitate	
	39.8%		84.2%		27.0%		84%		33.5%		96.5%		60%			
	d/n, A;	Int.	d/n, A;	Int.	d/n, A;	Int.	d/n, A;	Int.	d/n, A;	Int.	d/n, A;	Int.	d/n, A;	Int.	d/n, A;	Int.
Sodium Palmitate																
1	38	vs	38	vs	38	s	38	vs	38	s	38	vs	38	vs		
2	20.4	m	20.4	m	20.4	vw	20.3	m	20.3	vw	20.3	w	20.3	w		
3	13.4	s	13.43	s	13.4	m	13.4	s	13.4	m	13.4	s	13.4	m		
4	10	vvw	10.1	w												
5	8.05	w	8.06	m	8.1	vvw	8.06	w	8.1	vvw	8.06	w	8.06	w		
7			5.8	vw												
c sin β	40.5 ± 0.2[1]		40.5 ± 0.2[1]		40.4 ± 0.2[1]		40.4 ± 0.2[1]		40.4 ± 0.2[1]		40.4 ± 0.2[1]		40.4 ± 0.2[1]		39.6	
Minor Crystalline Components																
1	57	vw	57	m			54	w			53	w	52	w		
2	28	vw	28.4	m	30	vvw[2]	27.5	w	30	vvw[2]	27.3	w	27	vw		
c sin β	57		57		60		54.5 ± 0.5		60		54 ± 1		53 ± 1			
Side Spacing																
			7.8	vvw												
			7.1	vvw												
	4.71	s	4.71	vs	4.71	m	4.71	m	4.71	m	4.71	s	4.71	m	4.68	vs
															4.33	w
	4.17	m	4.17	s	4.16	vvw	4.15	w	4.06	vw	4.06	s	4.06	m	4.03	s
			3.88	w			3.93	vw			3.77	vvw	3.8	vvw	3.92	m
			3.63	vw			3.80	vw								
			3.43	vvw											3.23	w
	2.9	vvw	2.92	w			2.92	vw			2.92	vvw	2.92	vvw	2.95	m
			2.65	vw											2.68	vw
															2.52	vw
			2.35	vvw											2.39	vw
			2.22	vw											2.25	w

[1] The first orders of these patterns were not used in the averaging for the Bragg spacing because they were too intense for accurate measuring. The mean average deviation is also given.

[2] These first orders were present, but could not be measured accurately. The *c sin* β is calculated on the basis of what is believed to be the second order.



a) γ_1-sodium palmitate, 79.5% sodium palmitate in isopropyl alcohol.

b) γ_2-sodium palmitate, 75% sodium palmitate in *n*-heptyl.

c) γ_3-sodium palmitate, 84.2% sodium palmitate in *o*-cresol.

Fig. 1. Reproductions of x-ray photographs of systems of sodmm. Cu Kα radiation filter through nickel foil. Actual size. ium palmitate in organic liquids. Sample to film distance: 50.0

nent for gamma sodium palmitate, followed by 4.1, 6.9, 2.87, and 8.0 Å. Unfortunately, Buerger has published only photographs and not actual measurements so no direct comparison can be made with his work.

Because of the general similarity between x-ray patterns of these systems and that of γ-sodium palmitate, it was decided to designate these soap phases as γ_1, γ_2, and γ_3-sodium palmitate, Figure 1 shows reproductions of patterns from each phase. Figure 2 shows the long spacings of the soap and the minor crystalline component.

The composition of the "minor crystalline component" is not definitely known, but several things can be said about it. Since the long spacing from this component is longer than the calculated double length of the sodium palmitate molecule (46.6 Å), it cannot be another phase of sodium palmitate if the crystals are similar to the usual lamellar type of soap crystals. Since the ratio of the observed orders of the long spacing is 1:2, the component is lamellar. It might be a compound of sodium palmitate and the organic liquid, but, although this is conceivable in some cases, such compounds are difficult to imagine in all cases (e.g. with cetane). The component might be a lamellar liquid crystal of the soap with the organic liquid, the latter going into layers between either the hydrophilic or hydrophobic ends of the molecules, depending on its nature. This hypothesis gives the necessary latitude to explain the variation of the long spacing with concentration and organic liquid. This type of liquid crystal would be similar to the expanding lamellar type found for detergents in water (3).

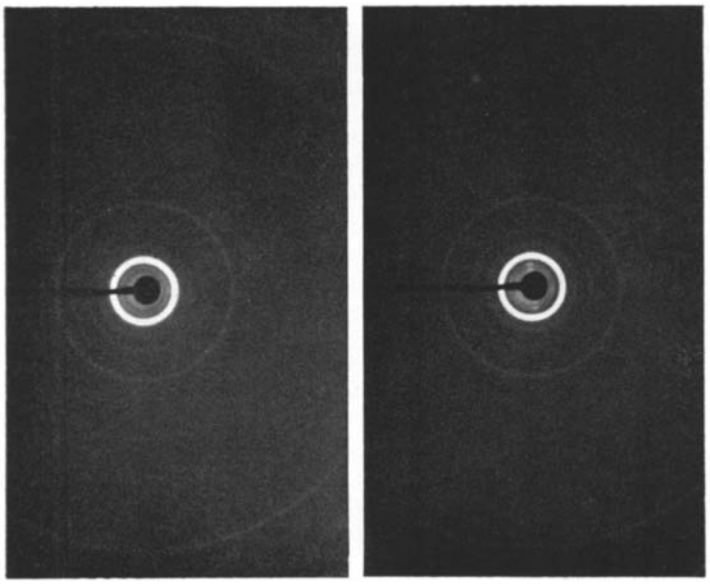


Fig. 2. Long spacings of systems of sodium palmitate in organic liquids. Sample to film distance: 100 mm. Cu Kα radiation filtered through nickel foil. Actual size.

a) 79.5% sodium palmitate in isopropyl alcohol.

b) 96.5% sodium palmitate in cetane. Note that the diffraction due to the "minor crystalline component" is partially oriented.

Cetyl Alcohol and Palmitic Acid Systems

It is interesting to note that sodium palmitate and cetyl alcohol, when allowed to cool from isotropic liquid, form separate crystals of the soap and alcohol, rather than any definite compounds or solid solution. This has been shown by the x-ray patterns of the system.

The x-ray photograph of the system of 84.8% sodium palmitate in palmitic acid consists of the pattern of γ_1-sodium palmitate superimposed on that of one of the acid sodium palmitates. Several of the latter have been reported in the literature (8, 9, 10), but unfortunately their Bragg spacings have not been included so that this one cannot be correlated with previous work.

Summary

The descendent phases of systems of sodium palmitate in 11 organic compounds have been studied by x-ray diffraction. These consist of: 1. sodium palmitate in one of the three gamma crystalline forms;

2. an unknown component which may be a lamellar liquid crystal; and 3. the free organic compound.

REFERENCES

1. Vold, R. D., Leggett, C. W., and McBain, J. W., J. Phys. Chem., *44*, 1059 (1940).
2. Leggett, C. W., Vold, R. D., and McBain, J. W., J. Phys. Chem., *46*, 429 (1942).
3. Marsden, S. S., Jr., and McBain, J. W., J. Phys. and Coll. Chem., *52*, 110 (1948).
4. Buerger, M. J., Smith, L. B., Ryer, F. V., and Spike, J. E., Jr., Proc. Nat. Acad. Sci., *1945*, 226.
5. Buerger, M. J., Smith, L. B., and Ryer, F. V., J. Am. Oil Chem. Soc., *24*, 193 (1947).
6. Ferguson, R. H., Rosevear, F. B., and Nordsieck, J., J. Am. Chem. Soc., *69*, 141 (1947).
7. Ferguson, R. H., Rosevear, F. B., and Stillman, R. C., Ind. Eng. Chem., *35*, 1005 (1943).
8. Buerger, M. J., Amer. Mineral., *30*, 551 (1945).
9. Ryer, F. V., Oil and Soap, *23*, 310 (1946).
10. Malkin, F., Ber., *63B*, 1807 (1930).

International Chemical Union

Minutes of Meeting of International Commission on Fats and Oils. Part I.

London, England, July 1947

Translated by C. L. Hoffpauir of Southern Regional Research Laboratory,* New Orleans, Louisiana.

THIS translation gives the minutes of the meeting in London during July 1947, incorporating the decisions made on the unified international methods and the plans for collaborative work to be done before the next meeting of the Commission. Methods under discussion included those for the sampling and analysis for moisture and oil specified for several oil-bearing seeds. They also included those for alkalis and rosin in soaps and those for soluble and insoluble volatile acids and sterols in fats and oil, also for the determination of thiocyanogen and peroxide numbers in fats and oil. The organization of and the representation on the present International Commission on Fats and Oils are also given.

INTERNATIONAL COMMISSION FOR THE STUDY OF FATTY MATERIALS

In accordance with the attached minutes of the London meeting, the following notes are offered:

SUPPLEMENT I$_1$—METHOD OF ANALYSIS OF OLEAGINOUS SEEDS

Having edited the text in accordance with the decisions taken by the Commission, we have taken the liberty, without submitting it to you for examination, to transmit it to the International Union of Chemistry so that it might be published in the booklet of unified methods, 1947.

SUPPLEMENT I$_2$—METHOD FOR DETERMINATION OF ROSIN

This method was adopted by the Commission and should be inserted in the published book.

The program of work you proposed is described as follows:

I—*Determination of Free Caustic Alkali in Soaps.* The text is given in supplement II$_1$.

We propose that the method be tried under the following conditions:

Weigh approximately 5 grams of fatty acid containing no trace of neutral oil into a tared flask. Add alcohol and exactly neutralize with an aqueous solution of sodium hydroxide, completing the neutralization with N/10 alkali. Remove all the alcohol and the major part of the water by heating and then placing in an oven. Add 5 ml. of aqueous N/10 sodium hydroxide containing in solution 20 mg. of anhydrous sodium carbonate. An analytical sample of a soap with a known content of free caustic alkali and free carbonate alkali is thus obtained. Add immediately the necessary quantity of absolute alcohol, previously boiled and neutralized at a temperature of 70°C. Finish the analysis according to the method and compare the free caustic alkali titrated to that which was effectively introduced.

II—*Determination of Free Carbonate Alkali.* The text of the method is given in Supplement II$_2$.

First Method: This method should be applied to the above analysis after titration of the free caustic alkali.

Second Method: Prepare neutral soap as described. Incorporate in it calcium carbonate and a known quantity of caustic alkali and of sodium or potassium carbonate (of the order of 1%). Apply the method to the soap so obtained.

III—*Qualitative Research on Rosin.* The text is given in Supplement II$_3$.

The technique should be tried on different products capable of producing the colors and on the same products mixed with 0.50% of rosin: lanolin, sulforicinoleate, degras, oxidized linseed oil, oil of grape seed, chinawood oil, or fish oil.

IV—*Soluble and Insoluble Volatile Acids.* The text is given in Supplement II$_4$.

The method should be tried on a sample of fatty material (a mixture of cow's butter and coconut oil) which will be distributed by the Swiss Commission.

V—*Phytosterols and Cholesterols.* The text is given in Supplements II$_5$ (Netherlands Commission) and II$_{5A}$ (Danish Commission).

The tests should be made on the sample mentioned in paragraph IV above.

VI—*Thiocyanogen Number.* The lead thiocyanate should be prepared by the two methods described in Supplements II$_6$ and II$_7$.

The thiocyanates so prepared will be compared by use of them as reagents in the methods of Supplements II$_{6A}$ and II$_{7A}$ as applied to a sample of semi-drying oil which will be distributed by the Swiss Commission.

Then comparisons will be made of methods II$_{6A}$ and II$_8$ as applied to the sample of tallow which

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