When a mixture of technical monoglycerides was partially crystallized from a solvent, the composition of the glycerides remaining in the solvent was relatively unaffected by changes in the concentration of the glycerides originally present in the solution.

REFERENCES

1. Arrowsmith, C. J., and Ross, J., U. S. Pats. 2,383,580-1 (1945).
2. Christensen, C. W. (to Armour & Co.), U. S. Pat. 2,022,493 (1935).
3. Edeler, A., and Richardson, A. S. (to Procter & Gamble Co.), Can. Pats. 340,803-5 (1934).
4. Feuge, R. O. and Bailey, A. E., Oil & Soap, *23*, 259-264 (1946).
5. Grün, A., in Chemie und Technologie der Fette und Fettprodukte, edited by H. Schönfeld; Springer, Vienna, 1936, Vol. I, pp. 276-278.
6. Handschumacher, H., and Linteris, L., J. Am. Oil Chem. Soc., *24*, 143-145 (1947).
7. Kawai, S., J. Soc. Chem. Ind. Japan, Suppl. Bind., *43*, 220-221B (1940).
8. Ross, J., Bell, A. C., Arrowsmith, C. J., and Gebhart, A. I., Oil & Soap, *23*, 257-259 (1946).
9. Weaver, E. R., J. Am. Chem. Soc., *36*, 2462-2468 (1914).

[Received December 16, 1949]

Palm Oil Substitutes for Hot Dip Tinning[1]

GEORGE G. FERENCE, W. R. JOHNSON, L. C. KINNEY, and JOHN M. PARKS, Armour Research Foundation of Illinois Institute of Technology, Chicago, Illinois

THE steel industry of the United States consumes annually appreciable quantities of palm oil, about 7,500 tons, in making hot dip tin plate. Over a period of years the price has fluctuated considerably, for example, rising from 3½c a pound before World War II to as high as 40c. Furthermore the quality of oil has been uncertain; it has contained variable amounts of water and foreign matter and has been received in various degrees of rancidity. In addition, all this oil is now imported over long shipping routes such that the United States is in a strategically unfavorable position should an emergency arise which might imperil shipping lanes. In view of these factors a study of palm oil substitutes was instigated at the Armour Research Foundation of Illinois Institute of Technology under the sponsorship of the American Iron and Steel Institute.

Requirements of a Tinning Oil

In the making of hot dipped tin plate, sheets of pickled steel are passed by means of rolls through a flux into a bath of molten tin and up through an 18-inch layer of hot (460°F.) palm oil floating on the tin. Three sets of rolls, operating in the oil, smooth and thin the tin coating (Fig. 1).

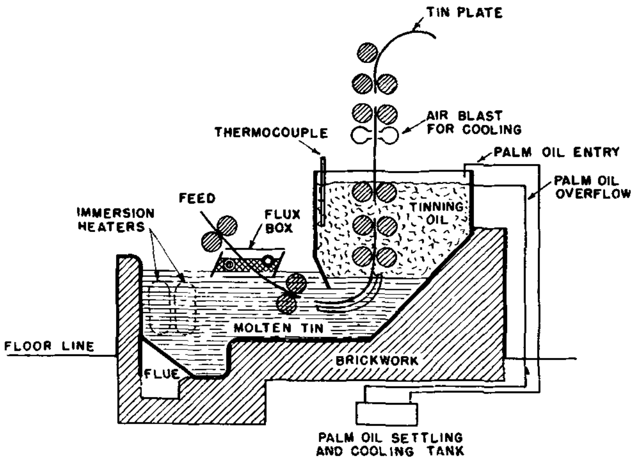

FIG. 1. Diagram of hot dip tin pot.

In order that an oil may operate properly in a tin pot, it should possess at least the following characteristics:

1. It should make smooth, bright, good quality tin plate.
2. It should drain rapidly and freely from the sheet.
3. It should be of low volatility.
4. It should have high flash and fire points.
5. It should neither oxidize nor polymerize readily.
6. It should be cleaned from the sheet readily.
7. It should be of low viscosity at 100 to 200°F. so that it may be pumped or poured without difficulty.

If a thin layer of oil is allowed to remain on the sheet, this oil affects the end use of the sheet. Consequently the oil should possess the following features:

1. It should be non-toxic, odor-free, and preferably edible.
2. It should not become rancid during storage.
3. It should not interfere with lithographing or lacquering procedures.
4. It should not interfere with soldering.
5. It should retard atmospheric corrosion.
6. It should assist handling in fabrication.

Finally, the oil should meet the following important economic requirements:

1. It should be readily available, preferably from domestic sources.
2. It should be inexpensive.

Palm oil has been and is a commercially satisfactory tinning oil; it has however several deficiencies. Its flash and fire points are low enough to create a fire hazard; it is quite volatile at tin pot temperatures and tends to increase in viscosity with time at tin pot operating temperatures. A primary disadvantage is its foreign source, and the strategic and financial problems which thereby arise.

Survey of the Problem

The actual operations of making tin plate have always been more of an art than a science, with the lore of the tin house being passed from one operator to the next without ever being recorded. Much of the information on tinning oil is available only in the memories of the operators, and the important details have been closely guarded by the individual. Only comparatively recently has information been made available on tinning oils, and much of that has been from British sources. In virtually all the literature little space has been devoted to evaluating or explaining the mechanism of the tinning oil action; most of the research has been devoted principallly to simulated service tests.

A review of the information gained in interviews of tin house operators revealed the following points of agreement:

---

[1] Presented at the 23rd annual fall meeting, American Oil Chemists' Society, Chicago, Oct. 31-Nov. 2, 1949.

1. The desirable viscosity for operating palm oil should be about 90 to 100 seconds at 210°F. (Saybolt Universal).
2. New or fresh palm oil is not suitable for a tinning oil. It must be heated at pot temperature first or mixed with old palm oil.
3. Tinning oil dragout increases with higher operating speeds, lower coating weights, and rougher sheet surfaces.
4. Hydrogenated fish oil and hydrogenated cottonseed oil have been used as palm oil substitutes but have not been widely accepted.
5. There was almost no information as to why one experimental oil worked and another did not.

Most of the previous work on palm oil substitutes has been carried out on materials whose composition and properties were similar to those of palm oil. This experimental work was primarily empirical, consisting of weight loss tests and full scale production trials. There was little correlation of specific properties and compositions with the tinning action.

In this investigation it appeared desirable first to analyze the specific action of palm oil and determine which properties were important as far as the tinning action was concerned.

FIG. 2. Petri dish test.

Theory of Tinning Oils

A. MECHANISM OF THE TINNING ACTION. 1. *Activity.* After considerable observation of tin pots in operation and a large number of laboratory experiments, a theory of tinning oil action was evolved. The basic phenomenon to be explained was the rapid draining of the oil in a coherent mass from the sheet as it rises from the oil bath. The measure of this tendency of the oil to dewet from the molten tin surface and leave a bright tin area may be called its activity.

The active component of a tinning oil was found experimentally to be compounds having a carboxyl group. All materials which were active dewetting oils had a carboxyl group or decomposed with heat to yield a carboxyl group. This group has an affinity for tin oxide and a powerful dispersing action on it.

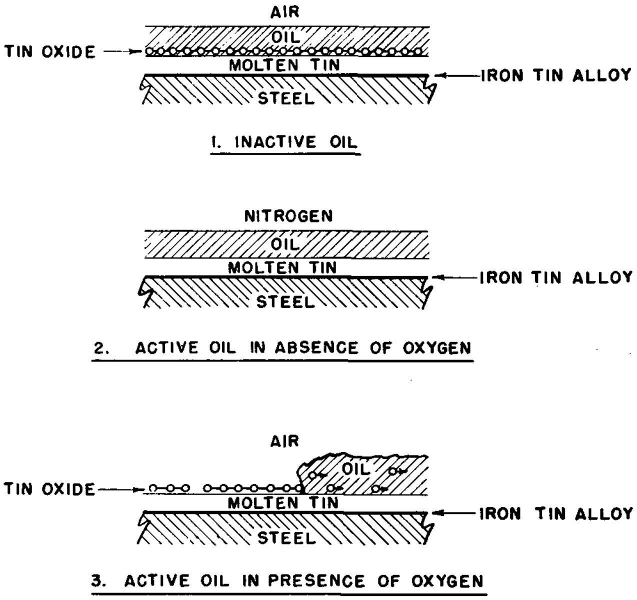

FIG. 3. Theory of dewetting petri dish tests.

If an active oil is placed on a layer of molten tin held in a petri dish and the surface of the tin briefly exposed to the air, an illustration of oil activity may be seen. As a thin film of oxide forms on the open spot of molten tin, the oil attempts to flow out across it. However the combination of the cohesive force in the main body of oil, the dispersibility of the oxide film in the oil, and the low friction between oxide and molten tin results in the film being pulled under the body of oil and dispersed, leaving a bright spot of tin which is free of oil (Fig. 2).

The action of oil attempting to run out on the oxide film which breaks and slides under it gives the appearance of a negative contact angle between oil and molten tin (Fig. 3). In spite of appearances, an active oil actually wets molten tin. If the petri dish is blanketed with nitrogen, the action gradually stops as the oxygen is displaced; the oxide film stops forming, thus permitting the oil to cover the molten tin completely. As soon as oxygen re-enters the system, the action resumes.

The dewetting action is dependent upon the formation of tin oxide. Aluminum, for example, dissolved in the tin, forms an aluminum oxide film, which has different characteristics from the tin oxide. Thus with aluminum dissolved in tin, no dewetting action occurs even with the most active tinning oils.

When the tin solidifies, the oxide film can no longer slide over the surface, and the oil covers the surface completely. The action of the oil appears to be physical rather than chemical in that the relatively stable tin oxide when on solid tin is not attacked but when on molten tin is absorbed by the oil and physically dispersed. On the other hand an inactive oil, which does not disperse the oxide, lies quiescent on the tin leaving no exposed bright area of tin (Fig. 2).

Applying the dewetting theory to hot dip tinning, the layer of oil drains from the sheet as it leaves the oil bath until the oil film is sufficiently attenuated for oxygen to diffuse through it to the molten tin. Once the oil break has started, it proceeds rapidly because the oxide film which forms instantaneously on the ex-

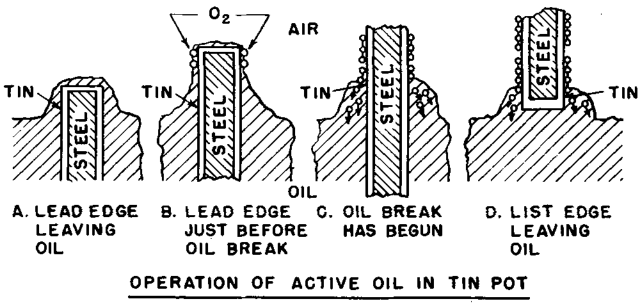

FIG. 4. Theory of dewetting tin pot.

posed molten tin slides rapidly down the sheet by the pull of the oil, thereby forming a negative contact angle between the tin and the oil (Fig. 4).

This theory is confirmed, in part, by the observation that, even with very low breaking oils in the tin pot, several inches of the lead edge of the sheet may emerge from the oil before the break occurs. The oil drainage proceeds by a tin oxide-tin shear, rather than by the shear of one oil layer over another, as is the case for drainage of an inactive oil such as mineral oil.

2. *Viscosity.* The theory on tinning oil activity presupposes that the oil will drain from the lead edge of the sheet sufficiently rapidly so that the oxygen can diffuse through and start the oil break. The operating viscosity of the oil is the major factor determining this initial drainage rate. In operation, tinning oils tend to increase in viscosity and consequently to be dragged out of the pot at increasing rates. It is common practice in the tin house to discard palm oil when its 210°F. viscosity rises above a specified control point determined by mill practice.

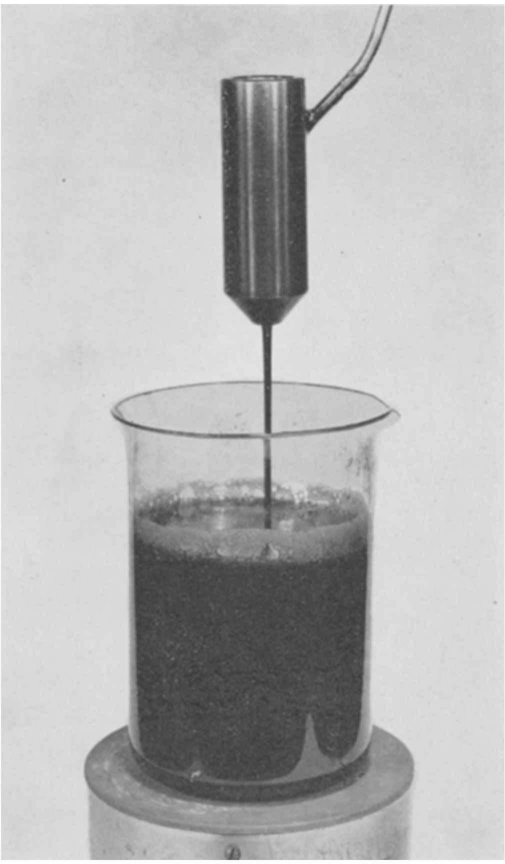

Fig. 5. Dip tester.

In an effort to separate the effects of oxidation, polymerization, and tin soap formation on heat bodying, samples of tinning oil were heated at 465°F. in the presence and absence of oxygen and tin. Results indicated that polymerization was the chief factor causing the viscosity rise.

In these experiments the need developed for a rapid means of measuring viscosity at the higher temperature (465°F.). A special dip tester, described in the appendix, was built for this purpose (Fig. 5).

B. POST TINNING FACTORS. 1. *Cleaning.* In normal tin pot operation, a quantity of the tinning oil is dragged by the sheet out of the bath into the catcher rolls. Additional oil accumulates on the rolls by condensation of the volatile products from the bath. The sheet emerging from the catcher rolls therefore carries a greater quantity of oil than can be tolerated. In most cases this is largely removed in an alkaline wet washer by a combination of emulsification and mechanical scrubbing. The remaining oil is partially removed and uniformly distributed by polishing the sheet in a branner. The low temperature viscosity and greasiness of palm oil combine to make these cleaning operations successful despite the occasional dragout of excessive amounts of oil; therefore these two properties must be inherent in any palm oil substitute.

The present cleaning procedures have been specifically developed for use with palm oil. Because of the capital investment in existing installations, a substitute oil should not necessitate extensive changes in the cleaning equipment and cleaning practice. The problem is further complicated by the fact that some mills depend entirely on the branning operation for cleaning while others wish to eliminate the branner entirely.

2. *Low Temperature Viscosity.* The viscosity of the tinning oil in the range of 100 to 200°F. is quite important not only because of the cleaning problem but also the handling problem. The oil must be pumped through lines and held in tanks; if it has a high melting point, lagging or steam jacketing of pipes—which is an expensive and troublesome operation—may be necessary.

Before processing tin plate into cans and other shapes, it is frequently stored for a few months in large stacks. This time under pressure may cause a pile of sheets to stick together, especially if the residual oil is tacky. Any sticking is highly objectionable because it prevents smooth feeding of the sheet to the can-making machines. Preferably the tinning oil should be fluid and non-tacky at room temperature.

Screening Tests for Tinning Oils

A. *Flash and Fire Points.* The first test that must be applied to a potential tinning oil is the flash and fire test for obviously the oil must be safe for operation above the melting point of tin. A potential oil should have a minimum flash point of 500°F. by the Cleveland open cup method, and a fire point at least 50°F. higher.

B. *Activity.* A separation of active and inactive oils may be made by the aforementioned petri dish test as described in the appendix. An indication of their potential life may be gained by the length of activity of a standard quantity of oil in this test.

C. *Long Term Heating Tests.* One of the most obvious methods of testing a tinning oil is to heat the oil in contact with tin for prolonged periods at 465°F., measuring its weight loss and viscosity periodically (Fig. 6). However this tends to give a misleading picture of actual operating conditions; in service a tinning oil undergoes a constant depletion due to volatile losses, dragout and bailout, and is periodically replenished. Consequently it is necessary to establish a regular daily removal and replenishment schedule for any long-term heating test.

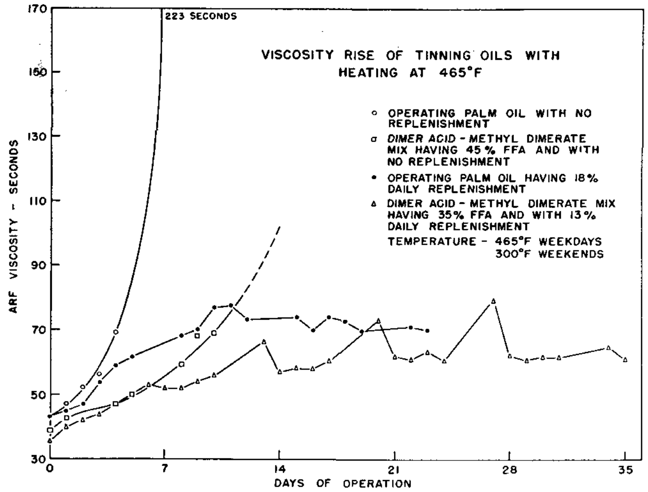

Fig. 6.

To test heat bodying it is recommended that 1,500 grams of oil be heated at 465°F. in contact with tin. Daily a measured quantity of oil should be removed and fresh oil added to make up both the bailout and the volatile losses. The minimum replenishment rate which gives a satisfactory equilibrium viscosity at 465°F. is the index of the heat bodying properties of a possible tinning oil. Some typical viscosity-time curves are given (Fig. 6). At present it is believed that equilibrium viscosities below 60 seconds at 465°F. as measured by the viscosimeter described in the Appendix would indicate an oil which would perform satisfactorily.

D. *Cleaning Tests.* Low temperature viscosity tests may serve to evaluate the ease of cleaning. In order to measure more accurately the low temperature viscosity of the oils, a modification of the dip viscosity tester described in the appendix was made with an orifice diameter of 0.200″ instead of 0.069″. This enabled oils to be tested at temperatures from 75°F. to 300°F. (Fig. 7). However these tests in themselves are not a sole criterion of ease of cleaning for oils which have a sharp melting point within the range of cleaning temperatures may give misleading values. The best cleaning test is to simulate mill cleaning by using bran to remove oil smeared on a tinned sheet.

E. *Miscellaneous Tests.* Tin plate made with a potential tinning oil must pass several other tests. One of the most important is a lacquer adhesion test to determine if the oil is compatible with the lacquer as far as spread is concerned and also if it interferes with its adhesion after baking. The oil must be nontoxic. This may be determined by conventional rat feeding tests.

F. *Model Tin Pot Tests.* A small scale tin pot obtained from the Jones and Laughlin Steel Corporation was set up for testing experimental oils. This pot has an oil depth of about 14″, in which three sets of rolls operate. It is heated by immersion heaters in the tin, supplemented by a Selas gas burner and additional immersion heaters in the oil, to be used when needed. Pretinned sheet is fed through by hand, no flux being used in the entry side of the pot (Fig. 8). Palm oil was run in the experimental pot for several weeks to give a standard for comparison. Although considerable trouble was encountered in making satisfactory coke tin plate due to mechanical difficulties in the tinning machine, enough information was obtained to be a basis for comparison with other tinning oils.

G. *Mill Tests.* At best mill performance can be only estimated by laboratory tests. The ultimate test of a tinning oil is a full scale production mill test run under conditions of commercial practice. Only such an evaluation can determine the true utility of a potential palm oil substitute.

Tinning Oil Formulation

A. Principles of Formulation. 1. *Active Agent.* It has been experimentally determined that a carboxyl group is necessary to an active tinning oil. A suitable active agent should be a substance containing a carboxyl group and having a satisfactory com-

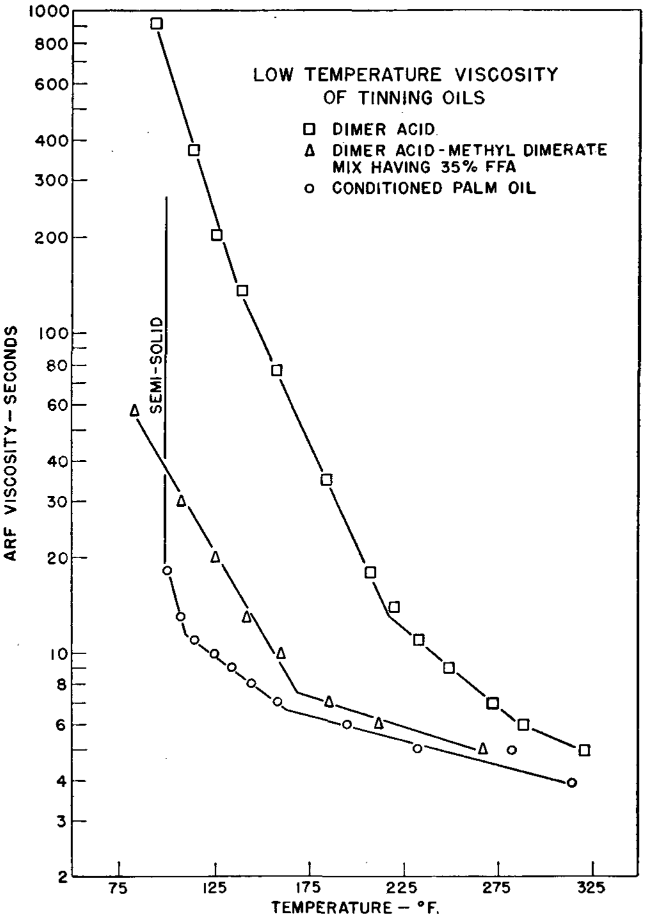

Fig. 7.

bination of low volatility and low cost. In addition, it should be non-toxic and edible.

2. *Diluent.* The diluent, or carrier for the active agent, must also be of low volatility, and compatible with the active agent. It should also possess, in combination with the active agent, favorable low temperature viscosity properties and resistance to heat bodying.

3. *Heat Bodying Inhibitors.* Theoretically heat bodying inhibitors offer considerable promise in lengthening the life of a tinning oil, but laboratory experiments showed all inhibitors tested were either toxic, too volatile, or too costly.

B. POTENTIAL OILS. 1. *Vegetable.* From the experimental requirement that a tinning oil have a carboxyl group and the operating requirements that the oil have a high flash point and low volatility, an oil—dimerized linoleic acid (dimer acid)—was selected from the many tested by the petri dish test. This material is a fatty acid product, only recently available in quantity. It is made from common vegetable oils by heating under pressure in contact with steam. The residue consists of pure fatty acids, dimerized linoleic acid, and a small percentage of trimers and higher polymers. The dimerized acid, separated by distillation, consists of two molecules of linoleic acid, linked together. It is substantially 100% free fatty acid. By virtue of its molecular structure, the material has a high flash point—600°F. as compared to about 470° F. for palm oil—and a volatility about one-third that of palm oil. Because the dimer acid lasted about seven times as long as palm oil in the petri dish test and because its price was in line with the then current price of palm oil, it was selected for further test.

Complete tests, including a mill test, were carried out on dimer acid as a tinning oil. The mill test revealed that while dimer acid was potentially an excellent tinning oil, actually it increased in viscosity excessively on heating. Due to its low volatility and the fact that no regular replenishment schedule was followed in the first mill trial, the viscosity rose to a point at which it was necessary to discontinue the test. In addition, the low temperature viscosity of dimer acid, particularly after heating, was so poor that the cleaning problem was tremendously complicated.

After these initial tests it became obvious that it would be necessary to alter the dimer acid to improve its low temperature viscosity and to increase its resistance to heat bodying. Mineral oils were found to be immiscible with dimer acid after heating, and synthetic polyalkylene glycols, although promoting mutual solubility between the mineral oil and dimer acid, accelerated the heat bodying of the dimer acid.

The best diluent was found to be a monohydric alcohol ester of dimer acid. Most of the work has been done with the methyl ester and a little with the butyl ester. This addition both lowers the low temperature viscosity and increases the resistance of the mix to heat bodying.

2. *Marine.* A new commercial product, similar in nature to the oil described above, has already had a successful mill test. This commercial product is composed of monohydric alcohol esters derived from marine oil as a diluent, with the active agent formed, in service, by the gradual decomposition of hydrogenated glycerol esters. It is more volatile than the dimer acid methyl dimerate mix and is solid at room temperatures, whereas the dimer acid mix is fluid.

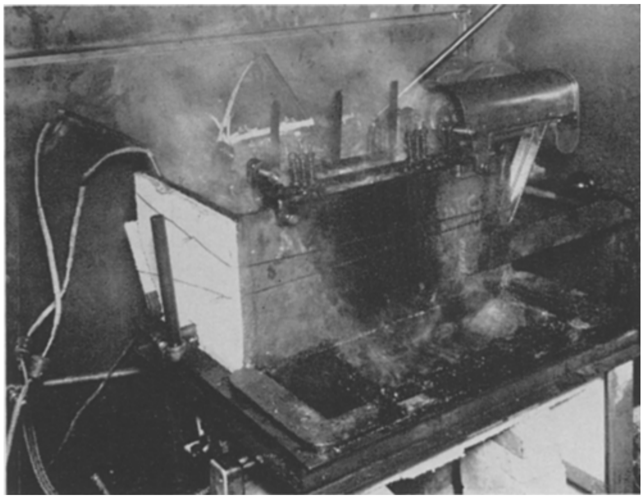

FIG. 8. Model tin pot.

3. *Animal.* Tallow has always been an obvious raw material because of its ample supply and low cost. It had been tried in the past and discarded because of its odor and non-uniform characteristics.

A sample of deodorized tallow was submitted for test. It had been prepared by steaming out the free fatty acids and adding back controlled amounts of acid. The percentage of linoleic acid was low, a fact which is desirable because this acid is believed to be one of the major contributors toward heat bodying. Work to date indicates specially processed tallow will make an economically successful tinning oil.

Summary

It is a difficult problem to formulate or discover a radically different oil to take the place of palm oil, doing an equivalent or better job in equipment specifically designed for palm oil. On the basis of the laboratory experiments two potential substitutes appear quite promising. Their advantages over palm oil are listed below:

Dimer Acid Mix	*Modified Tallow*
Lower oil consumption	Lower cost
Lower equilibrium viscosity	Lower equilibrium viscosity
Higher flash point	Higher flash point
Volatility low; less smoking	Does not polymerize to a solid as readily
Domestically available	Domestically available
Contains no water	Contains no water
Uniform supply	Uniform supply
Can be used without preheating	Can be used without preheating

A final evaluation of a tinning oil however is a mill production trial.

APPENDIX

Design of the ARF Dip Viscosimeter

Early in the project a tester was designed and built to measure oil viscosity at pot operating temperatures. It is made of stainless steel and its major internal dimensions and orifice are identical to those of the standard Saybolt viscosimeter. The walls are made ¼-inch thick to minimize heat loss, and a handle is welded on for ease of manipulation.

In operation the tester is immersed in hot oil until it has come to temperature; initially about 15 minutes is required. It is then removed and the oil drainage time is measured with a stop watch. The tester proved quite convenient for testing a row of individual stacks rapidly. At 465°F. values of 41 seconds for new palm oil to 62 seconds for palm oil ready for carding were obtained with this tester. Values could be checked to plus or minus one second; the test was sensitive enough to detect small additions of fresh oil to the pot. Such a method of testing proves to be more rapid than the present Saybolt test now in use and also gives a meaningful indication of actual operating conditions in the tin pot.

Tinning Oil Screening Tests

1. *Petri Dish Test.* A layer of tin is melted in a petri dish and held a little above its melting point, about 465°F. Sufficient oil is added to cover the tin completely in a thin layer. Then a portion of the tin is exposed to the air by holding back a portion of the oil so that a layer of tin oxide may form. If the oil is active, the exposed portion of tin will not be covered again by the oil but instead will remain bright, with the oxide continually being pulled under the oil. The oil will not lie quiescent but will move around in the dish. The length of time the spot of tin remains bright and the oil remains in motion is a measure of the active life of the oil.

2. *Long Term Heating Test.* A two-liter beaker containing 1,500 grams of oil and 500 to 1,000 grams of tin is maintained at a temperature of 465°F. The beaker is weighed daily to record volatile losses. A specified amount of oil is removed daily to simulate dragout losses, and fresh oil added to restore the oil weight to 1,500 grams. To simulate mill practice the beaker is maintained at 300°F. with no replenishment each Saturday and Sunday. Daily viscosity readings are taken with the ARF viscosimeter, and the test is continued until an equilibrium viscosity is reached—the equilibrium viscosity being defined as that viscosity value which does not change on indefinitely prolonged heating.

Acknowledgments

John Foster, Richard Crouse, Erik Nielsen, and John Barkley of the Chemistry and Chemical Engineering Department have contributed much to the success of the project. The authors wish to thank the members of the Steering Committee: R. A. Woofter, chairman, Jones and Laughlin; J. G. Donelson, Carnegie-Illinois; E. D. Martin, Inland Steel; and A. J. Krombholz, Weirton Steel, for their enthusiastic cooperation and many helpful suggestions. A great deal of credit also is due to the many interested men in the tin houses of the various mills, particularly those of Jones and Laughlin, who greatly aided in evaluating the experimental work.

[Received November 23, 1949]

An Improved Method for the Determination of Iodine Numbers[1]

G. HARVEY BENHAM[2] and LEO KLEE,[3] Department of Biology, Illinois Institute of Technology, Chicago, Illinois

THE determination of the iodine number for measuring the degree of unsaturation in fats and oils is of such universal importance that a clarification of the various methods is needed. Many halogen absorption methods are available; the Wijs (18) and the Hanus (5) are the most widely used. The Wijs method is recommended by the American Oil Chemists' Society, and the Hanus by the Association of Official Agricultural Chemists.

The German Dispensatory uses a modification of Winkler's method, as described by Awe, Skroch, and Demelius (1). The Kaufmann method (9) has not been applied to any extent although Thayer and Glass (17) prefer it to the Hanus procedure. The Rosenmund-Kuhnhenn method (13, 14) has been used only occasionally, and then usually in biological work for substances like cholesterol (2). Yasuda (19) claims that the Hanus reagent may not be used for cholesterol and advocates the Rosenmund-Kuhnhenn method.

The various methods do not give identical iodine numbers, especially in highly unsaturated oils. In general, the Wijs method gives higher, and the Kaufmann and Rosenmund-Kuhnhenn methods lower, values in oils whose iodine numbers are greater than 100. This fact alone causes some confusion when comparisons are made and necessitates control methods using two procedures, usually the Wijs and the Hanus.

The Rosenmund-Kuhnhenn method has been used by Govindarajan (4) for linseed, sunflower, and croton oils. He notes the ease of preparation and stability of the reagent but finds results lower than those obtained by the Wijs method. Earle and Milner (3) confirm this and cite low results for many oils above 100.

All the methods specify long absorption times, 30 to 60 minutes and even 2 hours in the Kaufmann method. This time is too long for rapid control of continuous plant operation, and inconvenient at all times. Hübl (7), as long ago as 1884, suggested the use of mercuric chloride as a catalyst. This idea was not developed until 1938, when Scotti (16) used mercuric acetate in acetic acid to shorten absorption times. This has led to the adoption of the rapid Wijs method, described by Hoffmann and Green (6) and the rapid Hanus method, described by Norris and Buswell (12). The absorption time is hereby reduced to 3 minutes, and this procedure has been adopted in some laboratories. Satisfactory results are obtained with methylene-interrupted systems, but low and erratic results are obtained with conjugated double-bond systems. Rowe, Furnas, and Bliss (15) have tried to overcome this for tall oil by lengthening

---

[1] Presented before the American Oil Chemists' Society Meeting, Chicago, November 2, 1949.

[2] Associate Professor of Biochemistry.

[3] Present address: The Griffith Laboratories, 1415 W. 37th Street, Chicago, Illinois.