leate. The difference between the total peroxides and hydroperoxide is 14.6% while that for the more highly purified methyl oleate preparation at the same temperature is only 7%. Samples of these two preparations differed primarily in methyl linoleate content but were handled in the same manner.

The nature and manner of formation of the non-hydroperoxide portion of methyl oleate peroxides is still not known. Swern and co-workers (9) have suggested that the non-hydroperoxide portion is probably cyclic, at least in part. Several of their oxidized methyl oleate samples contained significant proportions of non-hydroperoxides among the total peroxidic compounds. In one sample oxidized at 100° in the presence of ultraviolet to a peroxide content of 28.6%, as much as 28% of the total peroxide was not hydroperoxide.

The question of why the proportion of non-hydroperoxides among the total peroxidic compounds varies for different autoxidized methyl oleate preparations still remains unanswered. Comparison of the results obtained by us with the two methyl oleate preparations (A) and (B) suggests the possibility that the same impurities which shorten the induction period and accelerate the autoxidation also contribute to the complexity of the total peroxides formed. Further investigation is indicated.

Summary

Methyl oleate has been autoxidized at 100°, 80°, and 60° in the Barcroft-Warburg apparatus. Samples have been analyzed for total peroxide by the iodometric method and for hydroperoxide by the polarographic method. These peroxide values have been compared with each other and with total oxygen absorbed.

The relation of chemical peroxide (y_c) to oxygen uptake (x) is expressed by $y_c = 1.09x^{0.936}$. This equation is equally valid at the three temperatures for the first 150 millimoles (15%) of oxygen absorbed per mole of methyl oleate.

Similarly, the hydroperoxide content (y_h) for the first 150 millimoles of oxygen absorbed at 80° and 100° is given by the equation $y_h = 1.02x^{0.936}$.

The ratio of hydroperoxide to chemically determined peroxide was, on the whole, constant throughout the entire range of oxidation (15-300 millimoles of oxygen absorbed per mole), and averaged about 95%.

It has been shown unequivocally that the major portion of the peroxides formed in the autoxidation of methyl oleate are hydroperoxides, confirming conclusions of recent investigators. A small but significant amount of non-hydroperoxidic peroxide appears to be formed concurrently.

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The Effect of Polyunsaturation in Hot-Dip Tinning Oils

W. L. KUBIE and E. E. WERLE, Darling and Company, Chicago, Illinois

FIGURE 1 is a diagram of a hot-dip tin pot. The sheets of the pickled steel are passed by means of rolls through a flux box into a bath of molten tin at 600°F. The sheet is then carried up through about 18 to 20 in. of oil kept at 460°-465°F., where the rolls and brushes on rolls control the thickness of the tin coating. After passing through the oil, the molten tin on the sheet is solidified by a stream of low pressure air, and then the sheet is conveyed to the wet washer containing a sodium carbonate solution. The plate is finally polished in a branner, where excess oil is removed and the residual oil is spread uniformly over the plate. This residual oil amounts to only 0.1-0.4 g. per base box. (A base box is the tin plate industry's unit of area measurement and is equal to 31,360 sq. in. of tin plate. Since the plate is coated on both sides, a base box has 62,720 sq. in. of tinned surface. It contains approximately 100 lbs. of steel.)

In 1950 Ference *et al.* (1) published a theory on the tinning action of palm oil and showed that the activity was due to the dispersing action of the carboxyl group of the fatty acid on the tin oxide and the shearing action between the tin oxide and the molten tin.

In 1953 Fochtman *et al.* of the Armour Research Foundation, and Riemenschneider *et al.* (2), of the Eastern Regional Research Laboratory, reported that a mill test using refined, selectively hardened, and deodorized choice white grease containing 1% polyunsaturated acids had proved unusually successful.

In 1943 Bauer *et al.* (3) suggested that unsaturation may be harmful, owing to the increased possibilities of polymerization, and advocated the use of cottonseed oil selectively hardened to an iodine value of 50 with a linoleic acid content of below 2%.

The present paper indicates that the undesirable unsaturation is the polyunsaturation and that the mono-unsaturation is only required to the extent that it keeps the melting point of the fat in a range which makes it easy to remove in subsequent operations and soft enough not to clog feed lines and sewers or freeze the stacks of tin plate at relatively low temperatures.

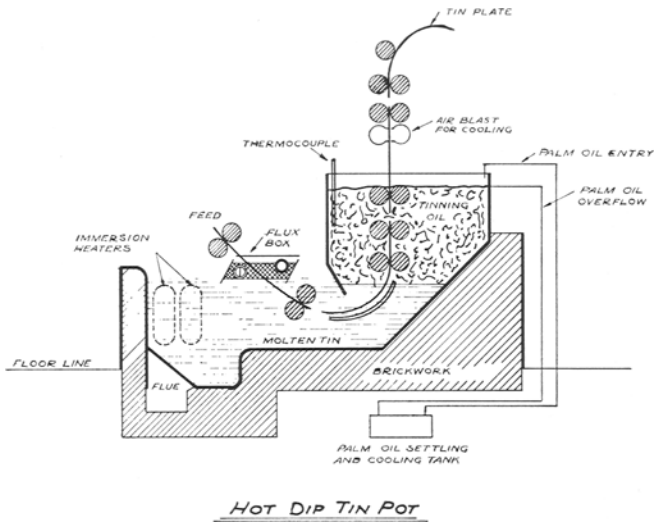

FIG. 1. Diagram of a hot-dip tin pot.

Theory

In the tin pot the following conditions conducive to polymerization are maintained.

Temperatures. High temperatures in the neighborhood of 465°F. are necessary. Below 455°F. the tin begins to solidify too rapidly on the plate. The rolls cannot remove the excess tin, and since the tin oxide cannot shear from the tin, the "oil break" does not take place. Above 470°F. a yellow stain may be formed on the plate.

Pressure. High pressures exist on the oil films between the rolls and plate. These pressures tend to polymerize any polyunsaturated materials directly on the plate, where it is least desirable.

Oxygen. Oxygen is a known catalyst for the polymerization of polyunsaturated compounds. It is also required in hot-dip tinning as the oil break will not take place in an inert atmosphere because the tin oxide formation on the surface of the tin must take place.

Metal Soaps. Metal soaps of tin, zinc, and iron are present in significant amounts. The soaps of other metals, such as manganese, chromium, and cobalt could be present in relatively small amounts. The catalytic effect of metal soaps on polymerization is well known. Some are even used as driers in paints.

Polyunsaturation. When palm oil is used, there is present under the above conditions as much as 10% of polyunsaturated acids.

Analyses of Virgin and Spent Palm Oil

Trevithick and Lauro (4) in 1932 reported analyses of virgin palm oil and spent palm oil from hot-dip tinning pots. The only sample the authors have found which had an acid content of 50%, similar to the spent oil reported by Trevithick, was a sample of condensed material taken from the walls of the cooling reservoir. Also it is hard to conceive how a sample of oil from a pot at 465°F. could have moisture and volatile matter as high as the 23% reported.

The analyses of three samples of palm oil, A, B, and C, and spent palm oil C, taken during this investigation, are shown in Table I.

As palm oil is used for hot-dip tinning, the following changes take place in the analyses:

TABLE I

Material	Palm oil			Spent C
Sample	A	B	C	
Color F. A. C.	39	19	21	Black
Acid, % (as oleic)	15.6	18.9	7.2	11.0
Moisture, %	0.25	0.10	.....	.....
Ash, %	0.04	0.00	0.5	1.11
Insoluble impurities, %	.....	0.04	0.02	0.05
Titre, °C.	46.8	47.1	46.0	43.1
Saponification number	198.8	199.2	203.2	183.9
Unsaponifiable, %	0.36	0.42	0.24	2.35
Iodine value	51.2	51.0	48.5	45.4
Viscosity S. S. U. at 210°F.	.....	.....	47	144
Total polyunsaturated acids, %	9.64	9.37	7.39	6.24[a]

[a] This value is probably not correct because of interference from color bodies. It does however represent the maximum which can be there.

1. At the spent stage the acid is usually higher than the original, from a fraction to 3 or 4%.
2. The iodine value drops, as much as 7 points.
3. The ash becomes appreciable; as much as 3% has been found.
4. The saponification value drops as much as 20 points.
5. The unsaponifiable percentage becomes appreciable but not great enough to account for the drop in the saponification value. We noted about 2% increase.
6. The viscosity increases; in some cases it was tripled.
7. The polyunsaturated acids definitely decrease.

The data of Bauer and Markley (3) also show the same changes except for ash, unsaponifiable and polyunsaturated acids, which are not reported.

Table II shows the analyses of five samples of reclaimed palm oil. Samples marked A to D are from the same processor and E from a different one. The reclaimed oils all have lower iodine values and polyunsaturated acid contents than virgin palm oil.

TABLE II

Material	Reclaimed Palm Oil					
Sample	A	B	C	D	E	F
Color F. A. C.	13	13	13	13	Dark	Black
Acid (as oleic), %	8.0	5.7	10.9	8.3	14.4	6.5
Moisture, %	1.00	0.05	0.21	.....	0.07	.....
Ash, %	0.03	0.00	0.00	0.07	0.00	1.60
Insoluble impurities	.....	0.01	0.02	0.01	0.00	0.13
Titre, °C.	44.7	44.4	44.0	44.7	45.8	44.6
Saponification No.	197.3	195.9	193.6	197.6	198.9	176.9
Unsaponifiable, %	0.62	1.27	1.32	0.91	1.39	1.75
Iodine value	45.7	48.6	48.0	44.5	43.0	42.8
Viscosity S.S.U. at 210°F.	.....	.....	.....	56	.....	84
Polyunsaturated acids, %	5.85	7.50	6.33	6.61	4.66	4.17

Sample F is used reclaimed Palm Oil D. The reclaimed palm oil is changed in the same directions as the original palm oil.

Table III shows the analyses of refined, hardened, and deodorized tallow as well as two samples of this material after long use, but not spent.

TABLE III

Material	Low Polyunsaturated Tallow		
Sample	Unused	Used (6 mos.)	Used (7 mos.)
Color F. A. C.	3	Black	Black
Acid, % (as oleic)	9.0	12.1	12.2
Moisture, %	0.05	.....	.....
Ash, %	0.00	3.35	2.50
Insoluble impurities, %	0.00	0.01	0.03
Titre, °C.	43.0	42.6	43.4
Saponification No.	197.2	184.8	189.0
Unsaponifiable, %	0.50	2.03	2.70
Iodine value	47.0	45.6	45.7
Viscosity S. S. U. at 210°F.	55	82	86
Polyunsaturated acids, %	1.28	3.49[a]	3.82[a]

[a] These figures are probably caused by color bodies, but they indicate approximately how much too high are the previous figures obtained by the same spectrophotometric method.

Plant Results

Sludge. During the drossing of tin stacks, sludge was removed and weighed from stacks on palm oil and on low polyunsaturated tallow. The results are shown in the following Table IV.

TABLE IV
Sludge Yield

Oil	Sludge, lbs.	Original polyunsaturated acids (%)
Palm	253	9.5
Low polyunsaturated tallow	35	1.3
Ratio	7.23	7.31

It appears significant that the sludge is directly proportional to the polyunsaturated acid content of the oils.

Consumption. Figure 2 shows the consumption of tinning oil per base box at two different tinning mills. It is to be noted that consumption increases with increasing polyunsaturation and that the curves for the two mills are parallel. The reason for the higher consumption in the second mill is due to a different mode of operation.

Factors that contribute to different consumptions are higher rate of formation of free fatty acids, maintenance of a lower level of viscosity, and greater speed of plate travel through the stack.

Ference and Johnson (5) report results which are similar to three of the points shown above for the first mill.

Prime Plate Yield. One of the mills kept accurate records of the prime plate produced during the experiments. The low polyunsaturated tallow resulted in an increase of over 5% in prime plate yield over the results with palm oil. Both mills stated that the tallow (low polyunsaturates) plate was definitely brighter.

Conjugation. In regard to conjugation it was found that reclaimed or spent oil which appeared to have a large conjugated diene content according to the official spectrophotometric method would not make good plate because of oil staining. However it was found that color which had been formed was interfering with the conjugated diene determination. Therefore the true conjugated diene content was unknown.

Summary

1. A theory was outlined, which predicts that low polyunsaturation should result in better tin plate at lower oil consumption.

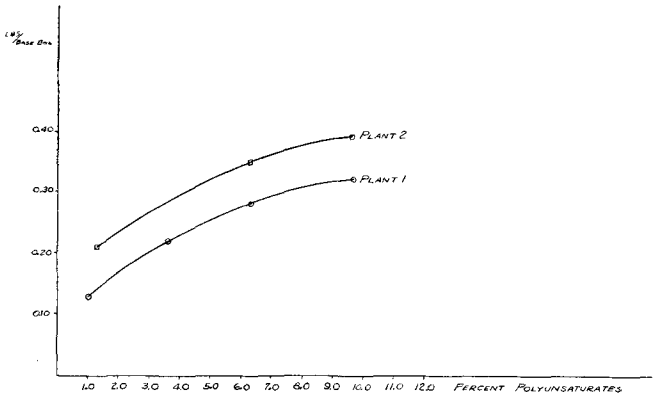

FIG. 2. Consumption of tinning oil per base box at two different tinning mills.

2. It has been shown that low polyunsaturation results in lower oil consumption in actual mill tests.

3. The percentage of prime plate is higher for lower polyunsaturation.

4. It has been demonstrated that percentage of polyunsaturation is lower in spent oils than in the original, indicating preferential reactivity of this fraction.

5. By actual mill test it has been shown that the percentage of sludge increases with the percentage of polyunsaturation in the original oil.

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Color Characteristics and Chemical Analyses of Oil from Frost- and Weather-Damaged Soybeans[1]

DUNCAN MACMILLAN and EUGENE H. MELVIN, Northern Utilization Research Branch,[2] Peoria, Illinois

IN an earlier paper (1) some spectrophotometric methods for grading green soybean oil were presented. These methods were based on measurements made on oil which had been extracted from soybeans of two varieties, grown in different fields and artificially frozen at several stages of ripeness. To make the methods more generally applicable, naturally frost-damaged soybeans from commercial sources were sought. Inquiries to several producers brought suitable samples of frost-damaged soybeans, and two cans of green oil. Localities represented in this group

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[2]One of the Branches of the Agricultural Research Service, U. S. Department of Agriculture.