# A Study of the Ellis-Jones Maleic Anhydride Method and Its Use In Testing Tung Oil*

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The present scarcity and high price of tung oil lend interest to methods of testing tung oil and tung oil substitutes, particularly if these methods are useful in evaluating tung oil for industrial use and in detecting its adulteration. Numerous halogen absorption methods have been suggested for this purpose. Recently, Von Mikusch and Frazier (1) have reviewed these methods and have offered a modified Hanus procedure to determine the total unsaturation of tung oil and of tung oil substitutes. Although this method and other methods such as hydrogenation and the method of Rosenumnd-Kuhnhenn are of interest from a theoretical standpoint, it is well-known that the intrinsic value of tung oil and similar oils depends upon their content of unsaturated acids having conjugated double bonds as well as upon their total unsaturation.

The procedure of Kaufmann and Baltes (2) for determining the diene value of tung and similar oils, from their reactions with maleic anhydride, appeared to offer a method of determining the amount of unsaturated conjugated fatty acids in these oils. However, several investigators (3,4,5) found that many hydroxylated compounds containing no conjugated double bonds reacted with maleic anhydride and gave significant diene values. They also reported that blown linseed, perilla, and soybean oils and even blown oleic acid gave sizable diene values. It was shown by McKinney and Jamieson (6) that elaeostearic acid does not react quantitatively with maleic anhydride in this procedure but only to 86.6 per cent of the theoretical amount, and that the elaeostearic acid content of a tung oil can be determined by dividing its diene value by 78.4, the determined diene value of pure elaeostearic acid. However, this procedure does not lend itself readily to routine laboratory use because of the necessity of sealing and opening the tubes.

The method of Ellis and Jones (7) for determining the maleic anhydride value of tung oil appeared not only to offer all the advantages of the Kaufmann procedure, but also to be well suited for routine laboratory use. Unfavorable reports (8) in regard to the accuracy of this method have probably prevented its use by the tung oil and allied industries.

Samples of tung oil obtained from tung fruits and kernels which had been subjected to elevated temperatures sometimes yielded higher iodine values by the Wijs procedure than did the oils from the unheated tung fruits and kernels. This increase in iodine value was attributed to an isomeric change in the structure of the unsaturated acids in the oil from a conjugated to a non-conjugated system. An effort was made to detect this change by means of the Ellis and Jones maleic anhydride procedure.

First attempts to use this procedure were unsatisfactory, due to the inability to obtain reproducible maleic anhydride values on tung oil with it. Probably the variation in values was due to loss of maleic anhydride during the refluxing, notwithstanding the precautions taken to prevent this. It was somewhat difficult to properly lubricate, with finely powdered graphite, the ground glass joint employed to connect the condenser with the flask, and it might have leaked. Moreover, rather vigorous bumping, with attendant possibility of loss of vapors, occurred during the refluxing. Later these difficulties were overcome. Half-way immersion of the reaction flask in a sand bath prevented bumping during the refluxing period. Satisfactory results have been obtained by lubricating the ground joint between the flask and condenser with a very thin layer of graphite grease together with a sufficient quantity of graphite powder to give a smooth layer; a condenser having a water-cooled joint was used. Satisfactory results were also obtained without the use of any lubricant on the joint between the flask and the condenser.

## Method

*Reagents Required.* (1) An approximately 6 per cent solution of maleic anhydride in toluene. This is prepared by dissolving 60 g. of maleic anhydride (melting point 52 to 54° C.) in warm toluene and diluting the cooled solution with toluene to one litre. This is prepared at least a day before it is required and must always be filtered through a fast filter paper immediately before use.

(2) Normal sodium hydroxide solution. This is standardized against 1 g. of pure maleic acid dissolved in 100 ml. of distilled water using phenolphthalein as the indicator.

*Procedure.* A sample of approximately 3 g. of tung oil is accurately weighed into a dry 250 ml. flask having a ground glass neck for connecting with a reflux condenser. Twenty-five ml. of the freshly filtered maleic anhydride solution is pipetted into the flask and the flask is connected with its condenser. The reaction flask is immersed half way in a sand bath to prevent bumping during the refluxing period. The contents of the flask are kept boiling very gently for three hours after which the flask is allowed to cool for a few minutes. About 5 ml. of distilled water is poured into the top of the condenser and the contents of the flask are then boiled gently for 15 minutes. The flask is then allowed to cool to room temperature; 5 ml. of ether is poured into the flask through the condenser, followed by 20 ml. of water. The flask is now detached from the condenser and its contents are poured carefully into a separating funnel having a ground glass stopper. The flask is

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rinsed—first with 20 ml. of ether used in three portions and then with 25 ml. of water, also in three portions. The funnel is shaken and allowed to stand until separation has taken place. The lower aqueous layer is run into a flask of 250 ml. capacity for titrating. The residual liquid in the funnel is further extracted successively with 25 ml. and 10 ml. of water and the water extract added to the 250 ml. flask. The mixed aqueous extracts are then titrated with normal sodium hydroxide, using phenol-phthalein as the indicator. A blank experiment is conducted in the same manner throughout to determine the concentration of the maleic anhydride solution used. The "maleic anhydride value" (M. A. V.) is obtained from the following equation:

$$\text{M.A.V.} = \frac{12.692 \times \text{ml. Normal alkali used}}{\text{Weight of sample in g.}}$$

Table I shows the maleic anhydride values and Wijs iodine values obtained on two samples of tung oil from kernels which had been artificially dried and one from undried kernels.

TABLE I

| Source of Tung Oil | Iodine Value (Wijs) | Maleic Anhydride Value |
|---|---|---|
| Undried tung kernels | 166.0 | 75.31 |
| Half kernels dried 1 hr.—105°C. | 166.3 | 72.86 |
| Ground kernels dried 1 hr.—105°C. | 165.9 | 72.86 |

These results are in accord with the results of Bradley and Richardson (9) who reported that heating tung fatty acids effected an isomerization, resulting in a decrease of conjugation, as well as polymerization. This effect was detected by means of a spectrograph.

Probably the most useful test on tung oil from a quality standpoint is the Browne (A.S.T.M.) heat test (10). However, it is rather difficult to maintain the heating bath at exactly 282° C. and it is well known that small variations from this temperature cause appreciable differences in the results, expressed in time required for gelation. It has been found that the Ellis-Jones maleic anhydride values of tung oils have an inverse relationship to the Browne heat test values, whereas the Wijs iodine values have no relationship to the heat test values. It is believed therefore that it may be possible to substitute the Ellis-Jones procedure for the Browne heat test for tung oils. The values obtained on samples of tung oil examined by the Ellis-Jones maleic anhydride procedure, by the Wijs iodine method and by the Browne heat test are given in Table II.

TABLE II

| Sample | I Value (Wijs) | Maleic Anhy. Value | Result of Browne Heat Test |
|---|---|---|---|
| | | | (Time required for gelation) |
| Tung Oil—1938 Crop | 162.9 | 67.66 | 9 min. 10 sec. |
| Tung Oil—1938 Crop | 164.4 | 68.94 | 9 min. 5 sec. |
| Solv. Extr. Tung Oil (1935) | 165.4 | 65.85 | 10 min. 15 sec. |

A previous study (6) of the Kaufmann diene procedure (2) showed that under the conditions specified the reaction of maleic anhydride with alpha elaeostearic acid is not quantitative but only 86.6 per cent of the theoretical. Therefore, it appeared desirable to ascertain if the reaction proceeded to the same equilibrium point when carried out by the Ellis-Jones procedure. Pure alpha elaeostearic acid was prepared according to Nicolet (11). Table III contains the

TABLE III

| Sample | Maleic Anhydride Value Determination | | Wijs Iodine Value Determination (1 hr.; 20°C.) | | Thiocyanogen Value Determination | |
|---|---|---|---|---|---|---|
| | Wt. sample gm. | MAV value | Wt. sample gm. | I value | Wt. sample gm. | SCN value |
| | ALPHA-ELAEOSTEARIC ACID | | | | | |
| 1* | 2.2774 | 89.0 | | | | |
| | 1.8165 | 89.4 | | | | |
| 2* | 2.1112 | 89.5 | 0.1561 | 189.9 | 0.1233 | 92.4 |
| | 1.9116 | 89.5 | 0.1422 | 190.9 | 0.1599 | 92.1 |
| | 1.8335 | 89.2 | | | | |
| | 2.4707 | 89.8 | | | | |
| 3* | 1.8583 | 90.1 | 0.1350 | 190.8 | 0.1226 | 92.0 |
| | 2.0001 | 89.8 | 0.1398 | 190.6 | 0.1253 | 91.9 |
| 4* | 1.9474 | 89.5 | 0.1229 | 189.2 | 0.0727 | 92.1 |
| | 1.7583 | 89.5 | 0.1183 | 190.7 | 0.0906 | 92.0 |
| | Average | 89.5 | | | | |
| | Theoretical | 91.2 | | 181.0 | | 91.2 |
| | METHYL ESTER OF ALPHA-ELAEOSTEARIC ACID Prepared from acid recrystallized three times | | | | | |
| | 1.6928 | 85.4 | 0.1351 | 181.7 | | |
| | 1.4690 | 85.7 | 0.1356 | 181.8 | | |
| | Theoretical | 86.8 | | 173.6 | | |

* Samples 1, 2, and 3 were recrystallized three (3) times from ethanol, while sample 4 was recrystallized five (5) times.

maleic anhydride values of a number of preparations of alpha elaeostearic acid and its methyl ester. Saponification of the tung oil separation and recrystallization of the acid, and the various tests were all carried out on the same day, in order to minimize the possibility of the acid undergoing any change.

It is apparent from the values in Table III that the reaction of pure alpha-elaeostearic acid with maleic anhydride in the Ellis-Jones procedure proceeds almost to completion (98.1 per cent of theoretical). The elaeostearic acid content of a tung oil sample can be calculated by dividing the found maleic anhydride value of the oil by 89.5 (the maleic anhydride value of the pure elaeostearic acid).

Mixtures of tung oil with linseed oil and with perilla oil were prepared and maleic anhydride values were determined on the individual oils and on the mixtures. Browne heat tests were made on the tung oil and on mixtures containing 80 per cent of tung oil. Table IV shows the results.

The maleic anhydride value obtained for a mixture divided by the maleic anhydride value of the tung

TABLE IV

| Sample | Maleic Anhydride Values 3 g. sample | Results of Browne Heat Test (Time required for gelation) |
|---|---|---|
| Tung oil | 70.59 | 11 min. 10 sec. |
| Perilla oil | 2.04 | |
| Linseed oil | 3.37 | |
| 20% Linseed oil; 80% tung oil | 56.80 | 13 min. 45 sec. |
| 50% Linseed oil; 50% tung oil | 37.62 | |
| 20% Perilla oil; 80% tung oil | 55.83 | 13 min. 45 sec. |
| 50% Perilla oil; 50% tung oil | 36.53 | |

oil (70.6) gives a fair approximation of the per cent of tung oil in the various mixed samples of tung oil with linseed or perilla oil. Calculating from the values obtained, it appears that the presence of 10 per cent of linseed oil in tung oil will lower the maleic anhydride values to 63.8. This value is distinctly lower than the maleic anhydride value obtained in this laboratory on any authentic sample of tung oil. Obviously then, determination of maleic anhydride value may serve as a means for detecting and roughly estimating adulteration of tung oil.

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# Report of the Governing Committee—1941-1942

By letter ballot and at the spring meeting the following matters were considered and decided by the Governing Committee:

### Constitution and By-Laws

It was voted to adopt the final draft of the changes in the By-Laws as submitted by the Committee on Constitution and By-Laws.

It was voted that up to $50 be allowed for printing of proxy cards sent to the membership in connection with the by-law changes.

The Secretary was instructed to insert the date of adoption of amendments to the charter at the head of such amendments when having new copies printed for distribution in the future.

### Financial

The financial report of the Secretary and the Auditor's report were read, discussed and accepted.

It was decided that the fee of $50 for the services of the Auditor for the season 1941-42 would stand as fixed by vote of the Governing Committee.

The Secretary was instructed to obtain a Certified Public Accountant to audit the books and accounts of the society for the year 1942-43 at a fee not to exceed $75.

It was decided that the status of the funds of the Chicago Local Committee and the funds of the Journal, OIL & SOAP, on deposit in Chicago be considered and some satisfactory arrangement made with the banks to record the signature of the Secretary and his authority relative to these funds.

It was voted to hold the $1600 National Union Mortgage Corporation bonds.

The Secretary was instructed to invest the surplus funds of the Society in U. S. Treasury bonds after first consulting with President Mitchell.

### Journal

It was decided that President Mitchell appoint H. L. Roschen as Chairman of the Journal Committee and Editor of OIL & SOAP for 1942-43.

It was voted that J. J. Haney be designated Managing Editor of OIL & SOAP and that he have authority to sign all checks for journal expenditures.

It was voted that J. J. Haney be bonded for $5000.

It was voted that the society continue the advertisement of the society's supplies in the Journal.

It was voted that all members in good standing called into the U. S. armed forces shall have the Journal sent them without charge and that a notice to this effect be published in the Journal.

### Meetings

It was voted that the Thirty-Fourth Annual meeting be held in New Orleans or vicinity on the Thursday and Friday preceding the next annual meeting of the National Cottonseed Products Association. It was suggested that President Mitchell contact the president of the N.C.P.A. relative to the above meeting.

It was decided to dispense with the services of a reporter to record the proceedings of the next Annual Meeting.

The Secretary was instructed to continue the practice of having Committee Reports mimeographed for distribution at the 1943 Annual Meeting.

### Membership

It was voted that all members of the society in good standing who are called into the armed forces of the U. S. be continued as members without having to pay dues.

It was voted that all members who were delinquent and had since paid their dues were reinstated in the society.

### Referee Board

It was voted that the Referee Examining Board for 1942-43 be composed of A. S. Richardson, Chairman; Lamar Kishlar; J. P. Harris; G. W. Agee; and H. S. Mitchell, member ex-officio.

### Secretary

J. C. P. Helm was nominated to the office of Secretary-Treasurer for the year 1942-43.

W. G. McLEOD
H. A. SCHUETTE
H. C. DORMITZER
C. H. COX
LAMAR KISHLAR
J. T. R. ANDREWS
J. J. GANUCHEAU
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