The Behavior of Soaps of Various Oils on Dilution

Castor Oil Soaps Exhibit Marketd Resistance to Hydrolysis with Water

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IN a paper read before the Society of Public Analysts, London, and published in the "Analyst" December, 1923, page 590, the author proposed a new test for castor oil, and the detection of any other oil which might have been added for the purpose of adulteration. This test is based on the observations made when soaps were diluted with water.

It is a well known fact that when even neutral soaps are dissolved in water, hydrolysis takes place and free alkali is formed. This was first discovered by Chevreul and has been confirmed by numerous observers. Chevreul found that when neutral sodium and potassium salts of stearic and palmitic acids were dissolved in large volumes of hot water, on cooling crystals separated having the composition of acid salts, i.e., half the sodium or potassium in the salts was replaced by the equivalent of hydrogen, the salts being represented by the formulæ $Na.H.R_2$.

Soap Solutions Unstable

The products of the ionization of ordinary salts in solution, for instance NaCl, Na_2SO_4, etc., do not give a pink color with phenol-phthalein. In both these cases a strong base is combined with a strong acid. The same may be said of the salts of many organic acids, including the lower members of the saturated fatty acid series—acetic, butyric, etc.—which, in solution in water, can be titrated to neutrality and estimated with phenol-phthalein as indicator. But with the soaps the problem is an entirely different one. The higher fatty acids are insoluble in water, and although they form neutral salts or soaps with alkalies, these are hydrolyzed more or less according to the amount of dilution, i.e., they separate into two phases, one of which is acid and the other correspondingly alkaline. A hot solution may be, and generally is, quite clear, but addition of phenol-phthalein shows that free alkali is present, the acid soap being too weak to exert the opposite effect on the indicator to any marked extent. On cooling the solutions usually become turbid and a suspension of the acid phase in an alkaline medium is the result. In the case of pure acids of high melting point, i.e., palmitic, stearic, etc., the acid phase separates in the form of fine crystals having a satiny lustre which remain suspended in the liquid, but which can readily be separated by filtration, the clear filtrate being strongly alkaline, containing half the total alkali, and practically free from soap.

With ordinary commercial soaps this separation is not so clearly marked, and it is impossible to separate, except incompletely, the two phases, but there is reason to believe that in these cases the change is substantially the same.

The pink color which develops on addition of phenol-phthalein to solutions of most soaps deepens as

dilution is increased, but the writer found that with castor oil soaps only a faint pink color was produced which did not deepen appreciably on dilution. On titrating these former solutions with standard acid it was found that the hydrolysis alkali increased up to a maximum at a certain dilution, (i.e. part of soap in about 150 parts of water), further dilution causing little or no change. The titrations are not entirely perfect since a faint pink color usually reappears showing that equilibrium is only momentary, but on increasing the dilution beyond that above mentioned the end point is more distinct, a faint pink color reappearing in some cases only after an appreciable interval of time. With most of the soaps examined by the writer the hydrolysis alkali amounted approximately to 50% of the total, but castor oil soap formed a marked exception, the hydrolysis alkali in this case amounting to not more than 5% of the total.

The following results, given in the original paper, will illustrate the behavior of various soaps with this test:—1 gram of soap dissolved in water and made up to 320 cc. for titration.

Soap	Free Na_2O found A	Total Na_2O found B	Per cent of total A × 100 / B
Stearic acid	0.056	0.111	50.5
Palmitic acid	0.057	0.119	48.0 (1 part in 160)
Oleic acid	0.049	0.103	47.5
Yellow bar soap	0.037	0.082	45.1
Olive oil soap	0.043	0.083	52.3
Castor oil fatty acids	0.004	0.093	4.3

The first three were made by dissolving the pure acids in the calculated quantities of sodium hydroxide solution, the first two contained slightly more than 1 gram of soap, but this in no way affects the experiments.

More recently the soaps of several other fatty acids have been examined, but, in order to simplify matters, instead of 1 gram of the salt or soap, 1 gram of the fatty acid was taken, dissolved in alcohol, neutralized with sodium hydroxide solution to phenol-phthalein and the liquid evaporated to dryness. The salt or soap was dissolved in boiled distilled water, diluted to 350 cc. and then titrated with N/10 hydrochloric acid until neutral to phenolphthalein, then in presence of methyl orange to complete neutrality.

The following results were obtained:

Salt of soap	Free Na_2O found A	Total Na_2O found B	Per cent of total
Acetic X	0.00329	0.5128	0.64
Butyric X	0.00282	0.3444	0.82
Caproic (normal) X	0.00187	0.2529	0.74
Lauric	0.006	0.1488	0.40
Myristic	0.0713	0.1360	52.40
Arachidic	0.0536	0.0992	54.00
Erucic	0.0468	0.0942	49.70

X Color change with methyl orange gradual, not sharp.

A Test for Castor Oil

It will be seen that there is no appreciable hydrolysis in solutions of sodium salts of the fatty acids, up to, and including lauric acid, but after this there is a complete break, the hydrolysis alkali in the soap of myristic acid and all higher acids amounting to approximately 50% of the total. Rosin acids behave similarly to fatty acids as shown in the table given below.

Briefly the test suggested for distinguishing castor oil from other oils and detecting adulteration is as follows: 5 grams of the oil are saponified by heating with slight excess of aloholic caustic potash solution, under a reflux condenser, phenol-phthalein is added, the liquid exactly neutralized with hydrochloric acid, and the alcohol evaporated off. Water is now added to the residue, and when solution is complete the liquid is cooled, made up to 100 cc., 10 cc. (—0.5 gram of oil) taken, diluted to 250 cc. with boiled distilled water, and titrated with decinormal hydrochloric acid, first in presence of phenol-phthalein and continuing after addition of methyl orange. With castor oil only about 0.5 to 0.8 cc. of decinormal acid was required in the first titration whereas most other fats and oils required 8 or 9 cc. There were, however, a few exceptions, notably butter, coconut, and palm nut fats, the results in these cases being easily explainable when we take into account the presence of the lower fatty acids and know their behavior. Slightly lower results were obtained with sunflower, cotton-seed and linseed oils which are not so easily explainable except on the assumption that they contain some hydroxylated fatty acids.

Since 95% of the acids of castor oil are composed of ricinoleic acid, a hydroxylated acid, it is evident that the salt of this fatty acid does not hydrolyze in solution to any considerable extent, and the difference in behavior between this soap and other soaps must be ascribed to the presence of this particular hydroxylated acid.

The value of the method is shown by the following tests on mixtures of castor oil and arachis oil:

Castor oil Parts	Arachis oil Parts	0.1NHCl required C.c.	Free KHO per 100 of Oil parts	Arachis oil calculated Per cent
100	0	0.5	0.56	...
90	10	1.4	1.57	9.9
80	20	(1) 2.3 (2) 2.3	2.58	19.8
70	30	(1) 3.2 (2) 3.3	3.58	29.7
60	40	4.3	4.81	41.7
50	50	5.0	5.60	49.5
40	60	6.1	6.83	61.5
30	70	6.95	7.78	70.9
20	80	7.8	8.73	80.2
10	90	8.7	9.74	90.1
0	100	9.6	10.75	...

The amount of free alkali found by titration, compared with the total combined alkali, was 3.1% in the case of castor oil and 56.7% in that of the arachis oil. A number of oils and fats have been examined by this method with the following results:

	Free KHO A	Total KHO B	A × 100 B
Castor oil, medicinal.....	0.672	18.48	3.6
	0.784	18.59	4.2
	0.78	17.81	4.6
	0.7	17.92	4.4
	0.7	17.92	4.4
Castor oil, medicinal	0.896	18.70	4.8
	0.898	18.93	4.7
Castor oil, medicinal	0.896	18.70	4.8
	0.896	18.59	4.8
Crude castor oil	0.56	18.14	3.1
(Free fatty acids 1.20%)...	0.56	18.14	3.1
	0.56	....	....
Castor oil, best seconds.....	0.896	18.70	4.8
	0.896	18.81	4.8
Castor oil, Madras.....	1.34	18.25	7.3
	1.45	18.48	7.9
Linseed oil	6.16	20.05	30.8
	6.27	20.05	31.3
Cottonseed oil	8.17	20.16	40.6
	8.29	20.16	41.1
Crude cottonseed oil.....	8.96	20.16	44.4
Dark red	9.18	20.05	45.8
(Free fatty acids 3.1%).....	8.96	....	44.4
End point difficult.....	8.62	....	43.0
Sunflower oil	7.73	19.49	39.1
Naphtha extracted	8.29	19.49	42.5
Alkali refined	....	....	....
Arachis oil	10.64	19.94	53.7
	10.76	19.94	54.0
Olive oil, medicinal.....	9.41	19.82	47.5
	9.52	19.49	48.8
	9.18	....	....
Rape oil (crude).....	8.96	17.58	51.0
	8.62	17.69	48.7
Rape oil (crude Jambo).....	8.85	17.70	50.0
(Free fatty acids 1.04%)....	8.74	17.81	49.0
Rape oil (adulterated).....	4.14	13.21	31.4
	4.03	13.33	30.3
	4.81	13.66	35.2
Pure sesamé oil.....	9.41	19.49	48.3
	9.41	19.49	48.3
Refined sesamé oil.....	9.86	19.49	50.6
	9.86	19.49	49.4
Crude sesamé oil.....	9.41	19.49	48.3
(Free fatty acids 2.9%).....	9.63	19.38	49.8
	9.41	....	48.3
Crude groundnut oil.....	9.52	19.26	49.4
(Free fatty acids 0.99%)....	9.63	....	50.0
	10.08	19.26	52.3
Crude Kapok oil.....	10.2	20.16	50.6
(Free fatty acids 5.2%).....	10.63	20.38	51.6
	10.53	20.61	51.1
	10.64	....	51.6
Palm oil	9.52	19.93	47.7
	9.63	20.16	47.7
	9.08	....	....

	Free KHO A	Total KHO B	A × 100 B
Lard	10.53	20.27	51.9
	10.30	20.38	50.6
Tallow	9.74	19.60	49.7
	9.85	19.82	49.7
Pure Premier Jus.	9.86	20.05	49.2
Tallow oil	9.74	19.71	49.2
(Free fatty acids 0.27%)	8.29	18.41	44.9
Pure British cod oil	8.29	18.59	44.6
Pure filtered	8.62	19.49	44.2
No. 1, whale oil	8.62	19.49	44.2
Pure filtered	8.73	19.49	44.8
Seal oil	8.85	19.38	45.7
Butter fat (1)	8.29	22.96	36.1
	8.85	23.18	38.1
Butter fat (2)	9.30	22.06	42.1
	9.18	22.40	41.0
Butter fat (3)	8.40	22.06	38.1
	8.51	22.06	38.6
Butter fat (4)	9.40	22.18	42.4
	9.18	21.95	41.9
Butter fat (5)	9.52	21.84	43.6
	9.30	22.18	41.9
Butter fat (6)	9.40	21.62	43.5
	9.40	21.73	43.2
Coconut oil	5.15	25.20	20.4
(Commercial)	4.93	25.65	19.2
Cochin coconut oil	3.92	24.98	15.7
(Free fatty acids 1.30%)	4.03	24.86	16.1
French Cochin coconut oil	3.92	24.75	15.8
(Free fatty acids 1.97%)	3.92	24.64	16.0
Ceylon coconut oil	4.59	25.09	18.3
(Free fatty acids 4.57%)	4.37	25.09	17.4
Pure coconut oil	3.81	24.42	15.6
(Free fatty acids 1.00%)	3.70	24.19	15.3
	3.92	....	16.2
Palm nut oil	5.93	25.87	22.9
(Commercial)	5.82	25.65	22.7
Palm nut oil	5.15	23.74	21.7
Alkali refined	....	....	....
(Free fatty acids nil)	....	....	....
Palm nut oil	5.26	24.53	21.5
(Free fatty acids 3.55%)	5.49	24.64	22.3
Palm nut oil	5.60	25.20	22.2
(Free fatty acids 4.93%)	5.49	24.86	22.1
Rosin	9.52	17.81	53.5
	9.52	18.03	52.8

Experiments were conducted with other indicators besides phenol-phthalein and methyl orange; e. g., thymol blue and alizarin red S., which, after allowing for the slight difference in pH for the color change, gave comparable results.

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