and amounts of the acids in the resulting fractions. The low temperature crystallization technic was shown to be useful in the separation of the complex mixtures of esters found in fish oils.

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Direct Oxidation Tests on Soap

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WHEN it became necessary to test certain cosmetic products for oxidative rancidity, the question arose whether the peroxide test of Lea could be used in preparations where the fatty substance, fatty acid, or soap is emulsified or hydrated in water. This test has been used for years in determining the rancidity of oils while the method of separating oil and testing it by means of the Kreis test is slow and susceptible to change during the separation of the fatty substance. Attempts to make the Kreis test a quantitative test have not until now proved satisfactory for cosmetic products.

The Peroxide Test for Soap Gels

It was to be expected in employing the peroxide test of Lea that the acetic acid used in the solvent mixture would suffice for separating the free fatty acid from the soap-gel sample, thus yielding a solution of free fatty acid in the solvent. It was also to be expected that in the presence of water the hydriodic acid which is liberated from the potassium iodide might split off some free iodine, thus unfortunately increasing the peroxide value. When oxidized fats were emulsified with water in the proportions 1:1 and 1:2 and tested in comparison with the original oxidized oil, it was found that an increase in peroxide value of 0.3 and 0.5 units developed. These increases, while important in cases of very low peroxide values, do not affect practical conclusions in the case of higher values.

Method. Five-tenths to 1.0 gram of soap or 1.0 to 3.0 grams of cosmetic emulsion was weighed into a 40 ml. test tube. The actual amount of sample selected will depend upon the expected peroxide value and upon the water content of the cosmetic emulsion. To the mixture was added 1.0 gram of potassium iodide followed by the mixture of glacial acetic acid: chloroform (2:1). The mixture was boiled until the soap was dissolved (requiring about 10 seconds), and then for exactly 30 seconds longer, timed with a stop-watch. It was then cooled under running water, diluted with 30 ml. freshly boiled water, and titrated with 0.002 N thiosulphate with starch solution as indicator.

A sample of old soapflakes was tested by this method with the following results:

PEROXIDE VALUE

	Sample from package surface	Average sample of mixed flakes
1	5.7	2.0
2	5.3	2.2
3	4.0	2.4
4	5.0	1.8
5	4.0	2.4
Average	4.8	2.16
Blank on reagents: zero.		

It will be noted that the greater differences occurred when samples were taken from the surface because of the unevenness of aeration of the various samples. Smaller differences occurred in the case of mixed samples, and it is reasonable to assume that only these are to be taken into account in judging the accuracy of the method.

The procedure described is identical with that of the Lea peroxide test with the exception that instead of oil one gram of soap is substituted. The result is calculated directly per gram of soap. If only the state or extent of oxidation of a soap sample is to be determined, the exposure of the sample need not be considered. If the tendency of the sample to become rancid, however, is to be estimated, it is necessary carefully to control the exposure of the product to the action of oxygen or air.

The following tables provide general preliminary figures concerning the development of peroxide rancidity under various conditions, using the test proposed in this paper:

TABLE 1

Marseilles Type (Peanut-Coconut, 25% Water, Shavings)

Under quartz lamp

Hours	0	1	2	3	then 24 in open air without lamp
P. V.	4.4	8.0	10.0	14.8	44.0

200-watt lamp

Hours	0	24	48	72	96	144	192	336
	0.0	19	50	60	61	84	120	80

Dark drying oven (at 105°C.)

Hours	0	8	18	36
P. V.	0	6.0	3.0	3.5

TABLE 2

Soap Flakes (Olive, Coconut Oil, 5% Water)

Under quartz lamp

Hours	0	8 with lamp 20 without	11 with 60 without
P. V.	0.0	86	144
Remarks	0.04% NaOH		2% FFA
Hours	16 with 100 without	23 with 100 without	23 with 2 wks. without
P. V.	175	230	130
Remarks		no discoloration	yellow 7.7% FFA

Under 200-watt daylight lamp (at 70°C.)

Hours	0	24	72	120	264	336	580
P. V.	0.0	13.5	22	42	120	62	118

TABLE 3

Milled Soap (Tallow-Coconut Shavings)

Under 200-watt daylight lamp

Hours	0	21	26	46	and 6 under quartz lamp
P. V.	0.0	8.0	10.0	12.0	114

TABLE 4

Powdered Soaps, in Air at Room Temperature

Hours	0	48	72	120	168	216
Marseilles type as above, P. V.	2.5	40.5	58	82	94	107.5
Milled toilet soap as above, P. V.	6.0	49.5	68	82	91	130.0
Milled toilet soap, P. V.	11.0	52.0	66	88	123	155.0
Olive oil soap flakes as above, P. V.	4.6	35.0	47	57	74	97.0
Milled olive oil soap, P. V.	8.0	41.0	54	65	70	87.0

TABLE 5

Comparison of Respective Development of P. V. in Oil and Its Soap Under Similar Circumstances

Under quartz lamp

Hours	0	2	6 with lamp 14 without	10 with 28 without	15 with 28 without	20 with 40 without	25 with 80 without	40 with 80 without
P. V. Olive oil	12.0	19.0	59.0	75.0	110.0	155.0	166.0	300
Olive oil soap	9.6	10.2	25.7	36.8	72.0	129.6	131.6	162
Coconut oil	2.3	8.0	23.5	30.5	40.0	53.5	57.0	65
Coconut oil soap	0.6	2.1	3.6	9.6	10.8	13.2	18.0	21

NOTE: Values for soap are in this table recalculated on fatty matter in soap for comparison with the oil.

TABLE 6

Influence of Sodium Carbonate Under 200-Watt Daylight Lamp

Hours	0	2	4	9
P. V. Marseilles type	7.0	20	32	48
Marseilles type plus 5% Na_2CO_3	13.5	23	42	60
Milled soap	7.0	18	36	60
Milled soap plus 5% Na_2CO_3	5.7	21	....	46

TABLE 8

Influence of Free Alkali Under Quartz Lamp

Hours	0	2	4	9
P. V. Milled soap containing olive oil	3.7	21.5	42.8	72
Milled soap plus 8% NaOH	2.2	16.5	31.0	57
Milled soap as before	6.0	27.0	49.0	80
Milled soap plus 8% NaOH	5.4	13.0	39.0	81
Marseilles type	6.5	20.0	30.0	68
Marseilles type plus 8% NaOH	1.1	22.0	28.0	56

TABLE 7

Influence of Free Alkali or Unsaponified Oil, Respectively, at 105° in Dark Drying Oven

Hours	8	18	36
P. V. Marseilles type	6.0	3.0	3.5
Marseilles type plus 8% NaOH	1.0	0.6	1.7
Marseilles type plus 10% oil	19.0 (dark)	18.0	13.0
Marseilles type plus 2% oil	4.5	3.0	3.5

TABLE 12

Cold Process Coconut Soap Under Quartz Lamp

Hours	0	2	13 with lamp 60 without
4.2% Unsaponified fat	0.0	5.0	6.0
0.4% Unsaponified fat, 0.24% free NaOH	0.0	6.5	11.0

Cold Process Coconut Soap Under 200-Watt Daylight Lamp

Hours	24	72	264
4.2% Unsaponified fat	1.5	10.5	24.5
0.4% Unsaponified fat, 0.24% free NaOH	0.6	3.4	22.0
0.6% Unsaponified fat, 0.05% free NaOH	1.2	4.0	13.0

TABLE 9

Influence of Free Alkali Under Quartz Lamp

Hours	24	48	72	96	144	192	336
P. V. Milled soap containing olive oil	11.8	20.0	30	33	68	104	80
Milled soap plus 8% NaOH	8.1	14.0	23	36	69	113	98
Milled soap as before	14.5	22.0	28	40	56	60	80
Milled soap plus 8% NaOH	13.0	17.5	26	39	52	69	99
Marseilles type	19.0	50.0	60	61	84	120	80
Marseilles type plus 8% NaOH	8.7	16.3	25	31	52	78	98

TABLE 10

Influence of Small Quantities of Free Alkali as Against Small Quantities of Unsaponified Oil Under Quartz Lamp

Hours	0	2	5	9 with lamp 48 without	14 with 48 without	20 with 72 without	24 with 96 without	30 with 120 without	35 with 120 without
P. V. Marseilles type plus 0.1% free alk.	0.8	10.5	26	36	80	81	100	130	135
Same, plus 0.4% free alk.	0.3	6.2	19	38	56	66	88	90	120*
Same, plus 2% unsap. oil	0.0	12.6	42	64	120	120	136	152	170

*Still containing 0.09% free alkali.

TABLE 11

Peroxide Value and Gradual Neutralization of Free Alkali Under Quartz Lamp

Hours	0	2	4	6 with lamp 12 without	9 with 12 without	14 with 12 without
P. V. Milled soap containing olive oil	0.0	8.0	16.5	28	51	60
F. A. Milled soap containing olive oil	0.04%	0.03%	0.03%	....	neutral	neutral
P. V. Milled soap	1.0	15.0	27.5	29	56	55
F. A. Milled soap	0.07%	0.04%	....	neutral	sl. acid	....
P. V. Marseilles type	0.4	13.2	28.0	35	72	84
F. A. Marseilles type	0.06%	0.04%	0.03%	neutral	neutral	sl. acid

TABLE 13

Influence of Known Antioxidants, Marseilles Type Soap, 0.7 P. V. Before Drying, Mixed With 0.5% Antioxidant and Dried Under 200-Watt Lamp for 48 Hours

Under quartz lamp

Hours	0	2½	5	11	15	24
Marseilles type soap, dried as above, without antioxidant	15.0	25.0	46	80.0	112	160
Same, $Na_2S_2O_3$	13.5	30.0	47	57.5	95	145
Same, $SnCl_2$	17.0	22.0	44	72.0	135	190
Same, sodium benzoate	16.0	26.0	45	72.0	105	150
Same, hydroquinone	5.5	5.5	10	22.0	25	50
Same. $Al_2(So_4)_3$	35.0	50.0	58	92.0	115	122

NOTE: Hydroquinone darkens the soap considerably at once after admixture. Aluminum sulphate was tried because it had been mentioned in literature as an antioxidant, but this was against our own judgment.

Under 200-watt lamp

Hours	48	300
Without antioxidant	14	90
$Na_2S_2O_3$	14	95
$SnCl_2$	17	87
Sodium benzoate	24	83
Hydroquinone	3	42
$Al_2(So_4)_3$	38	88

Summary

1. A direct method for quantitative estimation of peroxide content in dry and hydrated soaps and cosmetics is proposed.

2. Different methods of exposing the samples are discussed.

3. Soaps of different kinds are compared under similar conditions.

4. Development of peroxides in soaps is compared with their respective oils.

5. The influence of free alkali and unsaponified fatty matter is considered.

6. The influence of some chemicals mentioned in literature as antioxidants is tested.

7. We do not consider this experimental series as final, and further utilization of the proposed methods for the investigation of the factors mentioned in this paper and other factors influencing soap is to be made.

Catalytic Effect of Metals and Light on Fats and Oils[*]

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THE pro-oxidant effect of certain metals upon vegetable oils and fats has been known for many years, but the available information has been scattered and as a rule has been too incomplete to be of much help to the edible oil industry (1-8). The information presented in this paper was collected from laboratory data accumulated during studies upon the effect of the deodorizing process upon the keeping quality of hydrogenated vegetable oils. Steam deodorization, because of its place in the sequence of operations, as well as the relatively high temperatures employed, is one of the most critical steps in the quality processing of edible oils and shortenings. In most shortening plants it is the last processing operation before the product is packaged. At this point, not only the organoleptic properties but also the keeping qualities of the fat may be seriously impaired.

Before we can enter into any discussion of the experimental data, it is essential to state the method used in evaluating the keeping quality of the variously treated samples. For reasons of convenience and expedience an accelerated oxygen absorption test was used to measure oxygen absorption under standardized conditions for a definite period. The oxidized sample was titrated with 0.002N thiosulphate and the numerical values obtained expressed as millimoles of active oxygen per kilogram of fat. Under the specific conditions of this test most hydrogenated oils become rancid when a peroxide value of approximately 25 is reached.

The majority of the tests were carried out with hydrogenated cottonseed oil of a consistency suitable for an all-hydrogenated vegetable oil shortening. Various other oils have been subjected to tests of a more limited scope.

Table I shows the data obtained by deodorizing a hydrogenated cottonseed oil blend of 70 iodine value in the presence of various metals. Whenever possible, the metals were obtained as lathe turnings or approximately 10-mesh granules. In no case was a metal used in powder form as such practice might lead to erroneous results due to disproportionate surface effects and adsorption phenomena. Deodorizations were carried out at the indicated temperatures at an absolute pressure of 4-6 mm. Hg for a five-hour period, using 20% super-heated steam. Results of the previously defined oxygen absorption test are given for each sample before and after deodorization in pyrex glass, and also in the presence of the various metals.

Among the metals tested aluminum and nickel were the only ones found to be absolutely free of any pro-oxidant effect on the fat. Lead, manganese, copper, cobalt, and iron were the worst offenders, these

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[*] Presented at the Conference on Problems Related to Fat Deterioration in Foods, under auspices of the Committee on Food Research, Research and Development Branch, Military Planning Division, Office of the Quartermaster General in Washington, D. C., on June 20, 1945.