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, Na₂S₂O₃	13.5	30.0	47	57.5	95	145
Same, SnCl₂	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, Al₂(So₄)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
Na₂S₂O₃	14	95
SnCl₂	17	87
Sodium benzoate	24	83
Hydroquinone	3	42
Al₂(So₄)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

TABLE I.

Effect of Various Metals and Alloys Present During Deodorization.

Hydrogenated CSO Blend	Deodorization Temperature °C.	Metals		Peroxide Number After Acc. Test
		Amount	Type	
No. 1	......[1]		......[2]	10.6
No. 1	205		......[2]	9.5
No. 1	205	1%	Aluminum	8.7
No. 1	205	5%	Nickel	9.1
No. 1	205	5%	Tantalum	12.6
No. 1	205	5%	Tin	15.6
No. 1	205	5%	Chromium	27.3
No. 1	205	5%	Iron	36.4
No. 1	205	5%	Cobalt	37.9
No. 1	205	1%	Copper	45.9
No. 1	205	5%	Manganese	60.1
No. 1	205	5%	Lead	99.6
No. 1	205	1%	Inconel	17.5
No. 1	205	1%	Rezistal	20.0
No. 1	205	1%	18-8-3	27.0
No. 1	205	1%	18-8	43.2
No. 1	205	1%	Monel	51.1

Composition of Alloys

Alloy	Source	Fe	Ni	Cr	Cu	Mo	C
18-8	U. S. Steel Co.	74	7-9	7-19			.08-.2
18-8-3	U. S. Steel Co.	71	7-9	7-19		3	.08-.2
Rezistal	Crucible Steel Co.	68	21-25	7-10	1-1.5		.25
Monel	Int. Nickel Co.	1.5	68		28		.2
Inconel	Int. Nickel Co.	7.0	79	13	.2		.08

Boiler-Plate Steel

S	P	Mn	C	Fe
Less than .03	Less than .03	.34-.60	.08-.18	99-99.5

[1]Before deodorization.
[2]Glass blank

results falling in line with various other published data and also with the fact that some of these metals are commercially used as paint driers. Inconel and rezistal were the best of the alloys tested while monel was the poorest, probably because of its high copper content.

Although this information is interesting from a theoretical point of view, it is hardly complete enough to apply in a practical way to commercial equipment used in the edible oil industry. The cheapest, and consequently most widely used, material for oil processing-equipment is boiler-plate steel. Boiler-plate steel, sometimes known as "mild steel," is still universally employed for equipment designed to handle edible oils of low free-fatty-acid content. Table II shows some data regarding the behavior of two samples of boiler-plate steel as well as two of the most common stainless steels, 18-8 and 18-8-3, at temperatures of 180-230°C.

As may be seen from the data, there is a distinct decrease in keeping quality of the oil deodorized in glass as the temperature approaches 230°C., the highest temperature used. This is due either to destruction of the natural antioxidants or to pyrolytic breakdown of the fat itself. The pro-oxidant effect of the metals increases with the temperature. The critical temperatures vary with the individual samples of metals, probably due to such factors as crystalline structure, previous treatment, method of cleaning, etc. In practical deodorization operation these critical temperatures can usually be exceeded without impairing the quality too much because the equipment becomes conditioned by constant use and acquires a protective film of heat-bodied oil.

All previously described experimental data have been confined to hydrogenated cottonseed oil blends of approximately 70 iodine value. Consequently, a number of other common vegetable oils and fats were

tested and found about equally susceptible to the pro-oxidant effect of iron (Table III).

The mechanism of the catalytic pro-oxidant action of metals is not entirely clear at this date. While the preponderance of evidence points to metallic soaps as the most active catalyzers, inorganic metal salts are also very active. This, however, does not preclude the possibility that they may merely be an intermediary and that the actual formation of metallic soaps is essential for the oxidation to proceed at accelerated rates. Iron soap, in concentrations as low as 0.3 ppm, will materially decrease the keeping quality of a shortening with an original iron content of 0.3 ppm, the constitution of which is unknown.

In recapitulating, it may be stated that at the specific conditions described—

1. All metals tested, with exception of aluminum and nickel, exert some catalytic pro-oxidative effect on various fats and oils of a consistency and purity suitable for shortenings.
2. The metal effect as a rule becomes more noticeable with increasing temperatures.
3. As a mechanism, the formation of metallic soap is suggested by the interaction of the metal and the free fatty acid.

TABLE II.

Effect of Deodorizing Temperature on Pro-Oxidant Effect of Boiler-Plate Steel, 18-8, and 18-8-3 Stainless Steels.

Hydrogenated CSO Blend	Deodorization Temperature °C.	Metal Amount—Type	Peroxide Number After Acc. Test
No. 2	......[1]		17.1
No. 2	180	Glass Blank	16.6
No. 2	205	Glass Blank	17.4
No. 2	230	Glass Blank	25.2
No. 2	180	1% Boiler-Plate Steel No. 1	21.8
No. 2	188	1% Boiler-Plate Steel No. 1	23.2
No. 2	194	1% Boiler-Plate Steel No. 1	45.0
No. 2	196	1% Boiler-Plate Steel No. 1	51.3
No. 2	205	1% Boiler-Plate Steel No. 1	49.3
No. 2	230	1% Boiler-Plate Steel No. 1	50.7
No. 3	......[1]		12.9
No. 3	180	Glass Blank	13.8
No. 3	150	1% Boiler-Plate Steel No. 2	13.5
No. 3	160	1% Boiler-Plate Steel No. 2	16.3
No. 3	170	1% Boiler-Plate Steel No. 2	17.6
No. 3	180	1% Boiler-Plate Steel No. 2	44.9
No. 3	188	1% Boiler-Plate Steel No. 2	45.0
No. 4	......[1]		16.8
No. 4	180	Glass Blank	17.8
No. 4	205	Glass Blank	18.9
No. 4	230	Glass Blank	23.8
No. 4	180	1% 18-8-3 Stainless Steel	26.1
No. 4	205	1% 18-8-3 Stainless Steel	32.5
No. 4	230	1% 18-8-3 Stainless Steel	40.5
No. 4	180	1% 18-8 Stainless Steel	40.5
No. 4	205	1% 18-8 Stainless Steel	40.7
No. 4	230	1% 18-8 Stainless Steel	50.0

[1]Before deodorization.

II. The Effect of Light of Varying Wave Lengths

In a discussion of the effect of light of varying wave lengths upon fats and oils some generalizations are allowable, based upon a considerable amount of investigation in this field in recent years. According to the Grotthus-Draper Absorption Law, only light which is absorbed in the experimental medium can produce chemical changes.

Chemical changes in fats and oils can take two principal courses, (a) by affecting the peroxide formation and hence, the induction period of the oil, and (b) by altering the odor and flavor characteristics in a manner somewhat unlike that caused by rancidity development.

Experimental work by Greenbank and Holm (9), Coe and LeClerc (10), have shown that with light waves shorter than 540 millimicrons the absorption and the amounts of peroxides formed increased progressively with decrease of wave lengths. The magnitude of these decreases varied with the type of oil. Thus lard, with somewhat greater light absorption throughout more of the visible spectrum, produced less peroxides than unhydrogenated cottonseed oil when subjected to the same conditions. Butter oil under these conditions showed very little peroxide formation. It is reasoned that the rate of oxidation of the unsaturates was the same but that the degree of oxidation varied inversely with the iodine value of the oils. No evidence other than the formation of peroxides attested to the rate of destruction of the antioxidants.

In unhydrogenated refined oils the development of organoleptic rancidity has for the most part coincided with the peroxide formation and precluded observation of changes in odor and flavor attributable to other causes. However, in cases where the oils are protected from absorption of light of 500 millimicrons and below [Coe and LeClerc (10)], the peroxide development has at least equaled that of unprotected samples without development of rancidity. These latter unprotected samples developed a rancid odor.

Vegetable shortenings properly aerated and chilled absorb less visible light than do refined vegetable oils. Gudheim (11) has shown the absorption for shortening to be only 10% of the light between 400 and 675 millimicrons whereas refined oil absorbed about 75%.

Although the chilled shortening exhibited this wide difference in absorption, its absorption in the liquid state was in like manner somewhat less than that of the refined oil.

Tests simulating practical conditions were made by exposing ordinary glass jars of aerated shortening to daylight of three intensities, namely, 250, 50, and 5-10 foot-candles, the last representative of average store light.

Samples from each of these three sets were examined at weekly intervals, and the peroxide values of those stored at the two lower light intensities showed no change even after many weeks. The peroxide value (millimoles of oxygen per kilogram of fat) of the specimens kept at the high intensity was only 1.5 after 10 weeks' time. From an oxidation standpoint even this value is insignificant and very much less than those reported as being obtained for oils.

The odor and flavor of the samples stored at the lowest intensity remained substantially unaffected for the 10-week period and the ones kept at 50 foot-candles showed only a slight change. The specimens exposed to the highest intensity, however, exhibited a flavor and odor change after only a few weeks, and these were very pronounced at the expiration of the 10-week period.

This flavor and odor was quite characteristic and was by no means reminiscent of rancid fat as most of us know it. The failure to develop peroxides, even at the higher light intensities, indicates that indoor light has practically no influence on the oxidation of "white" shortenings in glass jars.

Gudheim (11) then proceeded to develop an accelerated-light testing-machine having about the same

TABLE III.
Comparison of Other Vegetable Oils.

Oil	I. V.	Peroxide Number[1] Before Deodorization	Peroxide Number[1] After Deodorization at 205°C. in Presence of 1% Steel
Cottonseed Oil	67.5	10.3	19.6
Cottonseed Oil	69.9	16.3	34.3
Palm Oil	44.5	8.2	14.4
Peanut Oil	65.1	2.0	9.5
Sesame Oil	62.3	.4	4.2
Soybean Oil	78.5	10.4	22.0
Coconut Oil	9.2	.8	2.7

[1]Accelerated oxygen test.

spectral energy distribution properties as daylight, at least down to 325 millimicrons.

Tests were carried out with this machine on shortenings in commercial one-pound metal-capped unlabeled jars by completely surrounding the jars with different sets of Corning Filters.

Each set of filters had different cut-off points, the first screening out all the light below about 380 millimicrons, the second below 420, and so on up to 590 millimicrons.

The samples surrounded by the first two sets of filters, that is, those cutting out below 380 and 420 millimicrons, had developed a noticeable flavor and odor change after about 200 hours, whereas the ones protected by the filters cutting out below about 460, 530, and 590 millimicrons showed little change. None of these samples, however, developed peroxide values higher than about 1.5.

These results indicate: (a) that the portion of the spectrum between 325 and 460 millimicrons is largely responsible for the flavor and odor change induced by strong light and (b) that light above 460 has comparatively little influence. Likewise, light below 325 millimicrons probably has a marked effect, but, as has been mentioned, from a commercial standpoint we are not concerned with radiation below this wave length.

In view of the low absorption and high reflectance properties of "white" shortenings in the visible range, it is not surprising, however, to find that even very strong light above 460 millimicrons has comparatively little influence on the flavor or odor.

Homogenized vegetable-oil shortenings have one reaction to light which is also common to refined unhydrogenated oils, namely, that the chemical effect of visible light is small compared with the effect of ultraviolet (12). This chemical effect varies, however, in that with refined oils the peroxide formation and rancidity development is rapid. In shortenings, light between 325 and 500 millimicrons is more effective than longer wave lengths in promoting odor and flavor changes but has no significant effect on the peroxide development.

It would be of interest but of doubtful practical value to investigate by actual analysis the destruction of antioxidants in unhydrogenated refined oils caused by light of varying wave lengths. It might be reasoned from work by Coe and LeClerc (10) that light has no effect upon their rate of destruction. Certainly, this latter conclusion could result from the work by Gudheim (11) in the case of "white" shortenings.

Much more important to the manufacturer and to the consumer is the organoleptic alteration of different oils and fats not attributable to rancidity. Methods are known for inhibiting the effect, but much work remains to establish the reason for and the absolute means of overcoming it.

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Typha (Cattail) Seed Oil

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TYPHA is an ancient name for plants of the cattail or Reed Mace family (Typhaceae). Cattails are well known throughout North America, Europe, and Asia. About 17 different species are known, two of which are fairly common in the United States. They are Typha latifolia Linn, which is the common cattail growing in marshlands throughout the temperate regions of North America, and Typha angustifolia Linn, which occurs less frequently and is found mainly in the eastern coastal area. These two species may be distinguished from each other by the difference in width and shape of their leaves. T. latifolia has leaves ¾ to 1 inch broad while T. angustifolia has narrow leaves, ¼ to ½ inch wide, that are somewhat convex on the back. Typha angustata Linn is a species of cattail well known in the Orient, called "Pu-hwang."

Typha seeds are light brown in color and are very small, being approximately ¼ to ½ mm. thick and 1 to 1½ mm. long, tapering to a point at each end.

Composition of Seed and Oil

In view of the fact that considerable amounts of Typha seeds accumulate as a result of the use of cattail head fibers in industry, investigations regarding possible uses of the seed have been undertaken at this laboratory and elsewhere.

A review of the literature revealed two reports of work on Typha seed oil, both in Japanese journals (1, 2). Kimura (1) found seeds of the species T. angustata to contain 10% oil and reported palmitic and stearic acids. He also reported a typhasterol in the unsaponifiable matter. Later Sinozaki and Takumi (2) reported a number of characteristics of T. angustata seed oil as shown in Table I. They claim to have obtained 20% of oil from seeds of T. angustata.

Data collected as a result of studies at this laboratory on the oil extracted from seeds of T. latifolia are reported in Table I. The oil content of these seeds,[2] determined by petroleum ether extraction, was found to be 17.9% by weight.

Production

According to recent surveys, approximately 500,000,000 pounds of cattails, not including stems, are available annually in the United States.

Cattail processing plants, with a capacity to handle in excess of 1,500,000 pounds of raw material annually, are being operated in Minnesota and Wisconsin. The fluffy, fibrous portion of the cattail head has been found suitable for use in the manufacture of numerous insulation and shock absorption materials. The seeds account for 35 to 40% of the total weight. With present capacity 600,000 pounds of seed are produced annually, with a possible yield of about 100,000 pounds of oil.

TABLE I.
Composition and Properties of Typha Seed Oil

Characteristics	T. angustata (Sinozaki and Takumi)	T. latifolia	
		Oil	Acids
Density	0.9256²⁵°/¹⁵°		
Refractive index	1.4740²⁵°	1.4730²⁹·⁵°	
Acid number		30.7	
Saponification value	193.96	186.0	
Iodine value	130.8	141.6¹	143.8¹
Acetyl value		10.8	
Reichert-Meissl value	0.22		
Polenske value	0.42		
Unsaponifiable matter, %	3.64	2.52²	
Thiocyanogen value		79.8³	81.6³
Linoleic acid, % (by isomerization)		69.2⁴	69.6⁴
Linolenic acid, % (by isomerization)		0.12⁴	0.20⁴
Linoleic acid, % (by CNS analysis)		69.5³	73.6³
Oleic acid, % (by CNS analysis)		14.2³	11.6³
Saturated acids + unsaponifiable, % (from CNS analysis by difference)		12.0	14.8

[1] A.O.C.S. 30-minute Wijs.
[2] A.O.C.S. procedure.
[3] A.O.C.S. 24-hour, 0.2 N(CNS)₂ solution.
[4] Quantitative Spectral Analysis of Fats. J. H. Mitchell, Jr., H. R. Kraybill, and F. P. Zscheile, Ind. Eng. Chem. Anal. Ed. 15, 1, 1943.

Analysis of Typha seed revealed the following percentage composition:

ANALYSIS OF TYPHA SEED*

Components	Percentage by weight
Moisture and volatile matter at 100° C	9.0
Crude protein (N x 6.25)	19.8
Crude fat	17.2
Ash	3.5
Crude fiber	15.5
Nitrogen-free extract	35.0
Total carbohydrates	50.5

*Data submitted by Mr. Harold Hamley, Burgess-Manning Company, Chicago, Illinois.