# Potentiometric Method for Determination of Acid, Saponification, and Rosin Acid Values of Tall Oil

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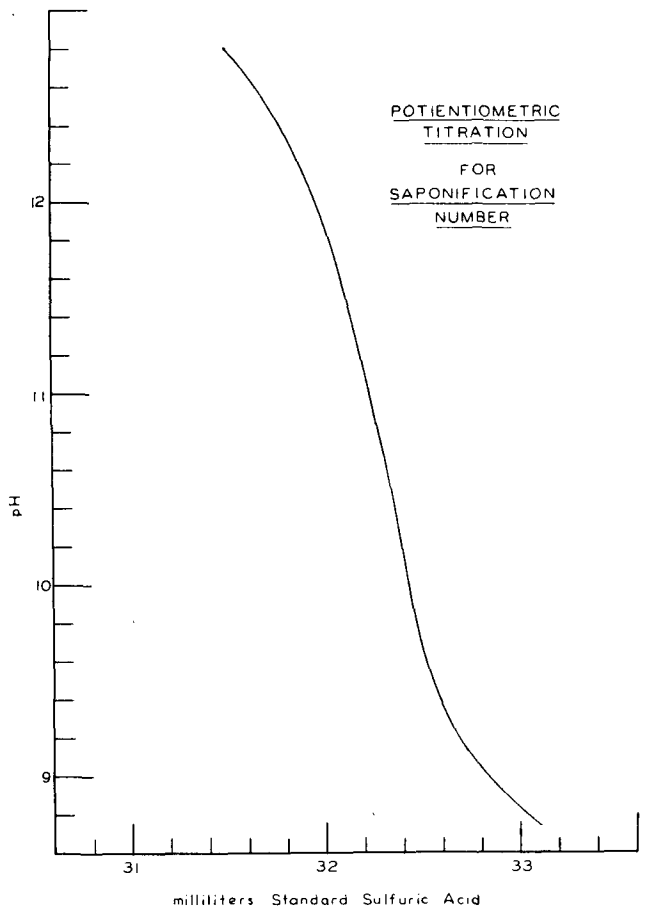
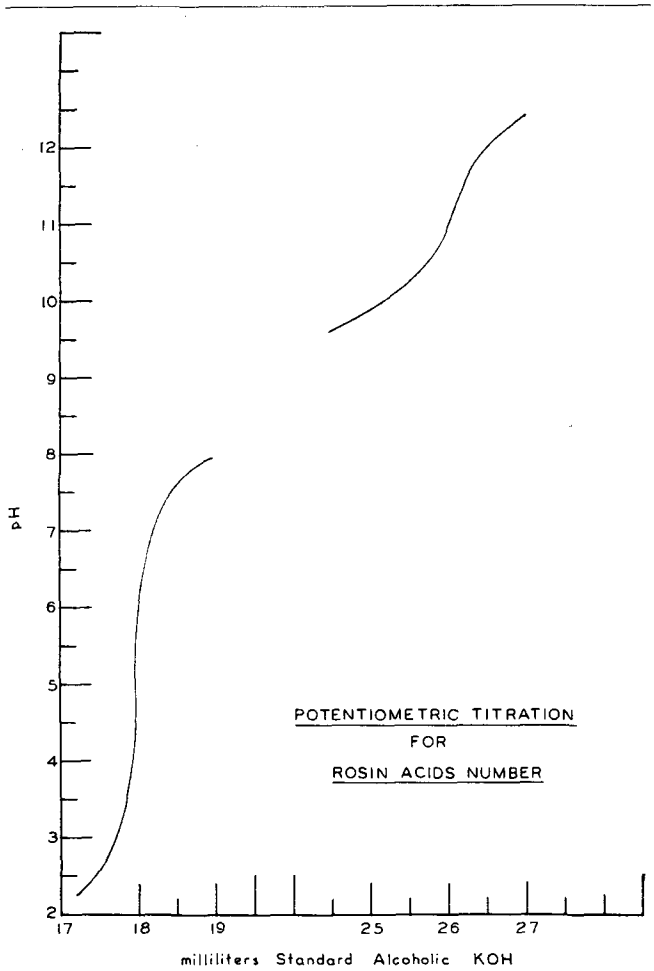
**Introduction**

Tests made on seven different samples of tall oil indicate that the use of a pH meter to determine the end-point in tall oil titrations eliminates the use of a doubtful visual end-point. The procedure given in A.S.T.M. Specification D803-44T can be used and pH 11 taken as the end point for acid value and saponification value. For rosin acid number two end-points are taken at pH 6 and pH 11.

THE difficulty of recognizing a colorimetric end-point in the titration of dark tall oils has plagued the analyst for years. The wide variation in results in A.S.T.M. cooperative tests shows that there is need for a better method. The A.S.T.M. has recently conducted tests using an electrometric end-point determination, and the results will soon be reported. Indications are that the results have been quite satisfactory (1).




Several months ago work was carried on in our laboratories in an effort to eliminate the visual end-point and to substitute an instrumental one. Seven tall oil samples from various sources were used in these experiments. They were:

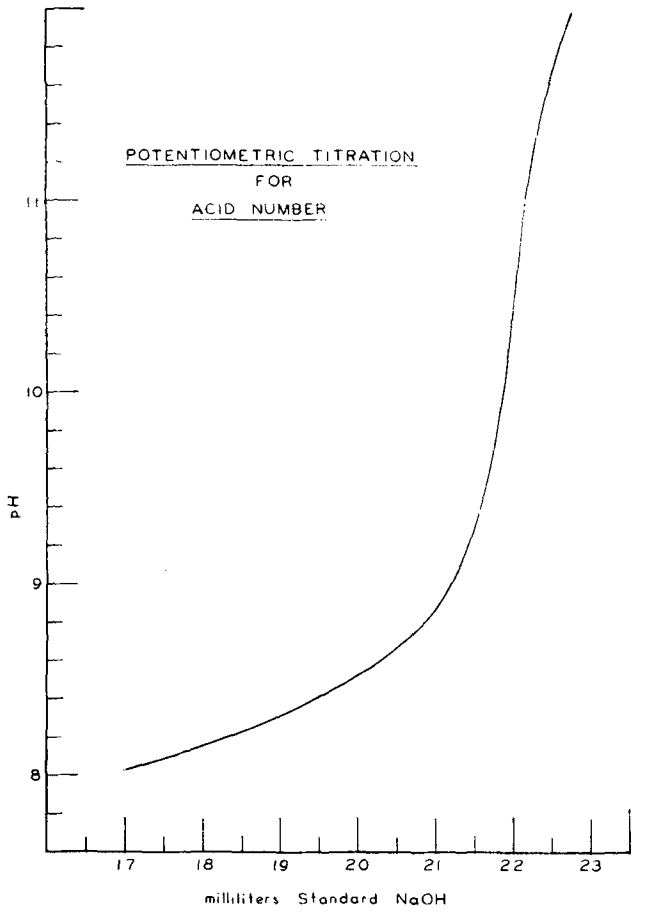



1. Indusoil—West Virginia Pulp and Paper Company.
2. Opoil—National Southern Products Corporation.
3. Facoil CS—National Southern Products Corporation.
4. Facoil FR—National Southern Products Corporation.
5. Ligro—West Virginia Pulp and Paper Company.
6. TOF—Champion Paper and Fibre Company.
7. TOFA—Champion Paper and Fibre Company.

These gave a wide range of color from the very dark Ligro to the relatively light TOFA.

Duplicate determinations of acid number, saponification number, and rosin acid number were made on each sample and were compared with the results obtained by the methods of the A.S.T.M. Specification D803-44T (2). The procedure used in the potentiometric method was identical with that given by the

above specification, the modified Wolff method for rosin acids being used. At the point where the sample was to be titrated the Type E electrodes for high pH of a Beckman Model G pH meter were introduced into the solution contained in a 250-ml. Beaker and the standard solution run in from a buret with vigorous stirring. pH readings were taken at 1 ml. intervals until the break in the curve was approached and at 0.1 ml. intervals until the break was passed. In the case of saponification number titrations, readings were taken only after the pH had fallen below 13. In the determination of rosin acid number readings started at about pH 1.5 and two inflections in the curve were obtained. The graphs show typical curves for each type of determination.




It is known that accurate pH determinations cannot be made in alcoholic solution. In setting up a potentiometric method for determining constants for tall oil the actual pH of the solution is not important. The important factor is the apparent pH at which a break or inflection occurs in the titration curve. A similar method for the determination of neutralization number of petroleum products has been used, in which the test sample is dissolved in butanol and titrated with a solution of potassium hydroxide in butanol and to breaks at about pH 5.50 and pH 10.0 to distinguish between strong and weak acids (3).

In the series of determinations made in this investigation (14 each for acid value, saponification value, and rosin acid value) it was found that the inflection in the curve varied by no more than one-half pH unit. This variation is due to the fact that at the point of inflection the pH changes so rapidly with small increments of standard solution that one drop at the end point may change the pH by several units. Taking an average from the determinations made these end-points were found to be:

| Determination | End-point |
|---|---|
| Acid Number | pH 11.0 |
| Saponification Number | pH 11.0 |
| Rosin Acid Number | pH 6.0 and 11.0 |

Using these values the various constants were calculated for the samples used and are compared in the following table with the values found by the colorimetric method.

Constants on Tall Oils
Comparison of A.S.T.M. (D803-44T) With Potentiometric Method

| Tall Oil Used | A.S.T.M. Acid No. | Potentiometric Acid No. | A.S.T.M. Saponification No. | Potentiometric Saponification No. | A.S.T.M. Rosin Acid No. | Potentiometric Rosin Acid No. |
|---|---|---|---|---|---|---|
| Indusoil | 169.0<br>169.5 | 168.1<br>169.0 | 185.7<br>188.2 | 182.5<br>182.7 | 57.2<br>56.2 | 58.0<br>57.7 |
| Opoil | 162.0<br>162.8 | 160.9<br>160.1 | 175.1<br>173.9 | 173.0<br>174.4 | 86.6<br>84.4 | 86.7<br>85.6 |
| Facoil CS | 164.0<br>163.0 | 165.2<br>164.3 | 177.6<br>176.2 | 177.1<br>179.1 | 76.7<br>74.5 | 75.1<br>73.1 |
| Facoil FR | 166.1<br>165.9 | 167.5<br>165.7 | 177.4<br>178.3 | 177.7<br>177.4 | 52.9<br>53.6 | 51.8<br>52.5 |
| Ligro | 157.0<br>157.2 | 157.2<br>157.8 | 173.3<br>172.1 | 170.8<br>171.4 | 73.3<br>73.9 | 71.9<br>72.7 |
| TOF | 155.0<br>155.3 | 156.2<br>155.7 | 171.2<br>170.7 | 168.3<br>168.1 | 58.4<br>58.2 | 59.6<br>58.3 |
| TOFA | 154.8<br>154.3 | 155.1<br>154.5 | 171.8<br>171.5 | 172.3<br>172.5 | 53.3<br>53.5 | 55.6<br>54.0 |
| End-Point | ..... | pH 11.0 | ..... | pH 11.0 | ..... | pH 6.0-11.0 |

The above procedure offers a simple method for analyzing tall oils. It eliminates the human factor in so far as it does not require that the operator judge a color change that is often difficult to observe in a dark sample. It would not be necessary to plot the curve for each determination but merely to add the standard solution until the required pH is obtained. The use of a direct reading pH meter would further simplify the operation. In all respects, other than the titration, the A.S.T.M. specifications can be followed.

## Acknowledgment

The author wishes to express his appreciation to the Champion Paper and Fibre Company for their cooperation in this investigation.

REFERENCES

1. Minutes of A.S.T.M. Committee D-17, June 1947.
2. A.S.T.M. Methods of Testing Tall Oil (D803-44T).
3. pH Bulletin Number B-10, National Technical Laboratories.