detected on general examination of the cores, particularly with regard to crumbling at the edges.

Attention is called to the high binding strength of tung oil. This oil was not seriously considered by us as the price differential usually favors linseed oil. Increasing production of American tung oil may change the aspect of this situation.

Aside from the binding properties rubberseed oil mixes easily with the core sand, does not gum up the core box, has good green bond and produces cores of satisfactory porosity. The baking time and temperature is the same as with linseed oil; in fact, other work seems to indicate that in the initial drying stages rubberseed oil absorbs oxygen at a faster rate than linseed. This will be made the subject of a subsequent paper. We could detect no adverse effects due to the high free fatty acid content of the oil.

The Availability of Rubberseed Oil

In a communication to the authors from the Chemical Division of the U. S. Bureau of Foreign and Domestic Commerce it is stated that certain quantities of the oil have been imported into this country, mostly for experimental purposes. There are, however, no official figures giving the amounts brought in.

Considerable interest has been manifested by the rubber planters and government agencies in Malaya, Dutch East Indies and Ceylon regarding the commercial exploitation of the oil. A large excess of seed over that required for replanting is now being produced and if a large commercial outlet is developed the oil could undoubtedly be produced in sufficient quantity. It should be procurable at a price substantially lower than that asked for linseed oil.

Our laboratory work leads us to the conclusion that para rubberseed oil may be substituted for linseed oil in foundry core binders. We hope that it will be an incentive for large scale foundry trials.

The authors are indebted to Dr. G. S. Jamieson, Chemist in Charge, Oil, Fat and Wax Laboratory, U. S. Bureau of Chemistry and Soils, for helpful suggestions concerning this paper.

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Oil and Fat Analysis by the Thiocyanogen Method

Chemical Division of The Procter and Gamble Company, Ivorydale, Ohio
By W. S. MARTIN and R. C. STILLMAN

Introduction

THIOCYANOGEN $(SCN)_2$ behaves chemically much as a halogen midway between bromine and iodine in activity. Its reactions with certain of the unsaturated fatty acids are, however, unique. Those reactions peculiar to this reagent form the basis of a very convenient method of fat analysis first outlined by Kaufmann.

It has been rather well established that oleic, elaidic, erucic and brassidic acids add $(SCN)_2$ mol for mol exactly as they add the halogens. It is probable that their isomers and homologues do likewise. This addition takes place easily and quantitatively in the case of either the free fatty acids or their glycerides.

Linoleic acid takes up $(SCN)_2$ at only one of its two double bonds, while it absorbs halogens, of course, at both of them. Kaufmann has published evidence to prove the reliability of this reaction, though some others have disputed his statement that this reaction is truly quantitative for all the isomeric linoleic acids which may be present in a natural oil.

The behavior of linolenic acid when treated with $(SCN)_2$ has been a matter of some question. Kimura found that the methyl ester of a purified linolenic acid absorbed between 1 and 2 mols of $(SCN)_2$ per mol of acid. Kaufmann, however, has published data to show that the "isolinolenic" acid, as he termed it, occurring naturally in linseed oil adds two mols of $(SCN)_2$ per mol of acid, while the linolenic acid made by debromination of the hexabromide of this "isolinolenic" acid shows a totally different behavior. Kaufmann's thiocyanogen analysis of linseed oil, whether strictly accurate or not, seems to have given fairly consistent and reasonable results in the hands of several investigators.

The original method for the thiocyanogen analysis of fats was outlined by Kaufmann.[3, 4, 5] Some modifications of this method were suggested by Gerber,[21] Stadlinger,[6, 20] and Barbour.[8] Despite the fact that there are numerous references to the method in the literature, there has never been a detailed analytical method for the thiocyanogen analysis published in English nor does there seem to have been much attention given to standardization of the method. The method here outlined in detail is that of Kaufmann, including, however, all the suggested modifications which experiments showed to be desirable, and such other changes as were indicated by the experience of 18 months' continuous use of the method.

Analysis of a Fat by the Thiocyanogen Method

I. *Reagents*

1. Lead Thiocyanate
2. Anhydrous Acetic Acid
3. Bromine

1. *Preparation of Lead Thiocyanate* $(Pb(SCN)_2)$

100 g. of the finest C.P. Neutral Lead Acetate $(Pb(Ac)_2 3H_20)$ is dissolved in 500 ml. of distilled water. Likewise 100 g. C.P. Potassium Thiocyanate (KSCN) is dissolved in another 500 ml. of water. The lead acetate solution is added slowly to the potassium thiocyanate solution with constant stirring. The precipitated $Pb(SCN)_2$ is filtered out in a Buchner filter and washed successively with distilled water, alcohol and ether. The $Pb(SCN)_2$ is dried as much as possible by drawing air through the filter cake, then it is stored in a desiccator over P_2O_5 for 8-10 days. This $Pb(SCN)_2$ should be a greenish or yellowish white crystalline product; if it is at all discolored, it must be discarded. Pre-

cipitated $Pb(SCN)_2$ can be kept for a period not exceeding two months.

2. Preparation of Acetic Acid

Acetic acid is suitably and conveniently dehydrated by refluxing with a slight excess of acetic anhydride. Two liters of C.P. glacial acetic acid (99.5-100.0%) and 100 ml. of acetic anhydride (90-100%) are mixed in a 3 l. round bottomed flask. A large test tube through which cold water circulates is set in the neck of the flask to serve as a condenser and the mixture is refluxed in an oil bath for 3 hours. After the acid has cooled to room temperature it is stored in clean, dry glass-stoppered bottles sealed with paraffin.

II. *Preparation of a 0.2 N Solution of Thiocyanogen.*

For the preparation of one liter of solution: 50 g. of dry $Pb(SCN)_2$ is suspended in 500 ml. of anhydrous acetic acid; 5.1 ml. of C.P. bromine is dissolved in another 500 ml. portion of the acetic acid. Two glass-stoppered bottles of 2 or 3 l. capacity are used for the purpose. The bromine solution is added to the $Pb(SCN)_2$ suspension slowly, in small portions, and the mix is shaken vigorously between each addition until the solution is decolorized. After all the bromine has been added, the precipitated lead bromide and the excess lead thiocyanate are allowed to settle out; the solution is then filtered as rapidly as possible, avoiding long exposure to the air. A 13 cm. Buchner funnel, qualitative paper and two 2 l. pressure flasks are used for this filtration. The entire solution is filtered by suction into one of the flasks, then the funnel containing the paper and cake is transferred to the other flask and the solution is refiltered. It should be perfectly clear after the second filtration. The solution is stored in glass-stoppered brown bottles and is kept in a dark place at 60° to 70° F. It is important that the temperature of storage be kept low.

III. *The Determination of the Thiocyanogen Value.*

The sample is weighed accurately in a dry 125 cc. glass-stoppered Erlenmeyer flask. 25 ml. of a 0.2 N solution of $(SCN)_2$ is pipetted into the flask, and the flask is held in the dark at 65° to 70° F. for 24 hours. The size of the sample should be such that the excess $(SCN)_2$ is 50% to 60% of the total $(SCN)_2$ added, i.e., 100% to 150% of that absorbed by the fat, though a somewhat larger excess appears to do no harm. At the end of 24 hours, 1 g. of dry powdered KI is added to the flask and the flask is swirled rapidly for 1½ to 2 minutes. 30 ml. of distilled water is added and the liberated iodine is titrated with a 0.1 N solution of $Na_2S_2O_3$, using starch as indicator. At least three blanks are stored side by side with the samples. The solution is titrated also at the beginning of the 24 hour period. If the titration of a 25 ml. portion of solution drops more than 0.2 ml. of 0.1 N $Na_2S_2O_3$ in 24 hours, the solution has decomposed too rapidly, and the results will not be accurate.

$$\text{Thiocyanogen Value} = \frac{(\text{Blank-titration})\ (\text{Normality } Na_2S_2O_3)\ (12.69)}{\text{Weight Sample}}$$

This is expressed as % "Iodine" in order to put it on the same basis as the Iodine Value.

IV. *Calculation of Fat Composition.*

The following formulae apply when both the Iodine Value and the Thiocyanogen Value of an oil or fat have been determined, and it is desired to express the percentage of glycerides of the various fatty acids which are present.

It is assumed that oleic and linoleic acids are the only unsaturated acids present.

I.V. = Iodine Value of oil
T.V. = Thiocyanogen Value of oil
S.G. = % Saturated Glycerides
O.G. = % Oleic Glycerides
L.G. = % Linoleic Glycerides

L.G. = 1.154 (I.V. — T.V.)
O.G. = 1.162 (2 T.V. — I.V.)
S.G. = 100.0 — (L.G. + O.G.)

When the iodine value and the thiocyanogen value of the mixed fatty acids are known, the percentages of the fatty acids in the mixed fatty acids are expressed as follows:

L.A. = 1.104 (I.V. — T.V.)
O.A. = 1.112 (2 T.V. — I.V.)
S.A. = 100.0 — (L.A. + O.A.)

V. *Notes on the Determination.*

1. All glassware and chemicals used in preparing standard $(SCN)_2$ solutions must be absolutely dry. Glassware is rinsed with chromic acid cleaning solution, distilled water, alcohol and ether, then dried for 1 to 2 hours at 105° C.

2. Any unnecessary exposure of $(SCN)_2$ solution to air, light, or heat must be avoided.

3. Kaufmann's original method recommends pouring the reaction mix into an aqueous KI solution before titration. The KI solution was not added to the $(SCN)_2$ because he feared that even a momentary contact with water might cause polymerization of $(SCN)_2$. By maintaining the KI always in excess he avoided this danger. Some other investigators claim that a rapid addition of a concentrated KI solution causes no appreciable loss of $(SCN)_2$ by polymerization. The authors have found, however, that the use of dry KI is superior to both these techniques, since, if water is not added before the decomposition of the free $(SCN)_2$ is complete, there is no danger of polymerization from this cause, and at the same time Kaufmann's rather hazardous transfer of the reaction mix from the reaction flask is also eliminated.

4. Hard fats are sometimes difficult to dissolve in the $(SCN)_2$ solution. The authors have found that if such a fat is melted, then cooled quickly to room temperature and the solution added while the fat is still in the form of a supercooled liquid, the fat dissolves much more easily. It may be necessary to use solutions more dilute than 0.2 N with some fats.

5. The 0.2 N solution of $(SCN)_2$ should be discarded as soon as its rate of decomposition exceeds 0.2 ml. of 0.1 N $Na_2S_2O_3$ per 25 ml. blank in 24 hours. A carefully prepared solution is usually sufficiently stable for analytical use over a period of at least a week.

Discussion of Application of the Thiocyanogen Method of Fat Analysis

For fats which contain no acids more unsaturated than linoleic, this method offers a rapid and convenient way of estimating the proportions in which oleic, linoleic and saturated acids are present. The analysis is not difficult for one practised in its technique and with proper care the thiocyanogen values of most oil samples can be reproduced to ± 0.2 units.

Compared with the Twitchell and other lead salt separations of the saturated fatty acids, the greater convenience of the thiocyanogen method is obvious. Both methods were used on a large number of samples, some hydrogenated and some not, and the thiocyanogen analyses ran consistently 2-5% higher in saturated and linoleic acids than did the corresponding Twitchell analyses. This agrees closely with the published results of Barbour and others. The Twitchell analysis tends to give low results for saturated and linoleic acids. It is probable,

therefore, that, of the two, the thiocyanogen analysis is the closer approximation of the true composition of a fat. Regardless of whether or not the method is absolutely accurate, its practical usefulness has been proved in over a year of continuous laboratory use.

The accuracy of thiocyanogen analysis of linseed oil has been a matter of discussion. We have had no occasion to apply the method to oils of that type.

The thiocyanogen method has proved to be particularly valuable for the analysis of fat mixtures containing oils such as coconut, palm, etc., which contain large percentages of low molecular weight saturated fatty acids. The Twitchell method is almost valueless in these cases, because the lead salts of these lower saturated acids are appreciably soluble in alcohol and ether. The method of Bertram, of course, can be used, but it is even more tedious than the Twitchell separation. The thiocyanogen method, with proper modifications of the formulae for calculating the fat composition, also serves nicely for the analysis of oils like mustard oil which contain high molecular weight unsaturated fatty acids forming lead salts insoluble in alcohol.

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The laboratories of D. W. Haering & Company, Chicago, continuing their research on corrosion problems have developed a highly efficient formula for controlling brine tank corrosion which utilizes colloidal glucosides to control electrolysis by buffer effect. The formula is adjusted to establish proper pH on initial treatment and the buffer action of the glucosides maintains this pH over extended periods of time without frequent additions of material. Oxygen is eliminated through direct chemical combination, a feature of all of the company's anti-corrosion products.

Japan—Fish Oil Industry

The fish oil industry of Japan is an important one, in that it provides fats for use in various manufacturing enterprises, and the residue from which the oil is produced becomes available for fertilizer in the farming districts. The principal producing districts are the Hokkaido, Niigata, and Ishikawa prefectures. By far the largest portion of the oil produced comes from the island of Hokkaido. The following figures show production of fish oils for the past five years:

	1927 Pounds	1928 Pounds
Sardine oil	36,418,511	28,614,209
Herring oil	10,688,677	10,470,529
Cod oil	1,880,006	2,013,316
Whale oil	6,963,580	7,723,058
Shark oil	4,027,284	6,051,777
Other fish oils	7,608,416	6,578,359

	1929 Pounds	1930 Pounds	1931 Pounds
Sardine oil	48,079,855	55,488,567	69,531,640
Herring oil	6,364,153	10,271,165	10,845,781
Cod oil	1,930,057	1,649,894	1,952,370
Whale oil	7,957,385	8,222,856	5,735,238
Shark oil	6,706,318	7,288,308	7,630,531
Other fish oils	7,883,006	5,714,381	4,030,714

Fish oil in Japan is produced by crude methods, the fish being boiled and then placed in open framework boxes, varying in capacity from 2½ to 4 cubic feet. The boxes are then placed in a press, which delivers the oil into barrels placed below the boxes. The oil is separated from the water, which also collects in the barrels simply by scooping it off as it rises to the top. The oil is then placed in second hand kerosene tins for shipment to its destination. Practically no fish oil is refined in the localities where it is produced.

Considerable quantities of fish oil are shipped to foreign countries, but due to the lack of tank steamers for this purpose the export of oil is not entirely satisfactory. The oil which is exported is shipped in barrels and tins, usually second hand kerosene tins packed two to the case. However, few firms are interested in exporting oil.

There are eight principal fish oil refiners and manufacturers in Japan. In manufacturing hardened oils these firms use principally herring and sardine oils. They produce from 4,500 to 5,000 tons of this oil a month. Production of hardened fish oil during 1928, 1929, and 1930 are as follows (1931 not available): 1928, 58,247,774 pounds; 1929, 87,881,699 pounds; 1930, 92,826,936 pounds.

In January, 1932, the manufacturers of hardened fish oil organized a Sales Association under the name of the Tokyo Kokwa-in Hanbai K. K. This association fixes sales prices, both for the domestic and export market.

Domestic consumption of hardened oils at present is estimated to be about 2,500 to 3,000 tons per month, the remainder being export, largely to Europe.

Mitsui Bussan Kaisha are the principal exporters of fish oils and hardened fish oils in this market.