(abstract) method was followed using the correction of the general directions for melting points. The method gave consistent results in a number of determinations. As can be seen from Tables I and II all samples conform to the standards set by the U. S. P. X (abstract) and "New and Nonofficial Remedies" with the exception of sample 2.

In recrystallizing the acid from chloroform, benzene, carbon tetrachloride, acetone, and alcohol, respectively, it was found that the melting point of the crystals from the various solvents did vary which seems to show that the apparent melting point is not a true melting point. The crystals obtained from chloroform, benzene, and carbon tetrachloride, were small, white, well-defined needle-like crystals, while those from acetone and alcohol formed large, beautiful tabular crystals, many of which were 10 mm. in length. However, the study of their optical properties showed that the crystals from all five solvents were identical in every respect, any difference in appearance of the powders being due to the variation in crystal size which depended upon the rate of crystallization from the solvent.

#### SUMMARY.

1. Acetylsalicylic acid varies in melting point when crystallized from various solvents.

2. The crystals obtained from various solvents are identical in optical properties and crystal form.

3. Commercial acetylsalicylic acid has a melting point of about 133-134° C. corrected, determined as per U. S. P. X (abstract) method.

4. In reporting melting points of acetylsalicylic acid it is necessary to give methods used.

5. The temperature at which acetylsalicylic acid melts is apparently not a true melting point.

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# SOME CRITICAL POINTS OF EMULSIFICATION IN OIL-SOAP EMUL-SIONS.\*1

# BY E. V. KYSER AND F. C. VILBRANDT.

The following is a continuation of previous work<sup>2</sup> on the emulsification of fixed oils in which the soap as the emulsifying agent is formed simultaneously with the emulsion.

For the determination of the critical points of emulsification in this series we have selected neutral cottonseed (Wesson) oil, to which we have added various percentages of sodium and potassium hydroxides, sodium and potassium carbonates and sodium silicate required to neutralize or saponify the oleic acid added.

<sup>1</sup> School of Pharmacy and Department of Chemistry, University of North Carolina.

<sup>\*</sup> Scientific Section, A. PH. A., Buffalo meeting, 1924.

<sup>&</sup>lt;sup>2</sup> Preliminary report on the Effect of Fatty Acids on Liniments and Emulsions, JOUR. A. PH. A., May, 1924, p. 433.

## May 1925 AMERICAN PHARMACEUTICAL ASSOCIATION

Where completed emulsification did not take place after the addition of unusually large amounts of oleic acid and hydroxides or silicate, it was decided that it was of no practical advantage to continue in this direction, because the resulting emulsion would become colored from the excess of acid and also because the amount of soap required to emulsify would be too large for palatable preparations.

In order to determine the value of the various soaps and practical application of the process for making the emulsions of various percentages of oil, soap, and water we made emulsions that contained ten, twenty, thirty, forty, and fifty per cent of oil respectively.

#### PROCEDURE.

Two-hundred-gram samples of each of the emulsions were made by the following method: the oil and oleic acid was weighed into a 300-cc. tall form beaker. The carbonates, alkalies, and silicates, previously calculated to neutralize the oleic acid, were added to the required amount of water and mixed. The oil and oleic acid were mixed and set in motion by means of a mechanical agitator, which consisted of a Cenco motor and a glass spiral stirring rod extending to the bottom of the beaker. A constant stream of water and saponifier was run slowly into the oil and acid. Agitation was continued for ten minutes after the addition of all of the ingredients. Emulsification was effected without the aid of external heat. For determining the viscosities of the oil and emulsions there was used a modified Sprengel viscometer consisting of a 100-cc. jacketed pipette calculated to permit water at 20° C. to pass from mark to mark in 14.1 seconds.

The tables of viscosities and separation show the percentage of oil, soap, saponifier, and water, also the kind of soap formed, the viscosity of the emulsion, the separation of the emulsion in terms of time started after emulsification, and when the separation was completed, the percentage of emulsified layer after 48 hours. Also the order in series of classification in the watery layer after complete separation of the emulsion. The percentage of water was calculated from the amount of water added and did not include water liberated by the action of the alkalies on the oleic acid.

TABLE OF VISCOSITIES AND SEPARATION.

			TABLE	OF VISCOSIT	IES AND	) SEPARA	TION.			
	%	%	Saponify-			Viscosity	Separa		Emul- sified layer	Order in series of clarifi- cation
Sample		n Oleic acid,	ing agent.	Soap present.	% soap.	in seconds.	Started.	Com- pleted.	after 48 hrs.	watery layer.
A-1	10	0.1	NaOH	Sod. oleate	0.11	16.5	10 min.	30 min.	10	3
<b>2</b>	10	0.2	NaOH	Sod. oleate	0.22	16.5	10 min.	30 min.	10	3
3	10	0.3	NaOH	Sod. oleate	0.33	16.5	10 min.	30 min.	10	3
4	10	0.4	NaOH	Sod. oleate	0.45	16.5	10 min.	30 min.	10	3
<b>5</b>	10	0.5	NaOH	Sod. oleate	0.56	16.4	10 min.	30 min.	10	3
6	10	0.75	NaOH	Sod. oleate	0.82	16.4	10 min.	30 min.	10	3
7	10	1.0	NaOH	Sod. oleate	1.11	16.4	1 <b>2 min</b> .	60 min.	10	3
8	10	1.5	NaOH	Sod. oleate	1.66	16.4	12 min.	60 min.	10	3
9	10	2.0	NaOH	Sod. oleate	2.23	16.4	30 min.	60 min.	10	3
10	10	3.0	NaOH	Sod. oleate	3.33	16.5	30 min.	60 min.	10	4
11	10	4.0	NaOH	Sod. oleate	4.46	16.6	30 min.	60 min.	10	5
12	10	6.0	NaOH	Sod. oleate	6.69	16.7	30 min.	60 min.	10	6
13	10	14.0	NaOH	Sod. oleate	15.96	18.5	30 min.	60 min.	10	7
B-1	10	2.0	KOH	Pot. oleate	2.40	16.3	10 min.	30 min.	10	7

	%	%	Saponify-			Viscosity	Separ	ation.	Emul- sified	Order in series of clarifi- cation,
Sample.	Wésson oil.	% Oleic acid.	ing agent.	Soap present.	% soap.	in seconds.	Started.	Com-	after	watery layer.
2	10	3.0	KOH	Pot. oleate	3.60	16.2	10 min.	30 min.	10	8
3	10	4.0	KOH	Pot. oleate	4.80	16.3	10 min.	30 min.	10	8
4	10	6.0	KOH	Pot. oleate	7.19	16.7	15 min.	60 min.	10	8
5	10	14.0	KOH	Pot. oleate	16.79	19.4	60 min.	120 min.	10	10
C-1	10	2.0	Na2SiO3	Sod. oleate	2.23	16.4	10 min.	30 min.	10	<b>2</b>
<b>2</b>	10	3.0	Na2SiO3	Sod. oleate	3 .33	16.4	10 min.	30 min.	10	3
3	10	4.0	$Na_2SiO_3$	Sod. oleate	4.46	16.5	10 min.	30 min.	10	4
4	10	6.0	Na2SiO3	Sod. oleate	6.85	16.6	10 min.	30 min.	10	5
5	10	14.0	Na2SiO3	. Sod. oleate	15.96	316.4	72 hrs.	72 hrs.	80	15
<b>D-</b> 1	10	<b>2</b> . <b>0</b>	Na <sub>2</sub> CO <sub>3</sub>	Sod. oleate	2.23	16.4	1 hr.	24 hrs.	20	1
<b>2</b>	10	3.0	$Na_2CO_3$	Sod. oleate	3.33	16.8	3 hrs.	24 hrs.	20	1
3	10	4.0	$Na_2CO_3$	Sod. oleate	4.46	17.2	24 hrs.	48 hrs.	20	1
4	10	5.0	$Na_2CO_3$	Sod. oleate	5.57	18.6	-	anent	100	0
5	10	7.0	Na <sub>2</sub> CO <sub>3</sub>	Sod. oleate	7.79	22.7	-	anent	100	0
E-1	10	2.0	K <sub>2</sub> CO <sub>8</sub>	Pot. oleate	2.40	16.3	1 hr.	24 hrs.	20	1
2	10	3.0	$K_2CO_3$	Pot. oleate	3.60	16.5	3 hrs.	24 hrs.	20	1
3	10	4.0	$K_2CO_3$	Pot. oleate	4.80	17.1	24 hrs.	48 hrs.	20	1
4	10	5.0	K <sub>2</sub> CO <sub>8</sub>	Pot. oleate	6.00	17.7	-	anent	100	0
5	10	7.0	$K_2CO_3$	Pot. oleate	8.40	21.2	-	anent	100	0
F-1	20	2.0	NaOH	Sod. oleate	2.23	16.3	15 min.	1 hr.	25 07	2
2	20	4.0	$N_{aOH}$	Sod. oleate	4.46	16.5	15 min.	1 hr.	25 97	3
3	20	6.0	NaOH NaOH	Sod. oleate	6.69	16.8	15 min.	1 hr.	25	4
4	20	10.0	NaOH NaOH	Sod. oleate	11.14	18.4	15 min.	3 hrs.	25 07	5
5 6	20	12.0	NaOH N. OH	Sod. oleate	13.37	20.1	30 min.	8 hrs.	25	8
7	$\frac{20}{20}$	14.0 16.0	NaOH NaOH	Sod. oleate Sod. oleate	$\frac{15.96}{18.19}$	$rac{21.3}{25.5}$	1 hr. 1 hr.	8 hrs. 8 hrs.	$\frac{25}{25}$	$\frac{12}{13}$
G-1	$\frac{20}{20}$	$\frac{10.0}{2.0}$	NaOH KOH	Pot. oleate	$\frac{18.19}{2.40}$	$\frac{25.5}{16.1}$	15  min.	3 ms. 1 hr.	$\frac{25}{25}$	3
2	$\frac{20}{20}$	2.0 16.0	KOH	Pot. oleate	19.19	$10.1 \\ 25.7$	15 mm. 1 hr.	6 hrs.	$\frac{25}{25}$	10
H-1	20	7.0	Na <sub>2</sub> SiO <sub>3</sub>	Sod. oleate	7.79	17.6	30 min.	8 hrs.(?)		6
2	20	12.0	$Na_2SiO_3$	Sod. oleate	13.37	111.1	24 hrs.	72 hrs.(?)		14
3	20	14.0	$Na_2SiO_3$ $Na_2SiO_3$	Sod. oleate	15.96	135.0	48 hrs.	72 hrs.(?)		14
-1	$20^{-0}$	1.0	Na <sub>2</sub> CO <sub>3</sub>	Sod. oleate	1.11	16.0	8 hrs.	48 hrs.	20	1
2	20	2.0	Na <sub>2</sub> CO <sub>3</sub>	Sod. oleate	2.23	16.0	8 hrs.	48 hrs.	20	1
3	20	3.0	$Na_2CO_3$	Sod. oleate	3.33	16.5	8 hrs.	48 hrs.	20	1
4	<b>20</b>	4.0	Na <sub>2</sub> CO <sub>3</sub>	Sod. oleate	4.46	16.6	8 hrs.	48 hrs.	<b>25</b>	1
5	20	5.0	$Na_2CO_3$	Sod. oleate	5.57	18.5	perm	anent	100	0
<b>J-</b> 1	20	1.0	$K_2CO_3$	Pot. oleate	1.20	16.3	2 hrs.	48 hrs.	20	1
<b>2</b>	20	2.0	$K_2CO_3$	Pot. oleate	2.40	16.3	8 hrs.	48 hrs.	<b>20</b>	1
3	<b>20</b>	3.0	$K_2CO_3$	Pot. oleate	3.60	16.7	8 hrs.	48 hrs.	20	1
4	<b>20</b>	4.0	$K_2CO_3$	Pot. oleate	4.80	17.0	8 hrs.	48 hrs.	25	1
5	20	5.0	$K_2CO_3$	Pot. oleate	6.00	18.4	perm	anent	100	0
K-1	30	5.0	NaOH	Sod. oleate	5.57	17.5	1 hr.	8 hrs.	50	<b>5</b>
2	30	7.0	NaOH	Sod. oleate	7.79	18.6	1 hr.	8 hrs.	50	6
33	30	10.0	NaOH	Sod. oleate	11.14	22.3	6 hrs.	8 hrs.	60	7
4	30	12.0	NaOH	Sod. oleate	13.37	23.6	6 hrs.	8 hrs.	60	11
L-1	30	5.0	KOH	Pot. oleate	6.00	18.9	1 hr.	2  hrs.	50	$\frac{6}{7}$
2	30	7.0	KOH	Pot. oleate	8.40	21.7	2 hrs.	8 <u>h</u> rs.	50	7
3	30 20	10.0	KOH	Pot. oleate	12.00	23.8	2 hrs.	8 hrs.	75	8
4 M 1	30 20	12.0	KOH	Pot. oleate	14.40	25.0 17.6	8 hrs.	24 hrs.	90 50	9
M-1	30 20	5.0	$Na_2SiO_3$ $Na_2SiO_3$	Sod. oleate	5.57	17.6	1 hr.	8 hrs.	50 50	6
$\frac{2}{3}$	$\frac{30}{30}$	7.0 10.0	Na2SiO3 Na2SiO3	Sod. oleate Sod. oleate	7.79 11.14	$\frac{18.4}{128.0}$	1 hr.	8 hrs. anent	$\frac{50}{100}$	6 0
э N-1	30 30	<b>3</b> .0	$Na_2SIO_3$ $Na_2CO_3$	Sod. oleate	3.33	128.0	2 hr.	8 hrs.	50	1
<b>11 1</b>	50	0.0	1.42003	Jou. orale	0.00	10.0	<i>ц</i> п.	о <u>ш</u> э.	00	•

Sample	% Wesson e. oil.	% Oleic acid.	Saponify- ing agent.	Soap present.	% soap.	Viscosit <u>i</u> in seconds.		ration, Com- pleted,	Emul- sified layer	Order in series of clarifi- cation, watery layer
<b>2</b>	30	4.0	$Na_2CO_3$	Sod. oleate	4.46	17.7	6 hrs.	8 hrs.	50	1
O-1	30	3.0	$K_2CO_3$	Pot. oleate	3.60	17.0	6 hrs.	8 hrs.	50	1
<b>2</b>	30	4.0	$K_2CO_3$	Pot. oleate	4.80	17.5	6 hrs.	8 hrs.	50	1
P-1	40	2.0	NaOH	Sod. oleate	2.23	17.9	1 hr.	24 hrs.	66	<b>5</b>
Q-1	40	2.0	KOH	Pot. oleate	2.40	17.9	•1 hr.	24 hrs.	66	5
<b>2</b>	40	6.0	KOH	Pot. oleate	7.20	21.4	8 hrs.	36 hrs.	75	5
<b>R-1</b>	40	5.0	Na2SiO3	Sod. oleate	5.57	19.4	8 hrs.	36 hrs.	75	4
S-1	40	2.0	$Na_2CO_3$	Sod. oleate	2.23	18.0	8 hrs.	24 hrs.	70	1
<b>T-1</b>	40	2.0	$K_2CO_3$	Pot. oleate	<b>2.40</b>	18.4	8 hrs.	24 hrs.	70	1
<b>U-1</b>	50	2.0	NaOH	Sod. oleate	2.23	19.8	1 hr.	36 hrs.	50	7
V-1	50	2.0	KOH	Pot. oleate	2.40	19.7	1 hr.	24 hrs.	80	5
<b>2</b>	50	4.0	KOH	Pot. oleate	4.80	22.5	1 hr.	72 hrs.	80	5
<b>W-1</b>	50	3.0	Na2SiO3	Sod. oleate	3.33	21.5	16 hrs.	72 hrs.	99	5
X-1	50	2.0	$Na_2CO_3$	Sod. oleate	2.23	19.8	8 hrs.	24 hrs.	90	1
<b>Y-1</b>	50	2.0	K <sub>2</sub> CO <sub>3</sub>	Pot. oleate	2.40	19.7	8 hrs.	24 hrs.	90	1

# SUMMARY OF RESULTS.

The use of sodium and potassium carbonates for the saponification of the 1. oleic acid produces permanent emulsions when added in relatively small amounts. Where separation takes place the more aqueous layer retains the emulsion to such an extent that it is difficult to determine the line of demarcation; where separation does not take place the soaps formed by these saponifications are superior as emulsifying agents to those formed by the hydroxide or silicate saponification. The addition of 5 per cent oleic acid and the required amount of either of the two carbonates will produce permanent emulsions of ten per cent and twenty per cent of oil and likewise a corresponding diminution in the amount of oleic acid and carbonates will produce permanent emulsions of 30, 40, and 50 per cent of oil. Sodium and potassium carbonates have an equal value as saponifying agents, and the emulsions produced from each are indentical in physical properties. The emulsions produced by the addition of the carbonates are very fluid and therefore desirable for internal administration.

2. Sodium and potassium hydroxides for the saponification of the oleic acid are not desirable, because the quantity of oleic acid required to completely emulsify the oil causes coloration of the emulsions and the amount of soap formed is too great for a palatable preparation. The saponification of oleic acid by the hydroxides—14 per cent in the 10 per cent emulsions, 16 per cent in the 20 per cent emulsions, 12 per cent in the 30 per cent emulsions, 6 per cent in the 40 per cent emulsions and 4 per cent in the 50 per cent emulsions, does not produce permanent emulsification. The value of the two hydroxides as saponifying agents are the same, and the emulsions from each present the same physical properties. The watery layer does not retain the emulsified oil to the same degree as the carbonate saponifications.

3. The saponification of oleic acid with sodium silicate, 14 per cent in the 10 per cent emulsions, 14 per cent in the 20 per cent emulsions, 5 per cent in the 40 per cent emulsions and 3 per cent in the 50 per cent emulsions, does not give complete emulsification. The use of sodium silicate in sufficient amounts to



No. 3.



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No. 6.

ILLUSTRATION SHOWING SEPARATION

No. 1. NaOH SAPONIFICATION

(1) 10% oil, 0.11% soap, (2) 10% oil, 0.22% soap, (3) 10% oil, 0.33% soap (4) 10% oil, 0.45% soap, (5) 10% oil, 0.56% soap, (6) 10% oil, 0.82% soap (7) 10% oil, 1.11% soap, (8) 10% oil, 1.66% soap, (9) 10% oil, 2.23% soap (10) 10% oil, 3.33% soap, (11) 10% oil, 4.46% soap, (12) 10% oil, 6.69% soap (13) 10% oil, 15.96% soap

No. 2. NaOH SAPONIFICATION

(14) 20% oil, 2.23% soap (15) 20% oil, 4.46% soap (16) 20% oil, 6.69% soap (17) 20% oil, 11.14% soap (18) 20% oil, 13.37% soap (19) 20% oil, 15.96% soap (20) 20% oil, 18.19% soap (21) 30% oil, 5.57% soap (22) 30% oil, 7.79% soap (23) 30% oil, 11.14% soap (24) 30% oil, 13.37% soap (25) 40% oil, 2.23% soap (26) 50% oil, 2.23% soap

No. 3. KOH SAPONIFICATION

(1) 10% oil, 2.40% soap (2) 10% oil, 3.60% soap (3) 10% oil, 4.80% soap (4) 10% oil, 7.19% soap (5) 10% oil, 16.79% soap (6) 20% oil, 2.40% soap (7) 20% oil, 19.19% soap (8) 30% oil, 6.00% soap (9) 30% oil, 8.40% soap (10) 30% oil, 12.00% soap (11) 30% oil, 14.40% soap (12) 40% oil, 2.40% soap (13) 40% oil, 7.20% soap (14) 50% oil, 2.40% soap (15) 50% oil, 4.80% soap

#### No. 4. Na<sub>2</sub>SIO<sub>3</sub> SAPONIFICATION

(1)	10%	oil,	2.23%	soap	(2)	10%	oil,	3.33%	soap	(3)	10%	oil,	4.46%	soap
			6.85%											
			13.37%											
(10)	30%	oil,	7.79%	soap	(11)	30%	oil,	11.14%	soap	(12)	40%	oil,	5.57%	soap
(13)	50%	oil,	3.33%	soap										

#### No. 5. K<sub>2</sub>CO<sub>3</sub> SAPONIFICATION

(1) 10% oil,	2.40% soap	(2) 10% oil,	3.60% soap	(3) 10% oil, 4.80% soap
(4) 10% oil,	6.00% soap	(5) 10% oil,	8.40% soap	(6) $20\%$ oil, $1.20\%$ soap
(7) 20% oil,	2.40% soap	(8) $20\%$ oil,	3.60% soap	(9) 20% oil, $4.80%$ soap
(10) 20% oil,	6.00% soap	(11) 30% oil,	3.60% soap	(12) 30% oil, $4.80%$ soap
(13) 40% oil,	2.40% soap	(14) 50% oil,	2.40% soap	

## No. 6. Na<sub>2</sub>CO<sub>3</sub> SAPONIFICATION

(15) 10% oil,	2.23% soap (16) 10% oil,	3.33% soap (17) 10% oil, $4.46%$ soap
(18) 10% oil,	5.57% soap (19) 10% oil,	7.79% soap (20) 20% oil 1.11% soap
		3.33% soap (23) 30% oil, 4.46% soap
		3.33% soap (26) $30%$ oil, $4.46%$ soap
(27) 40% oil,	2.23% soap (28) 50% oil,	2.23% soap

completely emulsify the oil has a tendency to cause granulation—that is, the emulsion does not separate into two layers but shows signs of partial gelatinization and separation of a granular nature This is evidenced by the use of 10 per cent oleic acid and sodium silicate in the 20 per cent emulsions. The relative position of sodium silicate as the saponifying medium lies between the carbonates and hydroxides.

4. The oil used gave a viscosity of 51.5 seconds, and with the exception of the sodium silicate emulsions all of the emulsions range in viscosity between that of water and that of oil. All of the emulsions contained sufficient soap to emulsify the oil completely. This was shown by the suds on top of the emulsions after agitation. This soapiness reduces the external adhesion of the mass for the outlet, so that any increase in the viscosity of the emulsions over that of water can be attributed to the percentage of solids present and the internal cohesion of the emulsified particles. Therefore, the oil lends itself to increasing internal cohesion. It is readily seen that the difference in viscosity cannot be due to any great extent to the oil, because in series U to Y, in which 50 per cent of oil is used, the viscosities have increased 8.4 seconds only above that of water, or, in other words, the emulsification of the oil has reduced the viscosity from 51.5 to 22.5 seconds. ľπ the case of the sodium silicate emulsions, which show signs of gelatinization or granulation, the internal cohesion is increased enormously when the percentage of soap is increased and the high external adhesiveness of the silicate is also evident. In general, the increase in oil content increases the viscosity when the percentage of soaps are increased above 4 per cent. This does not apply to the silicate emulsions, which were thrown out because of other influences.

5. A study of the rates of separation in connection with the viscosities shows that the soaps formed by the hydroxide saponifications are much inferior to the soaps formed by the silicate or carbonates as emulsifying agents. Although increased oil content increases the time limit before the separation of the emulsion starts, an increase in the amount of soap formed also increases the time before the emulsion completely separates. The difference in the time of separation decreases as the soap is increased in the same series, and it also decreases as the oil content is increased.

6. The per cent of emulsified layer after 48 hours as given in column 10 is a relative measure of the extent of separation after a given length of time when no further progressive separation is evident. The increasing percentage of emulsification as the series is extended by increasing the oil content is not a true measure of permanency, since a 10 per cent emulsion in the 10 per cent series is the best that can occur if all of the oil should separate; whereas in the 50 per cent series the least that can occur is a 50 per cent separation. However, this table of information is important in showing the relative permanency of the emulsification of the oils in Even in the 10 per cent series A, B, C, D, and E, the permanency rises each series. from 10 per cent in the hydroxide series A and B to 20 per cent for the lowest of the carbonate series. This shows that the formation of an excess of 5 per cent soap by the use of carbonates as the saponifying agent is doubly effective over the formation of so large a quantity of soap as 16.8 per cent by the use of the hydroxides. In the 20 per cent oil series F, G, H, I, J, and K eliminating the adhesive silicate results, we again obtain the same general result. Increase of oil where the per cent of soap remains constant or increase of soap where the oil remains constant tends to increase the permanency of the emulsion. Of course in this connection it should be borne in mind that the increase in oil and soap likewise decreases the per cent of water.

7. After the complete separation of the emulsions the aqueous bottom layers that prevail show some interesting variations. The degree of separation varies with the oil content, the percentage of soap, the percentage of water, and the saponifying agent used. The classification given in column 11, order in series of classification in watery layer, presents a relative degree of separation of the emulsified oil layer from the aqueous portion. It varies from a rating of 1, in which it is difficult to discern the line of demarcation, to 16, in which the watery layer is perfectly clear and transparent. That is, no emulsified oil is suspended in the aqueous portion. It will be noted that the emulsions in which carbonates were used are rated as 1 or 0, the latter indicating no separation. Then as the soap content is increased in each series, as in A, B, or C, there is an increase in the separation of the emulsified layer from the aqueous layer, that is, the emulsified oil rises to the top and leaves less emulsified particles in the aqueous bottom portion.

Relatively small amounts of soaps formed from the action of the car-8. bonates on oleic acid are decided superior as emulsifying agents to the soaps formed by the action of the corresponding hydroxides and sodium silicate. This presents an interesting subject for further investigation. The fact that the same percentage of soap formed with each of these saponifiers does not have the same value as emulsifiers may be attributed to one or many influences. It is apparent that the question of the ability of the soap to hydrate properly is one of the contributing factors in the stability of the emulsions. This is borne out by the fact that an increase in oil and a decrease in water requires less soap regardless of the saponifier used. The rapidity of the rate of saponification in the case of the hydroxides and the silicates when compared with that of the carbonates probably explains the difference in the extent of hydration. Where saponification is rapid there is a tendency on the part of the saponified or partially saponified mass to bunch, and where such bunching occurs hydration takes place slowly and it is more than likely that a percentage of the soap instead of hydrating and becoming colloidal, goes into solution in the water. Soaps vary in their physical properties depending upon the nature of the alkalies used in saponification, the temperature, and the conditions under which saponification takes place. Merklen<sup>1</sup> concludes that soap as an "absorption product" is capable of continual variation, and that the absorption of water by the colloidal soap depends upon (1) the structure and nature of the colloid; (2) the nature of the solvent; (3) the nature of the electrolytes present (salts and alkalies; (4) upon the temperature. One of these conditions, the nature of the solvent, may be eliminated. However, the other three, perhaps, have a direct bearing upon the inequality of these soaps as emulsifying agents.

Further experiments in this direction as well as in the direction of determining the value of soap as emulsifying agents will be considered at another time in connection with other fixed oils.

<sup>&</sup>lt;sup>1</sup> Etudes sur le constitution des savons du commerce dans sec rapports avec la fabrication, Marseille, 1906.