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Jack Harris Returns to Nuchar

The Industrial Chemical Sales Co., Inc., has been forced into a program of expansion of its sales service and development personnel through the amazingly rapid acceptance and demand for its activated carbon "Nuchar" and its precipitated chalk "Snowtop" in so many fields, and because of several new products which the Industrial Chemical Sales Company, Inc., now has ready for marketing.

And so John P. Harris has returned again to take charge of the Chicago office at 205 W. Wacker Drive. His constructive, aggressive leadership assures the same success in the new fields which has marked this company's previous sales expansion campaigns in the middle west under his direction.

Mr. Harris will be assisted by W. A. Welch, formerly chief chemist of the Industrial Chemical Sales Co., Inc., who is already well known for his development work.

Mr. Harris and Mr. Welch cordially invite all out-of-town OIL & SOAP chemists to make their offices, Suite No. 1511 of the Engineering Building, 205 W. Wacker Drive, their headquarters when visiting in Chicago.

A Study of The Composition of American Tung Oil

By ROBERT S. McKINNEY and GEORGE S. JAMIESON

A CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE

Tung oil is obtained from the seeds of two trees, Aleurites fordii, and A. montana, both indigenous to China. In comparatively recent years cultural experiments, chiefly with A. fordii, which is the principal source of the Chinese oil of commerce, have been undertaken in various more or less semi-tropical regions in Africa, Australia, New Zealand and North and South America. In numerous instances these plantings have been made with seed produced in Florida, the pioneer state in the attempt to establish a tung oil industry in the United States. Up to the present time more than 40,000 acres have been planted to tung trees in the States of Alabama, Florida, Georgia, Louisiana, Mississippi and Texas.

Since 1928 the seeds (commercially called nuts) not required for planting, produced in Florida, have been crushed for oil by the Alachua Tung Oil Company near Gainesville. Another mill at Bogalusa, Louisiana, is about to begin operation. Plans also are under way in several other places for the establishment of plants to handle the locally produced seed.

For those who desire a knowledge of the development and history of this new American industry, attention is called to publications*, which may be found in many libraries.

The present investigation was made on a sample of expressed Florida tung oil furnished by Henry A. Gardner of the National Paint, Varnish and Lacquer Association. As determined by the regular Hanus method, this oil gave an iodine number of 261, which is notably higher than the value (217) reported by Van Loon[1] as the "true" iodine value of tung oil. To calculate the unsaturated acids of tung oil from the thiocyanogen study it is essential to know the "true" iodine value of tung oil. Therefore, it was desirable to redetermine the "true" iodine value of tung oil. Although theoretically substitution is less likely to occur with the Hanus iodine bromide solution which we used than with the Wijs iodine chloride solution used by Van Loon, yet the following experiment was conducted to see if substitution could be the factor causing the high value which we obtained.

Several pairs of identical quantities of tung oil were subjected to the action of 25 cc. of Hanus reagent for one-half hour. To one of each pair potassium iodide and water were added, and the iodine absorbed was determined in the usual manner. About 70 cc. of water was added to the other one of each pair and the mixture extracted repeatedly with 35-cc. portions of chloroform until all the free halogen was removed, leaving the halogen acids in the aqueous layer. This procedure was repeated with blank determinations, using 25 cc. of the Hanus solution in the absence of tung oil. In the latter cases it was

[1] Ir. J. Van Loon, Farben Ztg. 1767–69 (1930).

*Questions and Answers on Tung Oil Production in America. H. A. Gardner. Circ. 446, National Paint, Varnish and Lacquer Association.
Trade Promotion Series No. 133, entitled "Tung Oil," by C. C. Concannon. U. S. Department of Commerce.
Miss. State Department of Agriculture Bul. No. 1. "Tung Oil," by E. Squire Brooks.
Florida Agricultural Experiment Station Bul. No. 247, "Variations in the Tung Oil Tree," by H. Mowry (1932); and Bul. No. 221, "The Tung Oil Tree," by W. Newell, H. Mowry and R. M. Barnette.

found very difficult to remove the last traces of bromine from the aqueous solution with chloroform. Consequently, a few drops of amylene were added, and then a final extraction with chloroform was made. In all cases the separated aqueous solutions were further acidified with nitric acid, the halogens precipitated with silver nitrate and finally weighed in the usual manner. To convert any iodide into the bromide, the silver salts were then heated to the fusion point in an atmosphere of bromide until no further loss in their weight took place. The silver salts of the blank determination consisted of a mixture of bromide and iodide, in which the former predominated, but in the experiments in which the Hanus reagent reacted with the oil the silver salt consisted entirely of the bromide. In the data which follow only the final weights of the silver bromide are given:

EXPERIMENT 1—0.1127 gram of oil gave an iodine number of 259 and 0.3645 gram of silver bromide from the aqueous solution. The blank analysis gave 0.3475 gram of silver bromide. The difference between the two weights of silver bromide, 0.0170 gram, is equivalent to an iodine number of 10.2, due to substitution. Deducting this from 259 gives the iodine number of 249.2 for the oil.

EXPERIMENT 2—0.1229 gram of oil gave in iodine number of 263.4 and 0.3835 gram of silver bromide. Of this quantity, 0.0360 gram were due to substitution, and this is equivalent to an iodine number of 18.4. Correcting the original value, 263.4, gives an iodine number of 244.6. The average of the two results corrected for substitution is 246.9.

As is well known, the standard Wijs procedure as applied to tung oil gives iodine values which range from 162 to 173, the majority of samples giving values from 164 to 167. The Rosenmund-Kuhnhenn method[2], the reacting agent of which is bromine in a solution of glacial acetic acid to which has been added *pyridine* and concentrated sulphuric acid, gave an iodine number of 162. We found that the reaction was not affected by increasing the excess of reagent, nor was it affected by extending the reaction time longer than the one-half hour used in the determination.

The quantities of saturated acids were determined by the Bertram[2] procedure as the lead salt ether method is not applicable in the presence of elaeostearic acid or the closely related acid found in Brazilian oiticica oil. The results obtained were (1) 4.45 per cent, (2) 4.34 per cent, and the average 4.40 per cent of saturated acids. Also, the total insoluble fatty acids in our sample of tung oil were determined and found to be 95.43 per cent, the average of two closely agreeing results. Van Loon[1] also determined the insoluble fatty acids in his sample of tung oil and found 91.2 and 91.5 per cent. In view of the large quantity (3.4 per cent) of volatile acids, etc., reported by Van Loon, a weighed portion of our sample was heated for one and one-half hours at 135° in an atmosphere of carbon dioxide, but no loss or gain in weight occurred.

The thiocyanogen value[2] of the oil was determined in duplicate, giving 82.6 and 82.9, the average being 82.75. With this value and the corrected iodine value, it is possible to calculate the percentages of unsaturated acids and also the saturated acids present in the oil, since the unsaturated acids consist, in so far as anyone has been able to find, only of elaeostearic and oleic acids as glycerides. Using the formula—

$$261.78x + 86.04y = 24690$$
$$87.26x + 86.04y = 8275$$
$$x + y + z = 99.53$$

x = 94.1 per cent of elaeostearic and glyceride

y = 0.6 per cent of oleic acid glyceride

z = 4.8 per cent of saturated acid glyceride

The alkaline solution of the sodium salt of tung oil fatty acids was oxidized according to the method of Lapworth and Mattram[3], and a total quantity of dihydroxystearic acid was finally obtained, which was equivalent to 0.8 per cent of oleic acid in the oil. No tetrahydroxystearic acid, which would be evidence of the presence of linoleic acid, could be detected.

A summary of the results obtained during the present investigation is given in Tables 1 and 2.

[2]G. S. Jamieson, "Vegetable Fats and Oils."

[3]Lapworth and Mottram, J. Chem. Soc. 127, 1628 (1925).

[4]Z. Nahr. Genussm. 46, 154 (1923).

TABLE I.

Refractive index at 25° C.	1.5165
Saponification value	193.6
Iodine number (Rosenmund-Kuhnhenn)	162.0
Iodine number (Hanus) corrected	246.9
Thiocyanogen value (Kaufmann)	82.75
Insoluble fatty acids, per cent	95.4
Unsaturated acids,* per cent	90.6
Saturated acids, per cent	4.40
Unsaponifiable matter, per cent	0.47
Iodine number of unsaponifiable matter	74.0

*Calculated using the thiocyanogen value.

From this investigation it appears evident that tung oil contains only a small percentage of oleic acid. The amount found (0.8 per cent) agrees with the approximate value (0.6 per cent) obtained from the thiocyanogen study. Van Loon estimated that his sample of tung oil contained 13.6 per cent of this acid, but this is based on the true iodine number being 217 for the tung oil in question, as is also the calculated percentage of elaeostearic acid (72.9 per cent). It is believed that the value which we found (89.5 per cent) for the elaeostearic acid content of tung oil, based upon the iodine number of 246.9, together with the thiocyanogen value of 82.75, is very close to the amount present, as this same calculation gives 4.56 per cent of saturated acids, a value which is in close agreement with that (4.40 per cent) obtained by the Bertram oxidation method. The true iodine value of this tung oil is therefore 246.9. With the Rosenmund-Kuhnhenn reagent the reaction is complete in thirty minutes. It is independent of concentration of reagent or any further time of reaction, only two of the three double bonds being attacked. This method, therefore, has the advantage over the Wijs reagent, whose reaction is influenced by time, temperature and excess of reagent. On the other hand, the Hanus reagent reacts readily with the three linkages of the elaeostearic acid glyceride present in tung oil and, as indicated by our experiments, a small but notable amount of substitution also takes place.

TABLE 2
Composition of the Oil

	Per cent	*Van Loon*	*Per cent*
Elaeostearic acid as glyceride	94.10	Elaeostearic acid	72.8
Oleic acid** as glyceride	0.8	Oleic acid	13.6
Saturated acids as glyceride	4.6	Saturated acids	4.9
Unsaponifiable matter	0.47	Volatile substances	3.4
		Glyceryl radical	4.7
		Unsaponifiable matter	0.5

**Calculated from the amount of dihydroxystearic acid obtained.