Of the frozen products those made with lard and combination powder had slight peroxide values (4 to 6) after the storage period whereas all others had no more than a trace. However, all eight judges rated lard and lard plus NDGA biscuits made with pyrophosphate powder better in odor than those made with combination powder, the difference between them being distinct (average 2 plus marks). The off odor in those made with the combination powder was described as “sharp” or “strong” rather than rancid and seemed qualitatively different from the distinctly rancid odor which developed during accelerated tests on the biscuit crumbs. It is possible that oxidation of some other constituent of the dough takes place during the early stages of fat peroxidation or that the decomposition of the peroxidized fat follows a different course in the moist frozen product. The odor scores on hydrogenated fat biscuits showed no significant difference for those made with combination versus pyrophosphate powder. With muffins all judges preferred the odor of the pyrophosphate products, whether the fat used was lard or hydrogenated vegetable oil.

Flavor scores, unlike the odor, were not significantly different for pyrophosphate powder versus combination powder products. It is probable that the “excess soda” taste associated with the greater alkalinity of products made with the pyrophosphate powder caused some of the judges to rate them down in flavor.

Summary and Conclusions. The effect on rancidity of heated residues of the four commercial types of baking powder was measured in artificial aqueous fat systems. The powders inhibited rancidity in such systems in the following order: combination, tartarate, monocalcium phosphate, and pyrophosphate—the combination being least effective and the pyrophosphate very much more effective than any other type.

The antioxidant effect of the pyrophosphate powder was shown to be due primarily to a synergism with tocopherol rather than to special ability of the pyrophosphate to bind traces of copper. The synergism was much more marked with tocopherol than with NDGA.

In accelerated tests on the dried crumbs, biscuits and muffins baked with a pyrophosphate powder had much greater resistance to rancidity than those made with a combination powder. When frozen, products made with the combination powder developed off odors more rapidly than those made with a pyrophosphate powder.

REFERENCES

[Received Feb. 24, 1949]

Comparative Study of the Oxidation and Polymerization of Linseed Oil by Application of Some Recently Developed Physical Techniques


Research and control of plant processing in the drying oil field have been in the past very much dependent on chemical analytical evaluation. Although the value of such work cannot be underestimated, there have been instances where the results of such analyses have not been reproducible nor applicable to a particular oil system. In recent years physical methods have found more and more application because of the accuracy and reproducibility of results as well as the simplicity of operating the various commercially available instruments.

It is the purpose of this paper to present three physical test methods which have been used in our laboratories for the study of polymerized and oxidized oils and which have found diverse application as research and plant processing control tools. These measurements are:

1. Molecular Weight.
2. Dielectric Constant.
3. Power Factor.

For the demonstration and investigation of these methods this study has been confined to experimental procedures performed with linseed oil although in the course of this and prior work a considerable amount of data was obtained for other vegetable and marine oils. Specifically, raw linseed oil was thermally polymerized and mechanically oxidized; samples were withdrawn from each batch at various intervals for analysis. The raw linseed oil used in these preparations had the following constants:

* Presented at the American Oil Chemists' Society Meeting, New York City, November 16, 1948.
Viscosity (25°C) .................................. 48 centipoises
Color ................................................................ 11 (Gardner-Holdt)
Iodine Value ............................................. 183.5
Refractive Index (25°C) ....................... 1.4788
Dielectric Constant (25°C, and 200 kilocycles) .................. 3.22
Power Factor (25°C, and 200 kilocycles) ........................ 0.1%

**Preparation of the Oils**

1. **Thermal Polymerization.** Heat bodying was conducted with 500 grams of oil at 300°C, under conditions which would insure low acid values and relatively good color.

2. **Mechanical Oxidation.** This process was carried out by blowing 500 grams of oil in a three-necked flask at 110°C. The air used for oxidation was purified by passing it through an absorption train containing concentrated sulfuric acid and calcium chloride. The rate of blowing was 0.12 cubic feet per minute for 500 grams of oil. Agitation was supplied by means of a mechanical stirrer having a tip velocity of 832 feet per minute.

No driers were used in either experiment.

**TABLE I**

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Viscosity (25°C)</th>
<th>Refractive Index</th>
<th>Iodine Value</th>
<th>Molecular Weight</th>
<th>Dielectric Constant</th>
<th>Power Factor</th>
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<td>3.22</td>
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* Combustion analysis of six-hour sample showed essentially no gain in oxygen content over raw oil.

**Determination of the Constants**

1. **Viscosity.** This property was determined at 25°C by inverting a Gardner-Holdt viscosity tube and timing the rise of the bubble. These values were correlated with the values determined for the standard tubes for which centipoise readings were known. Several values were rechecked on the Brookfield electro-viscosimeter. Excellent checks were obtained.

2. **Refractive Index.** Measurements were made with the Abbe Refractometer at 25°C.

3. **Iodine Value.** The conventional Wijs method was used.

4. **Molecular Weight.** The conventional Beckmann freezing point depression method was used.

5. **Dielectric Constant and Power Factor.** The bridge method was used. A special test cell of 10 ml. capacity, Schering type bridge, alternating current voltage source, and a detector made up the apparatus. The measurements were carried out at 200 kilocycles and 25°C.

6. **Oxygen Content.** Conventional combustion analyses were used for the determination of the carbon and hydrogen in the samples. The oxygen was then determined by difference.

Tables I and II give the various analytical constants obtained for the thermally polymerized and the mechanically oxidized oils.

**TABLE II**

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Viscosity (25°C)</th>
<th>Refractive Index</th>
<th>Iodine Value</th>
<th>Molecular Weight</th>
<th>Dielectric Constant</th>
<th>Power Factor</th>
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**Molecular Weight**

There is no need to discuss fully the various cryoscopic solvents which have been used for the determination of molecular weights of drying oils. The literature mentions many solvents and for the most part the results published are usually too low when compared with the theoretical value of the untreated triglyceride. Since in the derivation of the cryoscopic formula ideal behavior for solvent and solute are assumed, it is easily understandable that the choice of solvent can affect Raoult's law by preventing the formation of an ideal mixture because of a) different internal pressures of solute and solvent, b) polarity effects, c) compound formation, and d) association or dissociation.

The original work of Gay (4) with cyclohexane and the recent determinations of Bernstein (1) with the same solvent have indicated that an oil-cyclohexane mixture may approach this ideal behavior and for this reason should be applicable for number average or mean molecular weight determinations.

Cryoscopic determinations with cyclohexane have been further investigated and extended in our laboratory for thermally polymerized and mechanically oxidized raw linseed oil and for purposes of comparison determinations have also been made in benzene.

**Experimental**

The freezing point determinations were carried out in the commonly used Beckmann apparatus using ice and water as the cooling mixture. In all instances 25 ml. of solvent, pipetted at 25°C, were used. The respective weights for this volume at the given temperature were 19.36 grams for cyclohexane and 21.51 grams for benzene. The temperature depressions were read to 0.01°C, and by means of a magnifying device estimated to 0.001°C.

The solvents were purified by the following procedure: Commercial cyclohexane and thiophene free, reagent grade benzene were each passed through an adsorption apparatus 100 cm. in length and 35 mm. in diameter, containing approximately 400 grams of silica gel according to the method of Graff, O'Connor, and Skau (5). The purified materials were distilled through a Widmer column, and the cyclohexane fraction boiling at 80.8°C, and the benzene fraction boiling at 80-80.1°C, were collected.

Molecular weights of all samples were determined at a concentration of approximately 4.5-5%. At least three samples of each run were checked over a concentration range from 2-10% in cyclohexane and benzene. It should be mentioned at this point that all experiments were run in duplicate, but since results checked within narrow limits the analytical or molecular weight data of the check runs were not included in this paper.