

Hydrogenated Cottonseed Oil as a Substitute for Palm Oil in the Production of Tin Plate and Cold Reduced Sheet Steel¹

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Among the fats and oils imported into the United States palm oil ranks next to coconut oil in point of volume. The average annual imports of palm oil for the 10-year period of 1931 to 1940 amounted to 274.8 million pounds, and varied from 155.5 million pounds in 1934 to 411.1 million pounds in 1937.

Palm oil is produced from the fleshy pericarp of the fruit of numerous varieties and strains of the African palm, *Elaeis guineensis*. There is no domestic source of palm oil. The palm from which it is derived is extensively cultivated in the Netherlands East Indies, British Malaya, the Belgian Congo, and other regions in West Africa.

For many years the wild African palms furnished all of the palm oil of commerce, but in recent years large quantities of high-grade oil have been produced and exported from Sumatra. The oil palm was first introduced from West Africa into the Dutch East Indies in 1848, but it was not until 1910 that the present plantation system of production had its beginning.

Owing to the competition of plantation oil from Sumatra, plantations were established in the Belgian Congo beginning in 1924 and at the present time about 275,000 acres are under cultivation. Some 90 plants have been built for the extraction of the oil by hydraulic presses and centrifuges, and an elaborate transportation system has been developed to bring the oil from the plants to the seacoast.

In recent years most of the palm oil imported into the United States came primarily from the Netherlands Indies, although some imports originated in West Africa. Data relative to the volume and origin of palm oil imported for the years 1938 to 1940 are given in Table 1.

TABLE 1
Imports of Palm Oil, 1938 to 1940¹

Origin	1938	1939	1940
	<i>Pounds</i>	<i>Pounds</i>	<i>Pounds</i>
Total Imports.....	271,324,950	288,602,895	225,037,074
Netherlands Indies.....	228,309,060	236,957,996	180,242,873
Belgian Congo.....	27,073,974	32,681,472	32,724,450
Nigeria.....	12,257,316	15,855,167	4,844,448
Gold Coast.....	740,601	6,630,886

¹ U. S. Department of Commerce, Industrial Reference Service, Part 3. Foodstuffs, No. 22, page 7 (February, 1941).

Palm oil has in the past been consumed in the production of shortening, oleomargarine, and soap, and in the process of manufacturing tin and terne plate, and more recently in the cold reduction process of producing sheet steel. Its use in edible products has been decreasing in importance in recent years, and its use

in certain types of soaps though desirable is not indispensable. However, for use in the tin and terne plate industry it has been considered indispensable, and the belief has been widespread that no other oil can satisfactorily replace it for this purpose.

The essential importance of palm oil was recognized when it was added to the list of strategic materials in Amendment No. 2 of the General Imports Order M-63 issued by the Director of Priorities of the Office of Production Management, effective January 13, 1942. On March 20, 1942, General Preference Order M-59, issued by the Division of Industry Operations of the War Production Board, restricted the use of palm oil on and after April 1, 1942, to: (1) The manufacture of tin plate, terne plate, long terne plate, steel sheets, steel strip, and black plate; (2) any manufacturing process in which glycerine is produced where the amount of glycerine remaining in the product does not exceed 1.5 percent.

The relative amounts of palm oil consumed in the production of various classes of products during the five-year period 1937 to 1941, are shown in Table 2.

TABLE 2
Factory Consumption of Palm Oil¹

Year	Total	Food	Soap	Miscellaneous
	<i>1,000 pounds</i>	<i>1,000 pounds</i>	<i>1,000 pounds</i>	<i>1,000 pounds</i>
1937	331,054	125,684	141,358	33,303
1938	253,150	115,477	91,642	19,905
1939	271,046	114,451	102,146	29,681
1940	157,213	36,309	84,934	32,302
1941	278,487	93,147	129,871	49,768

¹ U. S. Department of Commerce, Bureau of the Census, "Animal and Vegetable Oils," 1942, page 23.

All but a very small amount (approximately one or two million pounds) of the total consumption reported under "miscellaneous" was consumed in the manufacture of tin and terne plate and in the production of cold reduced sheet steel. Actual consumption for these purposes is shown in Table 3.

TABLE 3
Consumption of Palm Oil in the Production of Tin and Terne Plate¹

Year	Thousand pounds	Percentage of total consumption
1937	30,708	9.3
1938	13,565	7.2
1939	29,130	10.7
1940	31,075	19.8
1941	42,059	15.1

¹ U. S. Department of Commerce, Bureau of the Census, "Animal and Vegetable Oils," 1942, page 23.

The factory and warehouse stocks of palm oil on hand on June 30, for each of the years 1938 to 1942,

¹ Presented before the American Oil Chemists' Society, Chicago, Illinois, October 8-9, 1942.

are given in Table 4. On the basis of the 1941 rate of consumption of palm oil in the tin and terne plate industry it is apparent that the available supply on June 30, 1942, would last for about 2.6 years if it were all allocated for this use and no imports were received.² Diversion of palm oil to other channels, or increase in its use in the production of tin and terne plate, or in the cold reduction process, would necessarily exhaust available stocks in a shorter period.

TABLE 4
Factory and Warehouse Stocks of Palm Oil
June 30, 1938, to September 30, 1942¹

Year	Crude and Refined
	1,000 pounds
1938	156,158
1939	137,008
1940	140,549
1941	118,560
1942 (June 30)	108,937
1942 (Aug. 31)	97,423
1942 (Sept. 30)	94,364

¹ U. S. Department of Commerce, Bureau of the Census, "Animal and Vegetable Oils," 1942, page 5.

The 1941 production of tin and terne plate increased almost a million tons over 1940 production. Production figures in short tons for 1940 were: tin plate 2,572,558, terne plate 166,023, long terne sheets 153,988, and for 1941 were: cold reduced tin plate 3,183,051, hot reduced tin plate 382,834.

What the production of tin and terne plate will be in 1942 and in subsequent years is not known, but it may not be appreciably lower than past years despite loss of tin resources in British Malaya and the Dutch East Indies. This assumption is predicated on the record pack of canned vegetables which has been projected for military, civilian, and Lend-Lease requirements for 1942, the reduction in the thickness of the tin coating, intensive scrap tin collection programs, and other conservative measures, prospective increase in Bolivian tin ore production and the erection of an American tin smelter in Texas for operation on Bolivian ores. Furthermore, the rapid change in recent years from hot reduction to cold reduction processes for the production of sheet steel has created additional demands for palm oil. In fact, more palm oil is probably being used in the cold reduction of the strip sheet than is consumed in the actual tinning operation.

Tin Plating Operation

The process of tinning sheet steel to form tin plate varies slightly in detail of operation and in the construction of the tinning bath depending on the type of product which is being produced, principally size of plate and thickness of the coating. The operation is carried out in a tinning bath, which differs only in minor details from the one illustrated in Figure 1.

Adequate descriptions of the process of tin plating are not numerous and are seldom very informative. One of the best descriptions is found in Bulletin No. 4 of the International Tin Research and Development Council (1) from which the following condensed description is taken:

Base plates, which have been rolled to the desired thickness, pickled, annealed, and cold-finish rolled,

² On August 31, 1942, stocks had declined to 97.4 million pounds or approximately a two-year supply.

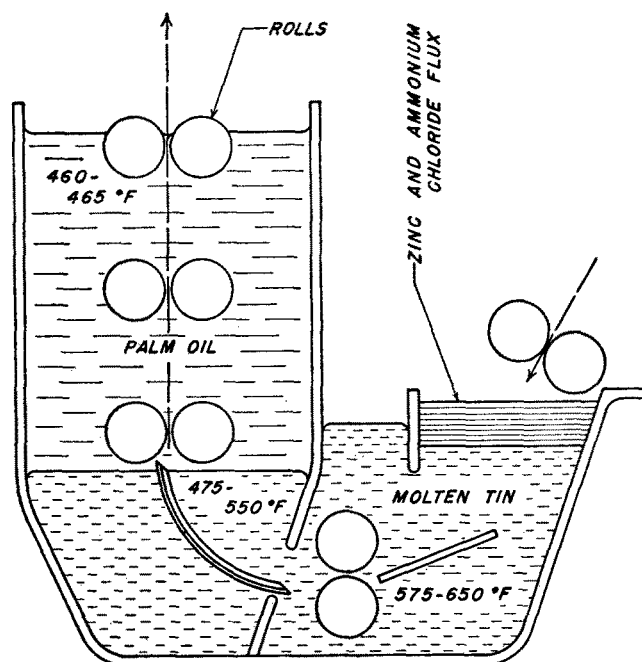


FIG. 1. Diagrammatic sketch of tinning apparatus.

are given a final preparation for tinning by white pickling in two to four percent sulphuric acid, washed, and stored under water in boshes (small portable tanks). In these they are moved to the tinning machines. The water is slightly acidified with hydrochloric acid to aid in preventing oxidation of the surface.

A tinning apparatus consists of a cast-iron subdivided pot suitably enclosed, and usually gas heated, into which a tinning machine fits. The pot is divided vertically to make two compartments, interconnected at the bottom. A molten bath of tin, two and one-half to five tons in weight, occupies the lower portion of the pot; a thin layer of molten zinc chloride flux floats on top in one compartment and a much deeper bath of palm oil occupies the other division. Many of the newer installations use immersion gas heaters inserted in the tin bath in the first or entering division of the pot. These automatically control the temperature very closely and are very efficient in fuel consumption.

The tinning machine is essentially a system of rolls for conducting the sheets singly down through the flux and tinning bath and up through the palm oil. A very important feature, however, is the manner in which the final rolls in the palm oil can be used to press off excess tin, thus regulating the thickness of coating. Pickled black plates are transferred from the water boshes several at a time to a small water-filled trough at the tinning machine where they remain immersed ready for feeding into the machines. If the machine is fed by hand, the operator manually inserts each plate into the first set of feed rolls. Most modern machines, however, are equipped with mechanical feeding devices whereby the operator needs only to insert a number of plates from time to time; magnetic rolls having limiting sleeves for admitting only one plate at a time, introduce and convey the sheets through the machine. Tinning units or pots may be wide enough for two or three sheets to be fed side by side simultaneously.

The flux of zinc chloride or a mixture of zinc and ammonium chlorides is heated by the molten tin bath underneath. Its purpose is to clean thoroughly the black sheet surfaces, remove moisture, and prepare the surface so that the tin will adhere uniformly.

Speeds at which the plate is conducted through the tinning bath may vary from 150 inches to about 350 inches per minute. The temperature of the tin bath, as measured by a thermocouple placed halfway down in the metal of the entering chamber, varies from about 575°F. to 650°F. depending on the operating speed, a higher temperature being needed for more rapid operation. Tin at the feed end of the pot is kept at a much higher temperature (by 100°F. or more) than that in contact with the palm oil. This is due both to the fact that the temperature of the palm oil must be kept relatively low, and to the necessity for quickly heating incoming cold plate to a temperature permitting rapid reaction with the flux and for quick tinning. The very short time in which the steel base sheet and tin are in contact prevents undue alloying before the tin freezes.

Palm oil used in the exit compartment of the tinning machine serves excellently as a medium in which to keep the tin coating molten while passing through rolls. This provides better distribution of the coating and aids in removal of excess tin. It also serves to protect the tin from oxidation or discoloration while being cooled.

The temperature of the palm oil is very important. At the top of the grease pot it should be kept at about 460-465°F., or only 10 or 15°F. above the melting point of tin. If temperatures of over 470°F. are reached, a yellow discoloration of the tin plate is apt to occur. Palm oil readily polymerizes if it becomes too hot, which results in poor work and high oil losses.

From the tinning machines the tin plate, coated with a film of palm oil, is conveyed by belt or roll conveyors to a hot aqueous cleaning bath or washing machine for removal of excess palm oil, then to dry-cleaning and polishing tables. In some plants the washing step is omitted, depending on the specifications or use to which the finished plate will be applied. The disposal of cleaning solutions containing saponified palm oil is often a serious problem. When this step is omitted, however, additional dry-cleaning machines are used.

The washing operation consists of scrubbing the plate in a hot dilute (about 0.2 percent) solution of sodium carbonate or other saponifier to remove most of the palm oil. Since some types of enamel cannot be used on tin plate coated with oil, a more complete oil removal than is usually accomplished by dry methods is necessary and quite widely used.

Dry tin-plate cleaners consist of two sets of flannel rolls, the first for oil removal and the second to remove dust and polish the sheet. Bran, middlings, or various mixtures of such oil-absorbing materials are passed over and lightly rubbed along the surface of the tin plate by the revolving rolls. After some recirculation of the bran until its oil-absorbing quality is largely gone, it is sold for stock feed. This is an advantage of using an edible oil rather than a mineral oil. The second set of flannel rolls removes any remaining bran mixture and gives the plate a lustrous polish. Since too much pressure on the cleaning rolls may cause

scratches on the plate, this operation is usually carried out in a manner designed to remove as much oil as possible without causing any serious scratches. The cleaned plates are mechanically stacked as they come from the cleaners.

A slight amount of oil is normally left on the tin plate unless it has been given an alkali wash. This has the advantage of preserving the finish or temporarily preventing corrosion during a possible period of storage before use. Sometimes considerable palm oil is purposely left on the tin plate when it is to be used for deep-drawing work, although other lubricants are more desirable.

Terne plate, short ternes, and long ternes are produced by similar methods except that the bath must operate at somewhat higher temperatures (700-725°F. at the intake) because of the higher melting point of the terne mixture which usually consists of 20-percent tin and 80-percent lead.

Recently, the method of electrically depositing tin on the strip steel in the form of continuous rolls has been introduced in the tin plate industry on a large scale. Following the electrolytic deposition of the tin, the coated steel is heated in a palm oil bath to reflow the tin to produce a uniform, smooth film.

The Cold Reduction Process

Although many improvements in equipment and method of manufacture of sheet steel or black plate have been made since the tin plate industry had its inception in the United States in 1890-92, a momentous development occurred in 1927 when the continuous hot-strip mill was introduced. Even more momentous was the introduction in 1932 of the continuous cold reduction of the strip furnished by the hot-strip mill. In 1941 approximately 90 percent of all the tin plate in the United States was produced from cold-reduced black plate.

Although the speed of rolling is less in the cold-reduction mill (700 to 1,600 feet per minute) compared with the hot-strip mill (about 1,800 feet per minute), the pressure exerted by the rolls is enormous and may exceed two million pounds. The work done by the rolls in reducing cold strip requires elaborate means of dissipating the heat generated. As a matter of fact, if such a mill were allowed to run dry for a very short time, the strip would soon reach a white heat and actually burn up. It is also essential to maintain a constant predetermined temperature on the rolls to hold their contour, since they determine the shape of the finished product. Consequently the rolls are cooled internally by circulating water and externally by application of a lubricant. Various oil emulsions are used for the external lubricant, one of which contains palm oil and especially spent palm oil from the tin bath.

The foregoing description of the tin and terne plating operations and of the cold reduction process for producing sheet steel indicates the dependence of the industry on a continuing supply of palm oil, or alternatively, the development of a satisfactory substitute. During the summer of 1941, when it became apparent that importations of palm oil might be drastically reduced or entirely cut off, the Southern Regional Research Laboratory was directed to undertake work

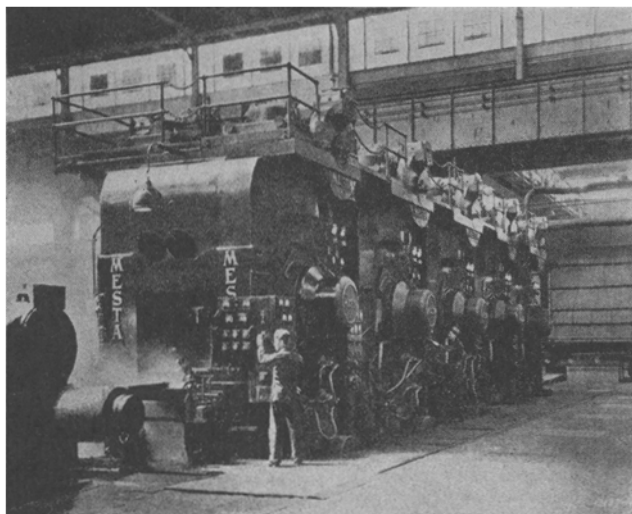


Fig. 2. Cold reduction mill. Note vaporization of palm oil as the sheet emerges from the rolls.

on the development of a substitute oil which could be produced from domestically available raw materials.

During World War I when the producers of tin plate were faced with the possibility of a shortage of palm oil a similar project was instituted in the Bureau of Chemistry, now the Bureau of Agricultural Chemistry and Engineering.

Collins and Clark (2) investigated, both on a laboratory scale and in an actual mill test, the performance of hydrogenated cottonseed oil as a substitute for palm oil in the tin bath. Two oils, hydrogenated to iodine values of 3.1 and 16.7 were used in these experiments, which covered a period of twelve weeks. The authors concluded that little or no difference was noted in their behavior in the tin bath following the first three days of operation. According to their report, the use of hydrogenated cottonseed oil gave somewhat better performance in the tin bath than did palm oil, and the consumption was distinctly less with the hardened oil. However, it was felt that the higher cost of the hardened oil offset any advantage to be obtained by its use. It is possible that other factors besides cost militated against the use of the particular type of oil which was employed in the above-mentioned experiments. Regardless of the reason, the fact remains that up to the present hydrogenated cottonseed oil has not replaced palm oil in the tin bath.

From time to time several tin-plate mills, as well as producers of commercial fats and oils, have carried out more or less extensive investigations on the development of substitutes for palm oil. Cottonseed, soybean, and fish oils have been the favorite oils used in these experiments. In most cases the oils were highly hydrogenated, in fact to a degree of hardness which permitted shipment in bags or bulk. One of the most successful of these experiments was carried out with hydrogenated cottonseed oil. A sample of this oil furnished the authors was found to have an iodine value of 8.8. During six months' test 187,300 base boxes of tin plate were produced and after fabrication into cans were successfully used in a wide variety of canning operations. However, certain difficulties have invariably been encountered in such oils, particularly freezing of the supply lines and circulat-

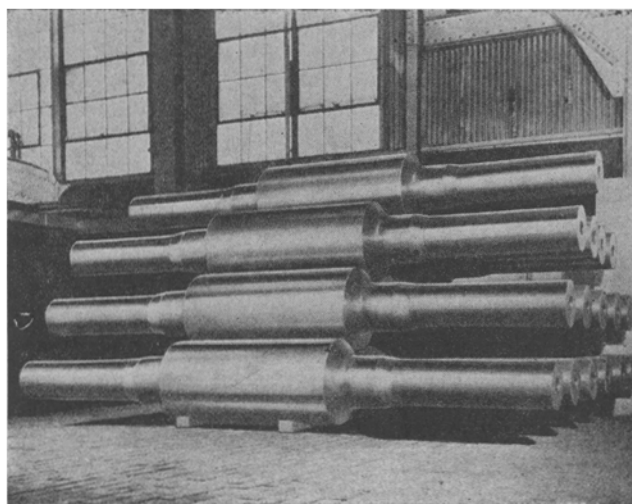


Fig. 3. Cold reduction rolls. Note provision for internal cooling.

ing systems, especially in winter and in northern climates. Often times supply lines are adjacent to gas mains and cannot be thawed without incurring undue risk of fire and explosion.

Before attacking the problem of producing a substitute for palm oil for use in tin and terne plating, efforts were made to learn why palm oil was apparently unique in its ability to function so effectively in this process. A search of the literature revealed little information of value and much that was contradictory. In the light of subsequent work it was found that many statements were also misleading, as for example the frequently repeated statement that the high free fatty acid content of palm oil was requisite to the proper functioning of the tin bath.

In view of the inadequate and contradictory information in the literature, the cooperation of a number of tin plate producers and consumers was enlisted in compiling technical information relative to the properties and behavior of palm oil in the tin bath, and the reasons for its use in preference to other oils. Responses on the part of the tin-plate producers were most generous with respect to both technical information and cooperation in furnishing samples of virgin and spent oils used in their respective tinning operations. The following paragraphs summarize the most pertinent information developed by these inquiries:

Manufacturer A. "The usually determined chemical and physical constants of palm oil, taken separately, do not fully measure its adaptability to the hot tinning of steel. . . . For proper operation a relatively low free fatty acid content is preferred, and the oil should not increase in acid number rapidly at the temperature required in practice, about 455°-465° F. On the other hand an oil with extremely low free fatty acid, if it does not break down at all, is deficient in fluxing value. The radical example on the low side is mineral oil; on the high side, rancid tallow.

"Low unsaturated acid content, or comparatively low iodine value, enhances the value of a tin-pot oil if other characteristics are right. The unsaturated constituents not only contribute to the fire hazard but they break down rapidly with attendant formation of fume and tar, both of which are deleterious. . . . Rate of change of viscosity, loss by evaporation, change of flash and fire points during operation, and the formation of tin soaps are pertinent considerations.

"The properties of the extremely thin film of oil that remains on tin plate after the commercial cleaning process are very important. Significant points are the adequacy of protection against blue and yellow staining, maintenance of new-bright surfaces during periods of shipment and storage, and the ease of soldering and lacquering in subsequent can-making operations. These matters are quite intimately related to the oil used in tinning, and any change at the tin pot entails careful investigation throughout all following steps, including the performance of the can in service. In the case of palm oil the fine points are known, with others the risk is on the producer until the new practice is as well established as the old. . . . A hydrogenated oil with free fatty acid value of approximately 0.5-1.0, iodine value 20-25, flash point above 500° F. new and 525° after use, fire point approximately 600° F., Saybolt viscosity 85 at 210° F. after heating for one week at 460° F., has given a good account of itself in the tinning operation. The 'Setting' characteristics of hydrogenated oil are different from those of palm oil; oil drag on the plates is increased; slower speed is sometimes necessary, resulting in reduced output; provision must be made against the freezing of hydrogenated oil in circulating systems and cooling boxes. These operating problems are cited as typical in a change from established procedure."

Manufacturer B. "The present practice of using palm oil in the tin pot apparently arose from a combination of necessity and convenience. The Wales tin-plate industry needed an oil to blanket its tin pots, and the British Empire had at its disposal a raw material that fitted this need.

"Tin-pot operations called for a relatively cheap material of high thermal resistance to prevent oxidation and evaporation; to furnish a medium in which the molten tin could flow; and one of such nature that the excess could be conveniently removed from the surface of the freshly tinned sheet.

"Palm oil met these conditions and has, by custom, enjoyed continued use.

"It is quite probable that the quality of the oils in use today is far superior to that used in the early days of the industry. The advent of the plantation systems, which put order into production and which utilizes latest scientific knowledge, has brought this about. However, it is still palm oil.

"Despite the large number of data available concerning the physical constants and chemical constitution of palm oil there has never been a satisfactory correlation made between these values and the performance of palm oil used for hot dip tinning. This is confirmed by the scant information in the literature. Aside from the fact that palm oil satisfied the conditions cited above, the functions of the various properties are a matter of conjecture.

"The only properties, therefore, that can be definitely said to be essential to the proper functioning of oil in the tin pot are: (1) High flash and fire point; (2) high resistance to thermal decomposition; (3) relatively low viscosity at high temperatures; and (4) easy control of amounts remaining on the freshly tinned sheet.

"Another consideration is that the oil and the products of its decomposition should be as non-corrosive as possible.

"The mere fact that an oil works well in a tin pot is not a criterion of its use as a replacement for palm oil. Any radical change in the type of oil may alter any one of the numerous operations of the tin plate fabricator. In this connection we must consider such operations as shearing, stamping, lithographing, lacquering, the application of sensitive and seam-coating compounds, labeling and even the service life of the filled container.

"While it is recognized that palm oil has not fulfilled all of the requirements of the various phases of fabrication, the attending shortcomings have not militated against its use over a long period of time."

Manufacturer C. "To be serviceable for use in the operation of hot dip tinning, an oil must consistently produce a high

grade of tin plate that has stability characteristics when tested with a variety of wet packs by the canners. Such tests necessarily require several years for their evaluation and are meaningless unless the tin plate is from an operating machine that is running under equilibrium conditions. The process of tinning is continuous, twenty-four hours per day and seven days per week. Even so, it may require from two to three weeks before complete equilibrium is assured in all cases.

"Among the essential properties of a satisfactory oil may be mentioned a flash and fire point well above the operating temperature, suitable wetting properties relative to steel and tin, and resistance to pyrolytic decomposition in the presence of metals and flux. The properties of the oil cannot be considered secondary and it is a fortunate circumstance in this case that they are found, possibly uniquely, in a low priced commodity."

Consumer A. "There are many sources of palm oil such as Lagos, Benin, Victoria, Cameron, Red Sierra Leone, Niger, Sumatra, and Congo. The better qualities contain the lower amounts of free fatty acids. For example: Lagos is one of the best and contains about 11 per cent of free fatty acid (palmitic acid). Many sources contain 18 to 38 per cent of free acid. When palm oil goes into use in the tin stack its acidity runs up rather rapidly to about 50 per cent.

"Where hydrogenated cottonseed oil is used as a substitute for palm oil the acidity of this oil increases but little and will not exceed 5 per cent.

"Palm oil fumes at 470° F. whereas hydrogenated cottonseed does not fume even when approaching 600° F., the approximate temperature of the bath.

"Hydrogenated fish oil might prove satisfactory as it has a high smoke point.

"We use a Sumatran oil with about 6 per cent fatty acid. In operation the oil gets heavy and every 8 hours old oil must be partially replaced by new oil. Hydrogenated cottonseed oil has been used and although it does not give quite as good a finish to the tin plate is certainly usable. The higher cost of hydrogenated cottonseed oil has been a deterrent to its use, but on account of its stability it goes almost three times as far as palm oil, offsetting its first high cost.

"By using palm oil or cottonseed oil with tin pot (always lead-free) and sieving the oily bran from slivers of tin, the product makes an excellent hog feed, and commands a fair price. Cottonseed oil bran would probably be better than palm oil bran because the free fatty acid is much lower."

Research Foundation A. "There is really no satisfactory way to judge a new oil except by actual operation with a tin bath. Some preliminary ideas can be obtained by using a small tin pot, such as a clay graphite crucible containing molten tin, heating being performed in an electric furnace of laboratory size. The temperature of the tin bath is controlled best by means of a thermocouple, such as alumel-chromel, encased in a closed tube of fused silica which is immersed in the molten tin. . . .

"The principal properties to be fulfilled by a tinning oil are as follows: (1) Ability to take up oxide on the tin bath; (2) ability to absorb any flux residues; (3) promoting the spread of tin on the base metal; (4) no difficulty in removal of residual oil; (5) no harmful effect, such as corrosion, on the tin coating if some oil remains; (6) reasonably long life; (7) low fire risk; and (8) no bad effect on subsequent lacquering, etc.

"Palm oil is considered good for items 1, 2, 3, and 5; fair for 4; bad for 6 and 7. It is also considered satisfactory for item 8, although there is definitely room for improvement.

"It is rather difficult, on the basis of present knowledge, to correlate the above properties of palm oil with its physical and chemical properties. However, it appears that a tinning oil must have some degree of chemical action, such as would be contributed by acid content. It is somewhat doubtful whether unsaturation in itself is of any benefit. In fact, it may be

harmful owing to the increased possibilities of polymerization, etc. at the temperatures used in tinning."

It is apparent from the above excerpts, as well as other information obtained from those interested in the problem, that the chemical and physical basis for the behavior of palm oil in the tin bath has not been known with certainty, and furthermore that palm oil is not the ideal product for the purpose but merely the cheapest and one of the best of those available. With these facts in mind efforts have been directed toward producing a product better adapted to the tinning operation and one which may be economical as well.

Experimental

Samples of virgin and spent palm oils were obtained from three commercial producers of tin plate, and analyzed to ascertain what effect the tinning process had on the chemical and physical properties of the oil. The results of these analyses are summarized in Tables 5 and 6.

TABLE 5
Chemical Properties of Palm Oils

Analysis	Sample A		Sample B		Sample C	
	Virgin	Spent	Virgin	Spent	Virgin	Spent
Free fatty acid as percent palmitic.....	6.75	7.66	8.55	7.28	9.49	10.15
Free fatty acid as percent oleic.....	7.43	8.44	9.41	8.02	10.46	11.20
Saponification No.....	198.0	192.0	197.0	200.0	197.0	193.0
Acetyl value.....	19.3	16.4	21.7	22.4	20.5	14.4
Iodine No. (Wijs).....	49.8	44.8	49.9	47.1	52.5	45.2
Thiocyanogen No.....	41.8	41.4	41.2	43.2	43.5	48.6
Neutral equivalent of total acid.....	270.5	302.3	272.2	283.5	270.7	303.2
Solid acids (percent).....	47.7	52.4	48.7	45.6	47.4	51.2
Neutral equivalent of solid acids.....	259.4	322.3	256.2	261.0	259.5	303.8

TABLE 6
Physical Properties of Palm Oils

Property	Sample A		Sample B		Sample C	
	Virgin	Spent	Virgin	Spent	Virgin	Spent
Surface tension dynes/cm ² at 118-120°C.....	28.4	28.4	28.0	27.3	28.0	27.3
200°C.....	22.2	22.6	22.0	21.9	22.1	21.8
250°C.....	19.0	19.8	19.1	19.4	19.1	18.8
Viscosity centistokes 60°C.....	27.93	65.18	23.26	26.35	21.12	45.54
100°C.....	10.32	20.87	8.57	9.46	8.00	15.05

Reference to these results reveals the fact that there is surprisingly little difference in the chemical properties of the virgin and spent oils. The slight increase in the free fatty acid content of the spent palm oils does not substantiate previous assumptions that breakdown of these oils during the tinning operation is accompanied by marked increase in the free fatty acid content of the oil. Only moderate and apparently insignificant changes are observed between virgin and spent palm oils in the saponification, thiocyanogen, iodine, and acetyl values. Evidence of decarboxylation is indicated in the neutral equivalent values of the acid fractions. Only slight changes in surface tension are evident, but there is a considerable increase in the viscosity of palm oils represented by samples A and C.

Preliminary investigations on the preparation of a tinning oil were carried out with the view of extending the present available stocks of palm oil by mixing

it in some proportions with hydrogenated cottonseed or peanut oils. A number of such mixtures were prepared and heated at elevated temperatures in the presence of surface-oxidized tin buttons. The heating unit consisted of six individual heaters wound with resistance wire and of such shape and size that they would accommodate a 50-ml. capacity porcelain crucible. The heaters were connected in series, imbedded in asbestos, and secured in place by means of plaster of paris. The temperature was controlled manually by means of a voltage regulator and measured with chromel-alumel thermocouples. Preliminary tests with Arochlor in the crucibles indicated that accurate temperature control could be maintained between 240° and 250°C. Thirty-gram samples of the oils were heated in the crucibles for three successive periods of 16 hours each, or a total time of 48 hours. The crucibles were weighed at the end of each 16-hour interval, and the loss of oil, tendency to polymerize, degree of removal of oxide film from the tin buttons, and the general appearance of the tin buttons were noted. After each 16-hour heating period sufficient fresh oil was added to the crucible to bring the volume to that of the original charge. The tin buttons were reoxidized by heating in air and then replaced in the oil, and the heating continued for another 16-hour period. The results and observations of these experiments with various mixtures of palm and hydrogenated oils are recorded in Tables 7 and 8, together with comparative results obtained with palm oil.

TABLE 7
Loss in Weight on Heating 30-Gram Samples of Oils at 240-250°C. in the Presence of Oxidized Tin Buttons

Oils	Iodine value.	Loss in weight of oil		
		16 hours	32 hours	48 hours
		Gms.	Gms.	Gms.
Palm.....	52.5	7.17	9.88	12.84 ¹
Palm.....	52.5	6.06	10.14	14.28 ¹
Cottonseed.....	53.8	2.15	5.10	7.49
Cottonseed.....	53.8	2.09	6.33	7.63
Cottonseed.....	48.0	2.29	5.47	7.89
Cottonseed.....	6.8	2.17	4.69	7.42
Cottonseed.....	6.8	1.67	4.19	7.11
Peanut.....	53.5	3.23	5.44	7.32
Palm + cottonseed (25:75).....	24.1 ²	1.35 ³	5.93	6.59
Palm + cottonseed (25:75).....	48.0 ²	3.95	6.54	7.95
Palm + cottonseed (50:50).....	48.0 ²	3.73	7.30	7.72
Palm + cottonseed (75:25).....	48.0 ²	2.93	6.01	8.13
Palm + cottonseed (75:25).....	24.1 ²	2.56 ³	6.45	9.27
Palm + peanut (25:75).....	19.4 ²	1.76 ³	4.65	6.59

¹ Polymerized to rubbery mass.

² Iodine values given are for the hydrogenated oils only.

³ Loss after eight hours' heating.

The various hydrogenated oils, when heated for prolonged periods in the presence of surface-oxidized tin buttons, exhibited less tendency to polymerize and had lower volatility losses than did palm oil or the mixtures of palm oil and hydrogenated oils under the same conditions. Removal of tin oxide by the hydrogenated oils was observed to be as good as or better than that obtained with palm oil or mixtures of palm and hydrogenated oils. The losses due to volatilization on heating observed with cottonseed oils hydrogenated to iodine numbers of 53.8 and 6.8, respectively, indicate that there is no decided advantage in using oils more highly hydrogenated than is sufficient to inhibit excessive polymerization. Though hydrogenated peanut oil proved to be a satisfactory tinning oil, no extensive investigation was carried out with it because of its limited supply, and its superior quality as an edible oil.

TABLE 8

Loss in Weight and Change in Appearance of Tin Button After Heating in Oils at 240-250°C.

Oils	Iodine value	Loss in weight of tin buttons			Appearance of button after heating		
		16 hours	32 hours	48 hours	16 hours	32 hours	48 hours
Palm.....	52.5	<i>Gms.</i> 0.04	<i>Gms.</i> 0.05	<i>Gms.</i> 0.07	Surface rough, covered with tin slag	Surface rough, covered with grey oxide film	Surface rough, covered with oxide film
Palm.....	52.5	0.05	0.06	0.08	Surface rough, covered with tin slag	Very little change	Surface bright, oxide film on edges
Cottonseed.....	53.8	0.02	0.07	0.08	Surface smooth and satiny. Tin slag on bottom	Surface smooth-satiny, small amount of grey oxide	No change
Cottonseed.....	53.8	0.02	0.06	0.10	Surface smooth, small amount of grey oxide on bottom	Surface smooth-satiny, small amount of oxide film
Cottonseed.....	48.0	0.01	0.05	0.05	Surface rough, covered with oxide film	Surface smooth, bright spots in grey oxide film	No change
Cottonseed.....	6.8	0	0.03	0.08	Surface rough, no change	Surface smooth, covered with grey oxide film	Surface covered with grey oxide film
Cottonseed.....	6.8	0	0.02	0.01	Surface rough, no change	Surface smooth, covered with grey oxide film	Surface smooth, bottom rough, covered with thick oxide film
Peanut.....	53.5	0.03	0.06	0.08	Surface smooth, covered with grey oxide film	Surface dull, covered with tin film
Palm + cottonseed (25:75).....	24.1 ¹	0.07	0.09	Surface shiny, no oxide film	Surface smooth, dull film of oxide
Palm + cottonseed (25:75).....	48.0 ¹	0.02	0.03	0.04	Surface rough, covered with thick oxide film	Surface shiny, oxide film on bottom	Surface rough, no change
Palm + peanut (25:75).....	19.4 ¹	0.06	0.08	Surface shiny, oxide film on bottom	No change
Palm + cottonseed (50:50).....	48.0 ¹	0.03	0.04	0.04	Surface rough, thick oxide film on bottom	Surface smooth, pitted with grey oxide film	Surface rough, bottom smooth and satiny
Palm + cottonseed (75:25).....	48.0 ¹	0.03	0.06	0.07	No change	Surface smooth, dull, shiny bottom, slight oxide film	Surface rough, covered with grey film
Palm + cottonseed (75:25).....	24.1 ¹	0.03	0.04	Surface rough, bottom bright and shiny	No change

¹ Iodine values are for hydrogenated oils.

Ordinary refined cottonseed oils and other oils of the same or a higher degree of unsaturation cannot be used because they are too volatile, and tend to polymerize too readily at the temperature prevailing in the tin pots. It was also observed that the more highly hydrogenated or saturated oils are not the most satisfactory ones for use in the tin bath because they lack ability to remove oxide coating. It is apparent that an optimum degree of unsaturation, and a certain degree of break down during heating are requisite to maximum operating efficiency of the oil in the tin bath.

Semi-hard, hydrogenated cottonseed oils. In view of the results mentioned above, and the objections raised by certain tin-plate producers to the hardness and high melting point of highly hydrogenated cottonseed oil, an investigation was made of the properties and action of cottonseed oil hydrogenated to the approximate degree of unsaturation occurring naturally in palm oil. Previous heating tests had shown that hydrogenated cottonseed oil of 55 iodine value or less was at least as good as palm oil in its ability to withstand prolonged heating and to dissolve tin oxide. A number of oils were prepared by the selective hydro-

TABLE 9

Composition and Properties of Hydrogenated Cottonseed and Palm Oils

Oil	Iodine value	Sapon. No.	Oleic acid	Linoleic acid	Saturated acids	Melting range	Smoke point	Fire point	Flash point
Hydrogenated cottonseed No. 26.....	58.9	193.5	<i>Percent</i> 62.0	<i>Percent</i> 3.2	<i>Percent</i> 34.8	<i>°C.</i> 38-41	<i>°F.</i> 395	<i>°F.</i> 615	<i>°F.</i> 685
Hydrogenated cottonseed No. 24.....	56.3	191.8	59.4	2.8	37.8	40-43	390	620	680
Hydrogenated cottonseed No. 25.....	50.2	192.3	56.5	0.9	42.5	43-46	390	620	680
Hydrogenated cottonseed No. 27.....	45.6	193.2	49.3	1.9	48.8	47-50	385	615	685
Palm ¹	48-58	196-205	43.2	9.5	47.0	27-50	240	480	560

¹Jamieson, George S., Vegetable Fats and Oils, American Chemical Society Monograph No. 58 (1932).

generation of cottonseed oil. The hydrogenations were carried out with a view to reducing the linoleic acid content without appreciably increasing the saturated acid fraction (3). The analyses of these oils are recorded in Table 9, together with the analysis of palm oil for comparison. The refined and deodorized cottonseed oil used throughout this investigation, and in the preparation of the hydrogenated oils had an iodine value of 102.3.

Oil No. 27 (Table 9) is quite similar to palm oil in the content and percentage ratio of oleic acid to saturated acids. However, the saturated acid fraction of the hydrogenated oil consists mainly of stearic acid, whereas the greater part of the saturated acid fraction of palm oil consists of palmitic acid. The average value of the smoke, flash, and fire points of the hydrogenated oils was found to be 390°F., 620°F., and 680°F., respectively, compared with 240°F., 480°F., and 560°F., respectively, for palm oil. The hydrogenated oil is therefore definitely superior to palm oil in this respect.

The various hydrogenated cottonseed oils were subjected to heating tests (230-250°C.) in the manner previously described. The results of these tests are recorded in Tables 10 and 11. Examination of the data in these tables again indicates that cottonseed oils, hydrogenated to an iodine value of approximately 50, are much less volatile and give as good or better tin oxide removal as virgin Sumatran palm oils.

TABLE 10
Loss in Weight of Oil and Tin Buttons During Heating at 230-240°C.

Oil	Iodine value	Loss in weight of oil			Loss in weight of tin buttons		
		16 hrs.	32 hrs.	48 hrs.	16 hrs.	32 hrs.	48 hrs.
		Gms.	Gms.	Gms.	Gms.	Gms.	Gms.
Palm.....	52.5	3.68	6.76	8.47	0.02	0.04	0.07
Palm.....	52.5	3.27	6.13	8.06	0.03	0.04	0.08
Cottonseed.....	56.3	2.25	3.92	5.95	0.01	0.05	0.07
Cottonseed.....	56.3	1.67	3.92	5.57	0.00	0.03	0.06
Cottonseed.....	56.3	2.29	4.28	6.30	0.03	0.06	0.09
Cottonseed.....	50.2	2.90	4.72	5.76	0.02	0.03	0.04
Cottonseed.....	50.2	2.43	4.85	5.61	0.04	0.08	0.10
Cottonseed.....	53.9	2.14	3.94	4.81	0.02	0.04	0.06
Cottonseed.....	45.6	3.39	5.85	7.42	0.01	0.04	0.07
Cottonseed.....	45.6	3.70	6.11	7.03	0.04	0.04	0.06
Peanut.....	43.6	1.85	3.57	4.81	0.03	0.07	0.09
Peanut.....	56.1	1.92	4.16	5.56	0.02	0.04	0.05

TABLE 11
Loss in Weight of Oil and Tin Buttons During Heating at 240-250°C.

Oil	Iodine value	Loss in weight of oil			Loss in weight of tin buttons		
		16 hrs.	32 hrs.	48 hrs.	16 hrs.	32 hrs.	48 hrs.
		Gms.	Gms.	Gms.	Gms.	Gms.	Gms.
Palm.....	52.5	7.17	9.88	12.84 ¹	0.04	0.05	0.07
Palm.....	52.5	6.06	10.14	14.28 ¹	0.05	0.05	0.07
Palm (acid free).....	3.85	6.60	10.01	0.01	0.02	0.03
Cottonseed.....	53.8	2.15	5.10	7.49	0.02	0.05	0.06
Cottonseed.....	50.2	3.11	5.38	7.60	0.03	0.05	0.08
Cottonseed.....	48.0	2.98	6.53	9.50	0.03	0.05	0.10
Cottonseed.....	48.0	2.29	5.47	7.89	0.01	0.05	0.09
Peanut.....	53.5	3.23	5.44	7.32	0.03	0.04	0.10
Peanut.....	53.5	3.41	5.69	7.90	0.03	0.06	0.08
Peanut.....	43.6	2.33	4.80	7.08	0.00	0.03	0.07

¹ Polymerized to rubbery mass.

Viscosity relationships. Through consultation with tin-plate producers and a visit to a large tin-plate mill it was learned that acceptable tin plate could be produced using modified cottonseed oils of 60 viscosity Saybolt (9.8 centistokes) at 210°F., whereas palm oil must have a viscosity of 85 (Saybolt at

210°F.), before suitable tinning can be accomplished. It is necessary, therefore, to preheat palm oil to a prescribed viscosity before it can be used in the tinning operation. This preheating period is avoided by most manufacturers of tin plate by mixing fresh and spent palm oils. By this practice the viscosity of the palm oil can be maintained between 85 and 102 Saybolt (about 15.8 and 21.0 centistokes, respectively) at 210°F.

Since the viscosity of the oil is an important factor in the tinning operation, the change in this property during heating was determined for both the hydrogenated cottonseed oils and palm oil. Two sets of experiments were undertaken, in one of which the oils were heated in the presence of surface-oxidized tin buttons at 230-240°C. in 50-ml. crucibles and the viscosity determined after 16 and 32 hours of heating. Viscosity measurements were made by means of a modified Ostwald-Cannon-Fenske viscometer at 98.9°C. (210°F.) with the results recorded in Table 12. In the other experiment 400-ml. samples of oil were also heated in the presence of surface-oxidized tin buttons in an electrically heated, insulated bath at 230-231°C. and samples were removed for viscosity determination at regular intervals. The result of these viscosity determinations are expressed graphically in Figure 4.

TABLE 12
Effect of Heating Oils at 230-240°C. in the Presence of Tin Buttons on Viscosity of Palm and Hydrogenated Cottonseed Oils

Oils	Iodine value	Viscosity in centistokes at 98.9°C.		
		0 hours	16 hours	32 hours
Palm, No. 1.....	52.5	8.42	29.30 ¹
Palm, (acid free).....	10.03	23.99
Cottonseed, No. 26.....	58.9	9.68	24.40	68.79
Cottonseed, No. 24.....	56.3	9.71	25.70	69.60
Cottonseed, No. 25.....	50.2	9.87	25.76	53.78
Cottonseed, No. 27.....	45.6	10.01	22.47	48.13

¹ Oil too viscous for determination.

The palm oil exhibited a greater increase in viscosity than did the hydrogenated cottonseed oils when heated in the presence of oxidized tin buttons. After 32 hours of heating the palm oil was too viscous to allow filling of the viscometer. While the hydrogenated cottonseed oils exhibited higher initial viscosities, the rate of increase was not as rapid as in the case of palm oil. The lower rate of viscosity increase is a definite advantage in favor of the hydrogenated cottonseed oil and results in a longer life in the tin pot. Little correlation was observed between the viscosities obtained after heating the oils in crucibles and those obtained after heating them in the insulated bath. The oils heated in 50-ml. crucibles were subjected to more drastic treatment owing to their greater evaporation area and the smaller volume of oil, than were those in the experiment where 400 ml. of oil was heated and small samples (ca. 15 grams) were removed periodically. The difference in the initial viscosities of palm oil (8.42 centistokes), and palm oil from which the free fatty acids had been stripped by steam (10.03 centistokes) cannot be explained on the basis of dilution of the oil by free fatty acids since recombination of palm oil fatty acids with the stripped oil gave no change in viscosity. Further work on the effect of free fatty acids and glyceride-degradation products on the viscosities of tinning oils will be reported in another communication.

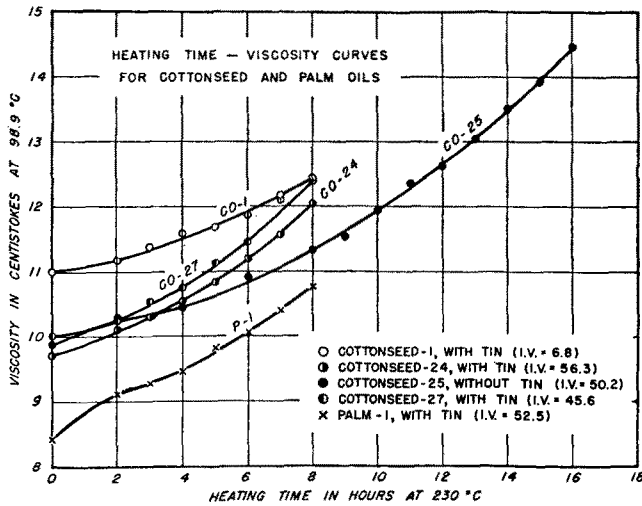


FIG. 4. Effect of heating on the viscosity of hydrogenated cottonseed oils and palm oil.

Reference to Figure 4 reveals the fact that while hydrogenated oils differ in initial viscosity, they all approach a common viscosity after about eight hours of heating and it is therefore immaterial what degree of hydrogenation is used so far as this property is concerned. In the case of the highly hydrogenated cottonseed oil (CO-1, I. V. 6.8) the viscosity increase per unit time of heating is less than in the case of the less highly hydrogenated oils but this slight advantage is offset by its greater hardness, higher melting point, and inferior oxide-removal properties. The higher initial viscosities of the hydrogenated oils is particularly advantageous in the tinning process since these oils may be used without the preliminary heating customarily required with fresh palm oil.

Effect of flux. While the actual quantity of flux, carried by the steel strip into the palm oil is small, it is conceivable that it might operate catalytically to promote break-down of the oil; consequently, the effect of zinc chloride on the volatility, fluxing properties, and free fatty acid formation of the palm oil substitutes was investigated.

Small amounts of anhydrous zinc chloride were added to palm oil, acid-free palm oil, and hydrogenated cottonseed oils, after which they were heated for 16 hours at 240-250°C. in the presence of surface-oxidized tin buttons. The oils darkened more readily in the presence of the flux than in its absence, but the oils were improved with respect to the removal of the tin oxide. Zinc chloride also seemed to retard polymerization, as the treated oils were less viscous than similar oils which were heated without addition of zinc chloride. The tin buttons after heating in the zinc chloride-treated oils possessed bright, shiny surfaces, and those from the synthetic oils appeared to have less oxide film than the buttons from the palm oil baths.

A similar heating test was made using various samples of the hydrogenated cottonseed oils to which 0.1 percent of anhydrous zinc chloride had been added in ether solution. Control samples, containing similar amounts of ether were also heat-treated in the same manner. It was again noted that while the oils in contact with zinc chloride gave better oxide removal than the untreated oils, they also darkened more read-

ily and exhibited greater losses in weight owing to volatilization. Zinc chloride flux apparently has a beneficial effect in facilitating the removal of tin oxide, but it also accelerates the breakdown of the oil and shortens its life in the tin pot.

Effect of free fatty acid. In view of the claims which have been made concerning the effect of free fatty acids on the action of palm oil in the tinning operation, the effect of such acids in the hydrogenated oils was investigated. It was assumed that the addition of free fatty acids to the hydrogenated oils would tend to make them more nearly resemble palm oil in composition and behavior in the tin bath. Palmitic and oleic acids were incorporated with the hydrogenated oils by simple mixing and by heating the mixture for five hours at 250°C. in the presence of 0.5 percent lead oxide. Also the effect of free fatty acids generated in the oil by Twitchellization was investigated. The fatty acids were generated in the oils by passing steam into a mixture of the oil in an aqueous solution of sulfonated phenylstearic acid (0.5 percent) until the free fatty acid concentration corresponded approximately to that of virgin palm oil.

Thirty-gram samples of the oils were then heated for 48 hours at 240-250°C. in the presence of surface-oxidized tin buttons as previously described. The results are summarized in Tables 13 and 14.

TABLE 13
Effect of Free Fatty Acids on Loss of Oil During Heating at 240-250°C. in the Presence of Tin

Oils	Loss in weight on heating 30 gm. samples of oil		
	16 hours	32 hours	48 hours
	Grams	Grams	Grams
Palm.....	6.06	9.88	12.84 ^a
Hyd. cottonseed ¹ + palmitic acid and mono-palmitin (mixed).....	3.87	6.95	9.40
Hyd. cottonseed ¹ + 8 percent palmitic acid (mixed).....	5.44	7.97	10.56
Hyd. cottonseed ¹ + 8 percent palmitic acid (heated).....	6.70	11.64	17.25 ^b
Hyd. cottonseed ¹ + 8 percent oleic acid (mixed).....	3.69	5.49	7.07
Hyd. cottonseed ¹ + 8 percent oleic acid (heated).....	4.55	8.18	12.01 ^b
Hyd. cottonseed ¹ (Twitchellized).....	3.84	5.87	7.60
Hyd. cottonseed ¹	1.67	4.92	6.57
Hyd. cottonseed ² (Twitchellized).....	5.00	7.87	10.29

¹ Iodine value 56.3.

² Iodine value 45.6.

^a Extremely viscous.

It is obvious from the results recorded in Tables 13 and 14 that free fatty acids are readily removed by distillation at the temperature prevailing in the tin bath, and consequently their addition to the hydrogenated oil is of no advantage. Furthermore, the rapid distillation of the acids precludes any unusual effective action on the tin oxide films. Oils differing widely in their initial contents of free fatty acids tend to approach the same value on prolonged heating, since heating has the effect, on the one hand, of developing free fatty acids in low acid oils, and, on the other hand, of removing free fatty acids by distillation from oils of high acid content. It is, therefore, evident that the greater volatility losses exhibited by palm oil result primarily from its high initial free fatty acid content. It is also apparent that the amount of free fatty acid in an oil should not permanently affect its utility in the hot-dip tin-

TABLE 14
Effect of Heating Oils at 240-250°C. in the Presence of Tin
on the Formation of Free Fatty Acids

Oils	Free fatty acid content of heated oil			
	0 hours	16 hours	32 hours	48 hours
	Percent ¹	Percent ¹	Percent ¹	Percent ¹
Palm.....	9.50	1.22	0.76	1.30
Hyd. cottonseed ² + palmitic acid and mono-palmitin (mixed).....	9.31	0.74	1.16	0.60
Hyd. cottonseed ² + 8 percent palmitic acid (mixed).....	7.85	0.90	1.23
Hyd. cottonseed ² + 8 percent palmitic acid (heated).....	8.25	3.24
Hyd. cottonseed ² + 8 percent oleic acid (mixed).....	7.48	0.96	2.56
Hyd. cottonseed ² + 8 percent oleic acid (heated).....	7.80	1.0
Hyd. cottonseed ² (Twitchellized).....	8.11	1.65	0.92	1.08
Hyd. cottonseed ³ (Twitchellized).....	9.50	1.08	0.90	1.18
Hyd. cottonseed ¹	0.04	1.19	1.00	0.91

¹ Calculated as palmitic acid.

² Iodine value 56.3.

³ Iodine value 45.6.

ning operation, since an oil of any given free fatty acid content will approach equilibrium with regard to the rate of acid formation by thermal breakdown of the oil and the rate of its removal by distillation from the tin bath.

Efforts were made to evaluate the effect of the molten tin upon the free fatty acid content and its rate of formation in palm oil during heating. Samples of the oil (400 ml.) were heated at 230-231°C. with and without oxidized tin buttons in an electrically heated, insulated bath. Small samples were withdrawn at intervals and the free fatty acid content was determined. The results of these determinations are presented in Figure 5 from which it may be seen that the decrease in the content of fatty acids of all the

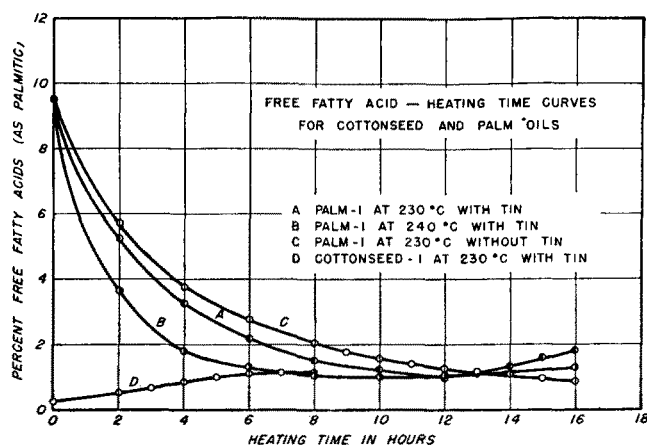


FIG. 5. Effect of heating on the free fatty acid content of palm and hydrogenated cottonseed oils.

palm oils is very rapid during the first eight hours of heating. The fatty acid content of the palm oils heated at 230°C. decreased rapidly in the presence of tin and remained at a minimum value for several hours of heating, after which it began to increase again. On another sample of palm oil heated at 230°C. in the absence of tin, a similar decrease in free fatty acid was observed during the first eight hours of heating. This was followed by a period in which the free fatty acid content remained constant,

and another period in which a gradual decrease in fatty acid content occurred. A third sample of palm oil similarly heated at 240-241°C. in the presence of tin exhibited the same phenomenon as was observed at the lower temperature.

The sample of highly hydrogenated cottonseed oil (I. V. 6.8) treated in the same manner exhibited a slight but steady increase in free fatty acids during the first eight hours of heating. It is significant to note that regardless of initial free fatty acid content and conditions of heating, all of the oils approached a minimum free fatty acid content after approximately 13 hours of heating. Additional results will be reported in a subsequent publication on the mechanism of free fatty acid formation in tin bath operations.

Based on the results of the investigation reported above, several types of hydrogenated cottonseed oils were prepared and submitted to interested tin plate producers for further testing and evaluation. Considerable interest was evinced in these products, and specifications were prepared for the procurement of a satisfactory substitute oil for the replacement of palm oil in the tin bath. These specifications are given in Table 15, together with the corresponding properties

TABLE 15
Specifications for a Hot-Dip Tinning Hydrogenated Cottonseed Oil
and Corresponding Properties of Sumatran Palm Oil

	Cottonseed oil	Palm oil
Melting point, C.° (Capillary tube).....	40-45	25-34
Free fatty acid, percent (as oleic).....	0.1-0.5	10.46
Flash point, F.° (ASTM Cleveland open cup method).....	615-620	480.0
Fire point, F.° (ASTM Cleveland open cup method).....	680-685	560.0
Viscosity, centistokes at 98.9°C.....	10.0-10.5	8.4
Iodine value (Wijs).....	48-52	52.5
Thiocyanogen value, (AOCS method) ¹	49-51	43.5
Saturated acids, percent (Lead soap-alcohol method).....	40-45	49.9
Oleic acids, percent ²	55-60	
Normal oleic acid, percent.....	35-40	39.2
Iso-oleic acid, percent.....	18-23	0.0
Linoleic acid, percent ²	1-2	10.9

¹ Modified by the use of four parts of carbon tetrachloride to six parts of glacial acetic acid solution to dissolve the oils.

² Values calculated from the iodine and thiocyanogen values using the empirical thiocyanogen values of Riemenschneider, Swift & Sando, Oil and Soap 18, 203 (1941).

of a sample of Sumatran palm oil currently in use in the tin bath of one of the largest producers of tin plate. The use of a hydrogenated cottonseed oil conforming to the above specifications should provide maximum performance in the tin bath, and the increased length in useful life of this oil compared with palm oil should compensate for the difference in cost between the two oils under all but the most abnormal economic conditions.

Summary

Work has been reported on the development of a substitute for palm oil, which is used to the extent of about 40 million pounds annually in the production of tin and terne plate, and in the cold reduction process for the manufacture of strip steel. This investigation included an examination of the chemical

and physical properties of virgin and spent palm oils, especially with respect to the effect of these properties on the action of these oils in the tin bath.

Based on the results of this investigation, and on information and cooperation of various producers and consumers of tin plate, efforts were made to produce from cottonseed oil a product which would be equal to or superior to palm oil with respect to its performance in the tin bath.

It was found that, of the various types of selectivity hydrogenated cottonseed oils which were investigated, one having an iodine number of approximately 50 was best adopted as a palm oil substitute for use in the tin bath. The effect of heating hydrogenated cottonseed oils on the viscosity, rates of free fatty acid formation, rate of volatilization, effect of flux, and other factors were determined.

Based on these results and further evaluation of the hydrogenated cottonseed oils by various producers of tin plate, specifications were formulated covering a product which it is believed will provide optimum performance and maximum life in the tin bath.

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A Nomograph for Emergent-Stem Correction of Mercury-in-Glass Thermometers

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Because it is not always possible to take temperature readings under the condition of total immersion of the mercury column, it is the usual practice to dip the bulb of the thermometer and a part of the stem in the material under investigation and then to make the necessary correction for the temperature observed. The formula (1) for calculating this correction (S) is $an(T-t)$, where a is a factor representing the relative expansion of mercury in glass, n is the number of degrees of mercury emergent from the bath, T is the observed temperature, and t is the average temperature of the emergent mercury column. The latter is measured by means of a second thermometer the bulb of which is placed about three-fourths the distance down the exposed mercury column. Although the value of a depends upon the kind of thermometer glass and the magnitude of the temperature being measured, its average value is taken as 0.00016 for Centigrade temperature and 0.00009 for Fahrenheit.

An occasional need for making temperature corrections probably does not justify the use of short cuts, but in those laboratories where many temperature readings are a part of routine control or of research, any aid which will reduce the labor of making calculations obviously is desirable. This aid may take one or more forms.

Assuming an average value of a , it is a simple matter although a somewhat laborious procedure to construct a stem-correction table covering the possible range of n and $(T-t)$. Better still, it is easier to con-

struct a nomograph which is much more convenient than a table and gives without undue extrapolation the required values to a degree of accuracy demanded even by an exacting worker.

Stem-correction tables may be found in standard reference works and elsewhere,* but apparently no mention has heretofore been made of a nomograph for this purpose. Such a nomograph has therefore been constructed and found to be of great help in this laboratory. It is reproduced here in the hope that it will facilitate the work of others.

In the construction of this nomograph, the equation (1) in question, was rewritten as $\log S = \log a + \log n + \log (T-t)$. Since a is constant, it contains only two variables, n and $(T-t)$. They were laid on two parallel logarithmic scales as shown at the x and y axes. The range for n and $(T-t)$ was taken as 10 to 100° C. Since the scales for x and y are made identical, a third axis (z), midway between them and parallel to both, gives the correction. The scale on z was constructed by taking $a = 0.00016$, a value which holds good for a range of temperature of 0 to 300° C.

It is not necessary, however, to construct a longer scale to cover this range; any value between 0 to 10° C. and 100° to 300° C. can be made to fall on the scale by a shift of the log cycle and a shift in the decimal point on the correction factor. Thus the x

* The widely published tables of Rimbach (*Z. Instrumentenk.*, **10**: 1890, 153) have but a limited application because his data were obtained by the use of a special thermometer in a distillation apparatus.¹