Studies on Congo Palm Oil

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PALM OIL is obtained from the pericarp of the fruit *Elaeis guineensis*. The palm tree is believed to have originated in Africa and still grows abundantly on the Atlantic coast of Equatorial Africa (1).

Production and Properties

Three wild species are known in the Congo. (a) *Dura* or *Macrocarya*, (b) *Tenera*, and (c) *Pisifera*. Fruits of the species Dura yield 10–25% oil. The Dura kernel is enclosed in a thick shell surrounded by a thin layer of pericarp, which constitutes only 20–50% of the fruit. Tenera, discovered some 30 yr ago, produces fruit with a very thin shell and a thick layer of pericarp constituting 80% of the fruit. The yield of oil in this species ranges between 35–40% of the fruit. Pisifera is a sterile variety seldom producing fruit.

Prior to 1944, cultivation of Tenera proved difficult because a pure Tenera seed segregated into 50% Tenera, 25% Dura, and 25% Pisifera. Studies at the Institut National d'Etudes Agronomigue au Congo Belge (INEAC) showed that Tenera is a hybrid obtained by crossing Dura with Pisifera (2). During recent years, through large scale hybridization, it has been possible to cultivate Tenera. In most of the Congo plantations, the controlled cultivation of Tenera is now well established.

Plantations in the Congo Republic extend up to 1000 miles from the coast along the Congo River and its tributaries. Palm trees (144 per hectare) yield up to 3 tons of oil per annum, whereas one hectare of natural palmeries would, in practice, yield only a a few hundred kilos.

Extensive studies have been carried out in order to improve the yield and quality of the oil. This program was carried out by the "Société Coopérative CONGOPALM" during the years 1951–1956 with the generous assistance of the Belgian Government Institution IRSIA. As a result, processing methods were greatly improved and a pure stable oil of low FFA content was produced. Present research on palm oil is centered mainly on improvement in refining and bleachability.

Composition. Palm oil is a semi-solid fat. The average composition of Congo palm oils is given in Table I. For these oils, which have normally an FFA content of between 1 and 4%, the temperature of complete fusion lies between 37 and 43C and the drop point between 26 and 30C. The iodine value ranges between 50 and 55.

Palm oil from wild trees possesses almost the same composition as the plantation oils; its unsaponifiable content is higher, the carotene percentage sometimes exceeding 0.1%.

Palm oil contains only a small portion of poly-unsaturated fatty acids and shows excellent stability against oxidation. The low amount of fully unsaturated triglycerides of high melting point makes it a first class raw material for margarine manufacture.

Processing. Bunches of wine red fruits develop in the leaf avils and are harvested when ripe. Oil from fresh ripe fruit contains only about 0.2% free fatty acid (as Palmitic acid). The fruit contains an active lipase with the result that, in bruised or damaged fruit the FFA value rapidly increases up to 50% within a few hours. Special care therefore is taken while harvesting as well as processing. The freshly harvested fruit is heated in sterilizers under 40 lb/sq in. of pressure for 1 hr. This step is necessary to destroy the lipase (3,4). The bunches are then stripped in drum or beater strippers. The stripped fruit is digested and the pericarpic oil is separated by basket centrifuging, water washing (wet process), or in hydraulic or screw presses, modern oil mills treating Tenera fruit favor screw presses. The crude oil is water washed, centrifuged and dried before shipment.

TABLE I

Average Composition of Congo Plantation Palm Oils

Myristic acid	1.2– 2.4%
Palmitic acid	41.0–43.0%
Stearic acid	4.4– 6.3%
Oleic acid	38.0–40.2%
Linoleic acid	9.9–11.2%
Linolenic acid	traces
Triglycerides S-S-S	about 6%
Triglycerides S-S-U	about 48%
Triglycerides S-U-U	about 43%
Triglycerides U-U-U	about 3%
Carotenes	.04–.06% (40% alpha–60% beta)
Sterols	about .03%
Tocopherols	about .05% (mainly alpha)
Phosphatides	.05–.1%

Palm oil from ripe, fresh very carefully processed fruit shows superior bleachability and generally good refining properties. Palm oil of this quality is produced now in the Congo, it is called SPB palm oil.

The *matte*, obtained from the bunches, is separated into fibers which are used as fuel, and palm nuts which are cracked to obtain the kernels. These contain a lauric type oil, totally different from palm oil. Although the extension of pure Tenera plantations results in a diminution in kernel content, original processes for their recovery have been elaborated in the last few years.

The transport of palm oil from the Congo is carried out entirely in bulk, by barges, railway tankcars and then by steamship. It takes 2–3 months before the oil reaches its destination.

Stability with respect to free fatty acids. Until a few years ago, the FFA content of palm oil increased by 1–2% during storage and transport. This was generally thought to be due to micro-biological or enzymatic action.

It has been shown that the action of the microorganisms is negligible once the oil is extracted from the fruit, and the increase in acidity is due solely to a chemical reaction between the triglycerides and the water dissolved in the oil. The kinetics of this reaction, in which the fatty acids act as catalysts, is now well known (5) and corresponds to the following formula:

$$k\Theta = 2.3 \log \frac{A}{A_0}$$

where k = velocity coefficient
Θ = acidification time
A_0 = initial FFA content
A = FFA content after a time Θ

If Θ is given in 10-day units, $k = 0.12$ at 60C and doubles for every 10C temperature increase.

The formula is applicable in general to all glyceridic oils and the velocity coefficients are nearly identical for palm oil, tallow, or groundnut oil when the oils are saturated with water.

Development of FFA is controlled by dehydration of the oil and avoidance of any contact with moisture. Hydrolysis stops almost completely if the moisture content is kept below 0.1%. As a result, the increase in FFA content between production centers and final destination is now completely negligible.

Melting point and plasticity. The study of hydrolysis also showed that with FFA content of up to 12% only diglycerides are formed. The monoglyceride content rises only subsequently (Fig. 1). This rapid increase in diglyceride content strongly influences the plasticity of the oil. Furthermore the plasticity does not follow a regular variation with FFA increase, but a pronounced minimum of hardness occurs at about 7% FFA content. At 5% FFA content for instance, spreadability threshold is 5C lower than at 2% FFA content (Fig. 2). This is due to eutectic formation between di- and triglycerides; the phenomenon persists even after alkali neutralization of the oil, which, under normally mild conditions, does not affect the plasticity (6). The plasticity is also dependent on the fatty acid composition of the oil and particularly on the total unsaturation. However, under the climatic conditions existing in the equatorial regions of the Congo, this variation is extremely small and has practically no influence on the plasticity. On the other hand, in badly damaged or rotten fruit, the diglyceride content does not vary in proportion to the acidity since hydrolysis goes on as far as the monoglyceride stage in that case.

Owing to the generalized controlled harvesting and processing, the plasticity and melting point of Congo palm oil vary solely with the FFA content.

Bleachability

Refining of palm oil can be divided into three main stages: (a) Neutralization, (b) Bleaching, and (c) Deodoration. Palm oil offers no special problems concerning neutralization and deodorization; it can be processed almost exactly like other edible fats, but major care has to be given to the bleaching problem, since the carotenoid pigments confer a dark orange color to palm oil. The average of 0.5 g of carotene per kilo of crude oil corresponds to an optical density of 110 as measured in a Lumreton 400-A Photocolorimeter with blue filter (420 $m\mu$). The residual color, after refining, must lie between 1 and 1.5 Red as measured in a 5¼ in. cell of a Lovibond Tintometer. Pronounced yellow shades can be tolerated for margarines provided they are not accompanied by greenish or brownish off-colors.

Bleaching Process. In practice, palm oil bleaching is usually carried out by a thermal treatment preceded or followed by a bleaching earth treatment, and also by the combination of these treatments.

Heat bleaching: By heating palm oil above 180C the carotene pigment is destroyed quite rapidly, yielding a yellow product nearly a thousand times less colored. The carotene destruction rate doubles for every 20C temperature increase (Fig. 3). Thus simple heating, under inert gas blanket, for 60 min at 220C or 3 min at 300C destroys over 98% of the total carotene present (7) and gives residual color value between 1 and 3 Red Lovibond in 5¼ in. cells for good quality SPB oils.

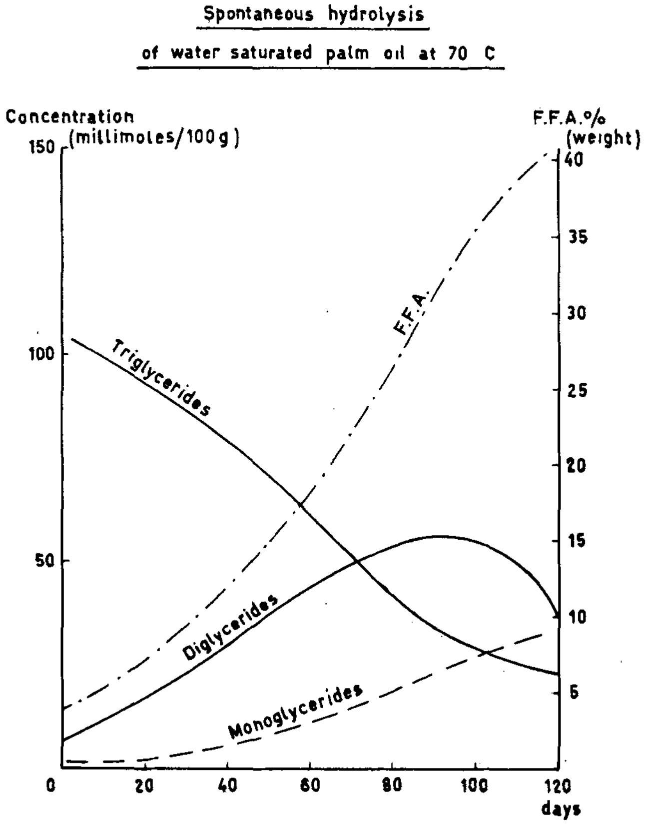

FIG. 1.

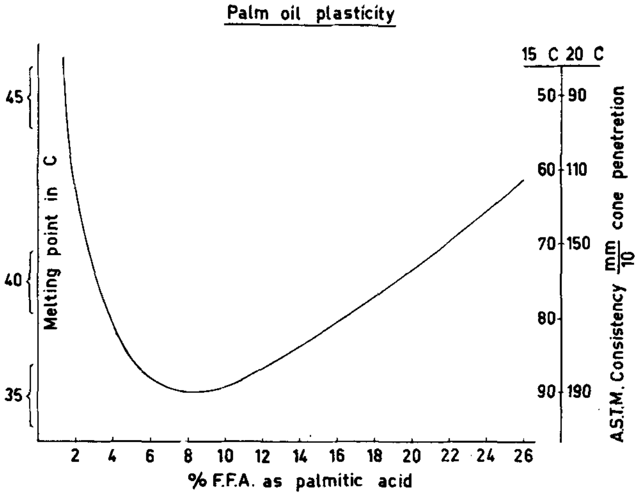

FIG. 2.

Earth bleaching: Acid activated bleaching earth not only adsorbs the carotene pigments but also catalyzes their chemical destruction. This effect becomes more pronounced with increasing temperatures. The "combined" bleaching treatment (utilization of bleaching earth at relatively high temperatures) is based on this property. Earth bleaching at low temperatures (100C) is considered a rather uneconomical process.

Factors influencing the bleachability of palm oil. Bleachability varies widely with the palm oil sample. Plantation

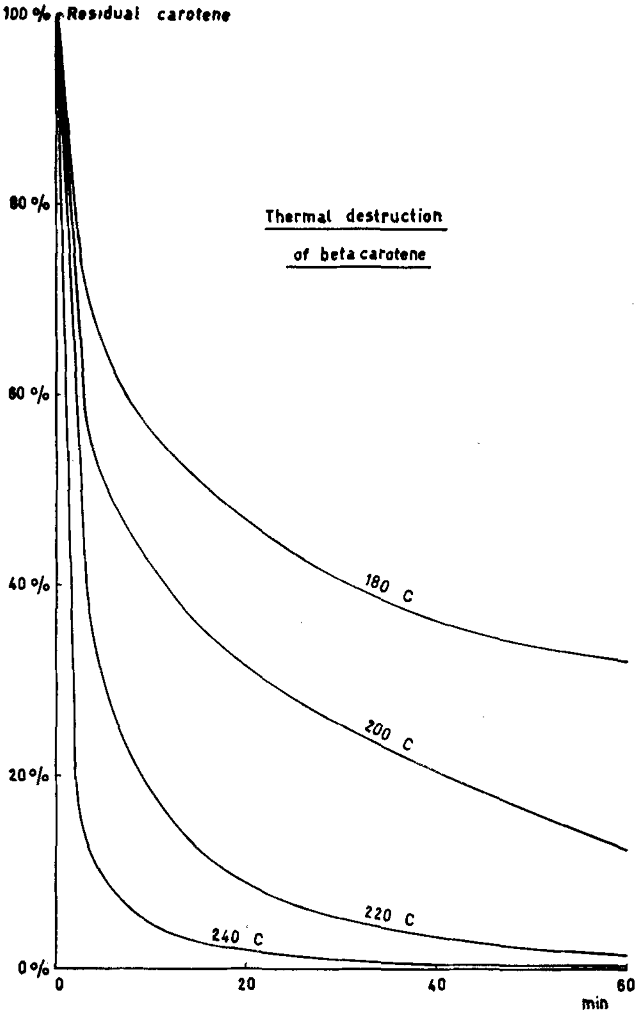

FIG. 3

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TABLE II
Relationship Between Bleachability and Oxidation with Limited Quantities of Air
Sample: Crude S.P.B. palm oil.

ml air for 100 ml palm oil	Oxygen oil v/v	Peroxide value millieq/kg	Residual color after standard bleaching test: Heat bleaching 60 min at 240C. Optical density at 420 mμ	Residual color after standard bleaching test: 1% Bleaching earth 20 min. at 110C. Lovibond color 5¼ in. cell
Blanc	....	4.5	.24	1.7 Red
After 50 hr at 80C in sealed phial				
+ 0 ml air	....	3.9	.27	1.8 Red
+10.6 ml air	.02	3.7	.27	1.9 Red
+31.5 ml air	.06	7.6	.29	2.1 Red
+98.5 ml air	.20	10.9	.29	2.3 Red

oils are on the whole, superior to oils from wild trees. It was found that for the production of good quality palm oil, the FFA content, oxidation, as well as contamination by external elements such as heavy metals and dirt, must be kept in check.

FFA content: Oils with high FFA content have poor bleaching qualities. For low temperature earth bleaching (around 100C) this is directly related to the competition in adsorption on the bleaching earth between the FFA (even the mono- and diglycerides) and the pigment. Residual colors are also affected by the FFA content of the oil in pure heat bleaching. The nature of the influence of the FFA content is not known. It is possible that certain concomitant phenomena occur which also depreciate the bleachability, such as lipoxydase action (8) parallel to the lipase splitting which gives rise to the FFA in the unsterilized fruit.

Oxidation: The oxidation of unsaturated fatty acid chains gives rise to compounds which react during heat bleaching with carotene. Colored substances are formed which are much more difficultly adsorbed on the bleaching earth than carotene itself.

Following test illustrates this influence of the oxidation process.

Palm oil was oxidized at 80C for 50 hr in the dark and subsequently bleached. The bleaching test used was also standardized and consisted of heat bleaching at 240C during 60 min under carbon dioxide, followed by earth treatment at 110C with 1% acid activated bleaching earth for 20 min (also under carbon dioxide blanket).

Table II shows the influence of oxidation with limited quantities of air. The oil was stored in sealed glass flasks and subsequently bleached.

A number of oxidized substances are believed to react with the carotene, however no correlation was observed between the amount of peroxides, hydroxyls or epoxides and the intensity of the residual color.

Influence of enzymatic oxidation on bleachability (7) has only a limited effect in modern oil plants, since the fruit is speedily autoclaved after harvesting.

Heavy metals: Copper and its alloys are very prejudicial to the bleachability of palm oil. Thus a copper rod dipped into crude palm oil for 50 min only at 80C, raises the residual color from 2.0 Red Lovibond to 4.8 Red Lovibond.

Iron also influences the bleachability as illustrated by Table III. The amount of metal soaps (40 ppm as iron) added to the oil in this test exceeds four to five times the amounts found usually in ordinary oils. SPB palm oils contain even less heavy metals (around 5 ppm). The heavy increase of residual color of ferric oleate compared to ferric stearate is doubtless due to the oxidation of the oleate itself induced by the iron present. A test comparing the influence of ferric and ferrous soaps gave results which were not clearly reproducible.

TABLE III
Influence of Iron Soaps on Bleachability

	Residual color after standard bleaching test[a] Lovibond 5¼ in. cell		
SPB palm oil	2.2 Red	22 Yellow	.2 Blue
Id. + ferric stearate (40 ppm iron)	5.9 Red	49 Yellow	3.0 Blue
Id. + ferric oleate (40 ppm iron)	19.0 Red	49 Yellow	9.9 Blue

[a] Standard bleaching test: 60 min at 240C, followed by 20 min at 110C + 1% bleaching earth.

TABLE IV
Polymer Formation in Palm Oil by Heating Under Abnormally Severe Conditions

Sample: Neutralized dried palm oil sealed under nitrogen	Temperature	Heating time	Polymers as linoleic acid
Palm oil	300C	5 hr	2.7%
Palm oil	250C	57 hr	1.5%
Palm oil + 5% acid activated bleaching earth	300C	5 hr	11.2%
Palm oil + 5% acid activated bleaching earth	250C	57 hr	14.3%

Adequate precautions are taken in the mills now as regards the apparatus and pipes which are in contact with the oil, and from which all copper and copper alloys have been proscribed.

Structural modifications of palm oil resulting from severe bleaching conditions. Owing to the presence of unsaturated compounds in the glycerides, prolonged heating at high temperatures can induce formation of heat polymers as well as trans-isomers.

Tables IV and V show the amount of polymers and trans-isomers formed by heating neutralized palm oil under nitrogen in a sealed glass phial at 250 and 300C for several hours.

It is quite evident that these very drastic experimental heating conditions are never even approached in practice, but they made it possible to accentuate the phenomenon in order to permit its measurement.

Polymers: The polymerization rate of the unsaturated fatty acid chains in palm oil doubles approximately every 10C (8). Owing to the fact that the temperature coefficient of carotene destruction is lower than the polymerization coefficient, a temperature increase produces a higher polymer content for a same bleaching effect. Acid activated bleaching earth strongly catalyzes both the thermal destruction of carotene and the heat-polymer formation at high temperature. Thus about 10 times more polymers were formed in palm oil heated in the presence of 5% bleaching earth as compared to the same oil heated under equal time and temperature conditions but without bleaching earth (Table IV).

It is possible in such a "combined treatment" to attain practical bleaching conditions which reduce the polymer formation to a minimum by reducing the heating time and temperature as well as the amount of bleaching earth. Extrapolations of the heat polymer formation results towards time/temperature relationship, such as attained in practice, are in fair agreement with others (9). At temperatures about 220–240C only traces of polymers are formed.

Trans-isomers: The trans-isomerization was measured by infrared spectroscopy which reveals the bending vibration of the trans-bond at 969 cm^{-1}. The figures in Table V are the result of comparing the integrated absorption intensities (10) of the sample and of elaidic methyl ester. (The latter was prepared from oleic methyl ester, trans-isomerized with

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TABLE V
Trans-Isomer Formation in Palm Oil by Heating Under Abnormally Severe Conditions

Sample: Neutralized dried palm oil sealed under nitrogen	Temperature	Heating time	Trans-isomers as elaidic acid methyl ester[a]
Palm oil	300C	5 hr	4.3%
Palm oil	250C	11 hr	1.3%
Palm oil	250C	57 hr	6.3%
Palm oil + 5% activated bleaching earth	250C	11 hr	18.5%

[a] Measured by I. R. Spectroscopy: Peak at 969 cm^{-1}. I. R. Spectrophotometer Hilger H 800. KBr prism. Slit .17 mm at 1100 cm^{-1}. ASC 35, G 3, D 3, V 30. Path length .1 mm. Solvent CS_2.

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TABLE VI

Residual Color Obtained by Different Bleaching Processes on Neutralized SPB Palm Oil
(FFA of the crude oil: 2.1%)

Bleaching conditions	Heat bleaching			Earth bleaching		Combined *treatment*	Pre-earth treatment		Post-earth treatment	
	1	2	3	4	5	6	7	8	9	10
Temperature	240C	220C	210C	105C	100C	150C	105C	100C		
Bleaching time	60 min.	60 min	60 min	45 min	45 min	45 min	20 min	20 min		
% Bleaching earth	....	....	......	5%	5%	2%	2.5%	2.5%		
FFA content	.13%	.13%	.13%	.12%	.22%	.21%	.11%	.09%		
Optical density at 420 mμ	.38	.78	.35	2.5	6.15	3.0	4.1	17.4	cf 2	cf 3
Lovibond 5¼ in.	.3R,30Y	1R, 49Y, .4 Blue	5.5R, 49Y	4R, 49Y	6R, 49Y	3R, 49Y	8R, 49Y			
Temperature							210C	220C	100C	100C
Bleaching time							60 min	60 min	20 min	20 min
% Bleaching earth							....	....	.5%	.5%
FFA content							.11	.10	.10	.10
Optical density at 420 mμ							.70	.50	.50	3.0
Lovibond 5¼ in.							2.2R,45Y	1R, 30Y	.5R, 22Y	3R, 49Y
Residual color in Lovibond 5¼ in.	.3R,30Y	1R, 49Y, .4 Blue	5.5R,49Y	4R, 49Y	6R, 49Y	3R, 49Y	2.2R, 45R	1R, 30Y	.5R, 22Y	3R, 49Y

selenium catalyzer and recrystallized until pure.) (Purity was checked by the melting point.)

The palm oil heated to 300C as well as to 250C in presence of bleaching earth acidified partly during heating. The interfering acid peak at 976 cm^{-1} was eliminated from the I.R. spectrum by methylating these samples with diazomethane.

Table V shows that acid activated bleaching earth catalyzes also strongly the trans-isomerization.

In practice the trans-isomerization is reduced to negligible amounts by decreasing the time/temperature relationship.

Bleaching in practice. A variety of tests were performed in order to determine the best practical bleaching conditions, to avoid any structural modification of the palm oil. The aim was to check the application of especially mild conditions for bleaching of palm oil to be used in margarine manufacture.

Residual color: Successful bleaching under mild conditions can only be achieved with good quality oils (such as SPB palm oils). These oils, which have been produced in the Congo as a result of the present investigations, have a low FFA content (below 2%) and possess good bleachability. Oils of more average quality give rise to brown and greenish off-colors which need a more intensive treatment; bad quality oils cannot be bleached properly at all.

The tests summarized in Table VI illustrate clearly the temperature effect in both the heat treatment and the earth treatment. They show that heat treatment at only 220 or even 210C, preceded or followed by earth treatment with a small amount of bleaching earth at 100 or 105C gives quite satisfactory results. The important difference between the bleaching earth effect at 100 and 105C is perhaps due to the interference of water on the adsorption of the pigments.

The "combined treatment" leads also to reasonable residual colors. It should be borne in mind that increasing of the temperature in presence of acid-activated bleaching earth favors the polymerization and trans-isomerization of the oil. Under present experimental conditions though, these effects are negligible.

Heat bleaching has to be carried out in stainless steel apparatus, whereas earth bleaching and the "combined treatment" can be performed in ordinary steel.

Keepability: SPB palm oil is fairly stable. Naturally occurring tocopherol acts as an anti-oxidant. Other factors which influence the keepability of the refined oil are: (a) The quality of the crude oil. In SPB palm oils, for instance, care is taken to avoid oxidation and heavy metal contamination in view to improve the bleachability. (b) The refining conditions. Bleaching operations are controlled to give an oil with low amounts of pro-oxidant elements and at the same time retain as much as possible the natural antioxidants.

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• *Local Section News*

Southwest Section

The Southwest Section held its last meeting of the current season with the traditional Ladies Night. The program consisted of two sound, color films: "Essential Oils of Africa," by Ernest Guenther of Fritzsche Bros., Inc.; and the second on the perfume industry in France. Ben Kapp, of Process Chemicals Company, gave a short talk on the "Psychology of Perfumes." Appropriately enough to this type of program, samples of perfume were distributed to all members and guests.

The following officers were elected, May 9, for the 1963–64 term: R. W. Atwood, Chairman; C. P. McClain, Vice Chairman; F. C. Woekel, Secretary; W. J. Park, Treasurer; and J. B. Michaelson, Program Chairman.

Tentative schedule of meetings for the coming year are: September 12, November 14, January 9, 1963, March 12, and May 14.

North Central Section

On Wednesday, May 1, the North Central Section closed their scheduled meetings with a Ladies Night Dinner Meeting at the Builder's Club in Chicago. Featured speaker was C. W. Powe, Jr., Whirlpool Corporation, with an intriguing title, "Out, Damned Spot?" Mr. Powe is experienced in the testing of laundry detergents and processes and in talking about them; he has also authored a number of technical papers on the subject. He compared the different methods of measuring how clean your clothes are . . . affording a better understanding of advertising claims of the soap commercials.

New officers (listed in the April Journal) were installed for the coming year.

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