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, tartrate, 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.

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

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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:

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Viscosity (25°C.)	48 centipoises
Color	11 (Gardner-Holdt)
Iodine Value	183.3
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

Polymerized Oil Constants

Time 300°C.	Visc. cps.	Refr. Index	Iodine Value	Mol.Wt. Cyclohexane	Dielectric Constant	% Power Factor
hrs.						
0	48	1.4788	183.3	883	3.22	0.10
1	145	1.4821	158.1	907	3.20	0.23
2	410	1.4841	144.2	1325	3.22	0.43
3	950	1.4858	136.8	1630	3.22	0.67
4	1700	1.4871	133.2	1997	3.22	0.90
5	2540	1.4889	124.4	2410	3.21	1.32
5.5	9600	1.4897	125.7	2970	3.22	1.48
6*	19000	1.4902	121.2	3125	3.21	1.57

* 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

Oxidized Oil Constants

Time 110°C.	Visc. cps.	Refr. Index	Iodine Value	Mol.Wt. Cyclohexane	Dielectric Constant	% Power Factor	% O_2 Combustion
hrs.							
0	48	1.4788	183.3	883	3.22	0.1	11.4
3	130	1.4815	157.0	1216	3.82	0.95	15.8
4	300	1.4830	139.3	1668	4.34	1.84	17.1
5	690	1.4842	127.3	2081	4.65	2.62	17.8
5.75	1340	1.4852	115.4	2680	4.86	3.83	18.3
6.25	2350	1.4861	111.3	3155	5.06	4.30	18.8
6.75	3450	1.4862	107.3	....	5.14	4.68	19.0

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 21.81 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.

Results and Discussion

In Figure 1 the molecular weights of the polymerized and oxidized samples determined in cyclohexane and benzene are plotted arithmetically against viscosity. A comparison of these curves shows a wide variation of the numerical values obtained in cyclohexane and benzene. This applies to the original oil as well as to the oil samples polymerized or oxidized to higher viscosities. The molecular weight value of the raw oil in cyclohexane agrees well with the calculated theoretical value of 878. This confirms the findings of Gay and Bernstein. Moreover, the abnormally low value (700) found in benzene also has been reported in the literature on many occasions.

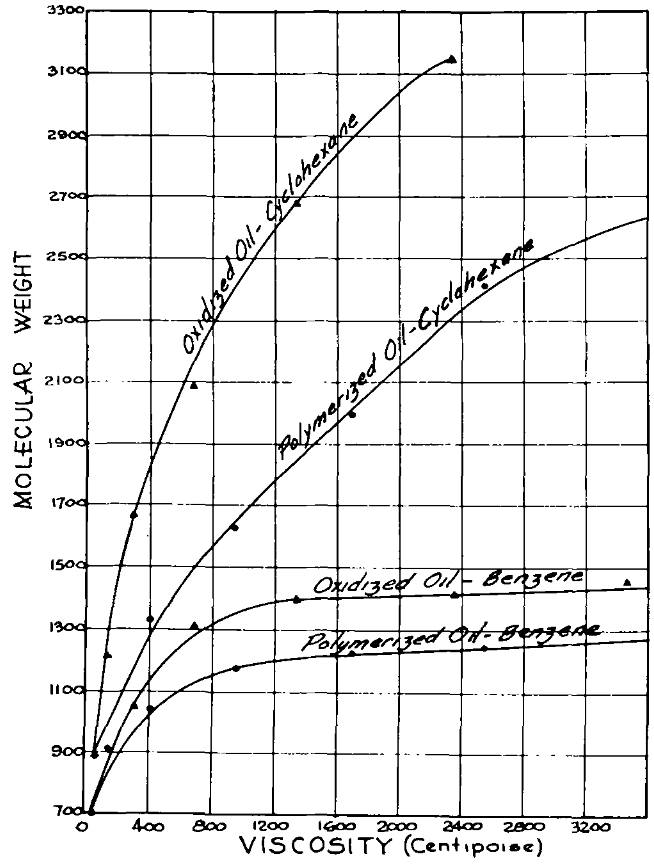

FIG. 1.

A relatively constant molecular weight value is obtained at comparatively low viscosities when benzene is used as the cryoscopic solvent. Under the experimental conditions employed in the thermal polymerization of the oil, this value reaches approximately 1200 at a viscosity of 1700 centipoises and does not change appreciably on reaching 19,000 centipoises. For the oxidized oil the molecular weight value approaches 1400 and again is fairly constant in the viscosity range of 1200 to 3500 centipoises.

Molecular weight investigations by Caldwell and Mattiello (2) on polymerized linseed oil using nitrobenzene as the cryoscopic solvent have shown that oils heat-bodied at different temperatures approach different constant molecular weights at relatively low viscosities. Thus, at a polymerization temperature of 329.4°C. the value was approximately 1550; at 304.4°C., 1300; and at 287.7°C., 1000. Our experiments indicate that benzene yields similar results. These constant molecular weight values, which extend over a wide viscosity range, indicate that any theoretical significance of these determinations in benzene would be questionable.

The use of cyclohexane as solvent presents an entirely different problem. There the molecular weight increases rapidly as the viscosity increases, and the polymerized oil at approximately 2500 cps. approaches an average molecular weight of the trimer stage. For the oxidized oil the tetramer stage is approached at a viscosity of 2400 cps. The value continues to increase slowly at the higher viscosities and apparently does not become constant in the liquid phase. Above approximately 2500 centipoises the method cannot be employed for oxidized oils because of insolubility. The question of whether results obtained with cyclohexane are true mean molecular weight readings is still open for discussion. It is believed that if values could be duplicated by using different cryoscopic solvents more positive statements concerning the true nature of the mean molecular weight could be made.

Nevertheless, theoretical and actual considerations lead to the assumption that cyclohexane is an almost ideal solvent for cryoscopic measurements. Four facts may be pointed out in support of this statement:

1. Molecular weights of raw oil agree closely with theoretical calculations.
2. Different concentrations of oil in cyclohexane give nearly identical molecular weight readings. In benzene it was found that in only some instances are good check determinations obtained at different concentrations. Mostly, however, the molecular weight values in benzene decrease as higher concentrations of solute are used.
3. Cyclohexane, as opposed to most other solvents tried, is a chemically and physically inert substance. Association with similar substances or with the solute is minimized since the compound does not possess valency stresses. The material is an excellent solvent for polymerized oil and for oxidized oil up to about 2500 centipoises, and it has a sharp freezing point in the pure state.
4. The molecular weights obtained for polymerized oils at high viscosities or near the gel point agree closely with the theoretical number average value predicted statistically by Flory's theory for three dimensional polymers (3). According to this theory, a gel should be obtainable with an oil polymer having an average molecular weight approximately three times that of the original oil. In the case of the polymerized oil near the gel point this factor is about 3.5.

It is illustrated in Figure 1 that for any given viscosity the oxidized oil has a higher molecular weight than the polymerized oil. That is true in cyclohexane as well as in benzene. These results however must be regarded with some caution. They are representative of the oils processed under the conditions outlined previously and consequently no generalization should be attempted. It is conceivable that different experimental conditions could affect the reactions taking place during the oxidation or polymerization and therefore could alter the molecular weight-viscosity relationship.

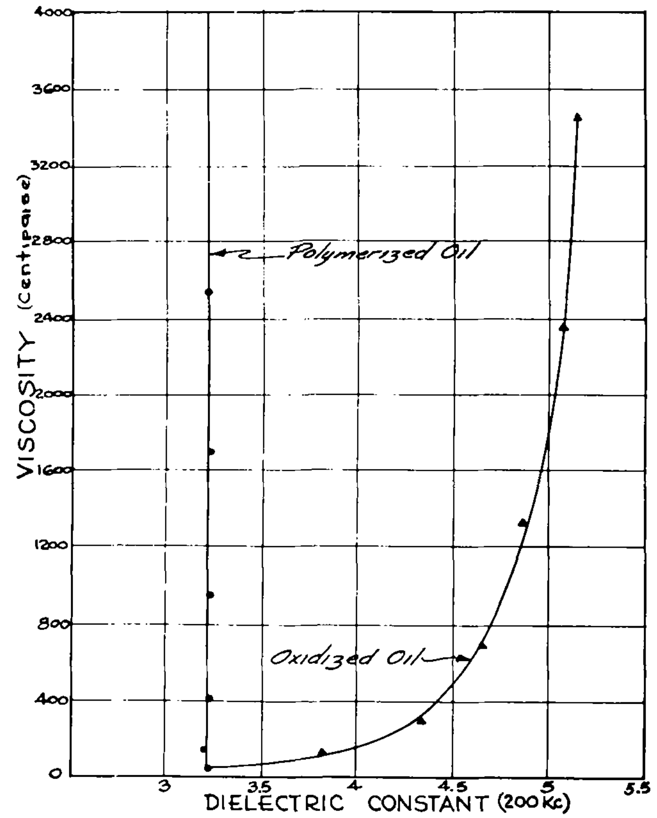

Fig. 2

Dielectric Constant

The method for the determination of the dielectric constant and dielectric theory have been fully described and discussed by Hazlehurst (6).

The experimental values (Figure 2) show that the dielectric constant rises from 3.22 to 5.14 as oxidation proceeds to a viscosity of about 3500 cps. This has enabled us to exercise continuous control over the oxidation of oils since a definite relationship exists between the dielectric constant and the amount of oxygen in the oil for any given set of conditions. Moreover, the approximate amount of oxygen in any unknown oil sample can readily and simply be estimated from its dielectric constant without resorting to laborious and time consuming combustion analyses. It is to be remembered however that for different oxidation conditions, especially temperature, the dielectric-oxygen content curve will vary somewhat. The relationship of oxygen content to dielectric constant for this batch is shown in Figure 3.

The dielectric constant of the thermally polymerized oil (Figure 2) remains constant at any degree of polymerization, illustrating that the dielectric value at any given temperature is dependent only on the amount of oxygen absorbed and the structural complexity induced in the oil because of this absorption. This has also been mentioned by Hazlehurst in an earlier paper from this laboratory (6).

These results indicate the value of dielectric constant measurements in the blowing of drying oils, and it is our belief that the knowledge of this oxidation reaction will be greatly furthered by use of this tool.

Power Factor

Another informative measurement for oil evaluation is the power factor. This indicates the amount of energy which is dissipated, as the molecules align themselves in an electrical field, because of the frictional resistance of the medium. Thus, as viscosity increases, the power factor takes on more impor-

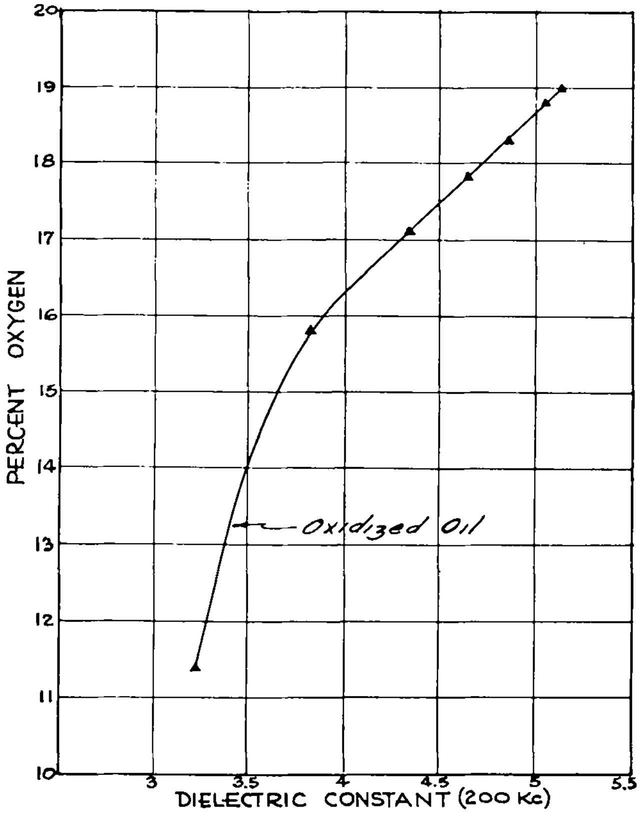

Fig. 3

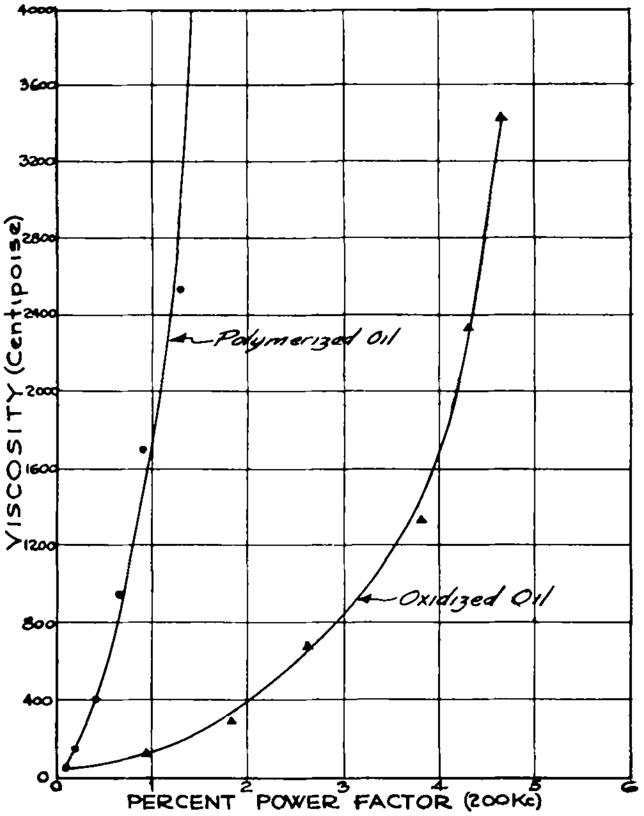

Fig. 4

tance since high viscosity media offer much greater sources of frictional resistance than the lower viscosity materials.

This comprises a very convenient determination since in the evaluation of the dielectric constant on balancing the A. C. bridge, the resistance as well as the capacitance must be balanced and, therefore, two determinations are made at one time. Figure 4 presents the per cent power factor change for the polymerized and the oxidized oils.

Examination of the arithmetic plot of viscosity-power factor shows that for any given viscosity the power factor of the oxidized oil samples is considerably greater than that of the polymerized oil. Consequently, power factor is mainly dependent on two variables: viscosity and oxygenated structure, the latter of which apparently contributes more. This could very well be another tool to be used to great advantage in the study of oxidation and oxidative polymerization during the processing of drying oils.

Summary

Three physical test methods for drying oils have been described. They are:

1. Molecular weight determinations in cyclohexane for thermally polymerized and mechanically oxidized oils. Results have been compared with those obtained in benzene. Theoretical and factual reasons have been given for the apparent validity of average molecular weight determinations in cyclohexane.
2. Dielectric constant determinations for treated oils. It has been shown that the dielectric increases as an oil is oxidized but that no increase in dielectric occurs on thermal polymerization. The dielectric constant is mainly a function of the oxygenated structure of the oil.
3. Power factor determinations. The power factor increases on polymerization and on oxidation. The values obtained for any given viscosity are considerably greater for the oxidized samples.

Molecular weight and dielectric constant determinations have been used to advantage in our plants and laboratories. Our knowledge on power factor determinations, however, is as yet not extensive but it is felt that with more background data on this constant a potentially meaningful tool for oil evaluation can be developed.

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Calcium Oxide-Soybean Oil Paints Having Reduced Tack and Increased Durability[1]

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Introduction

THE utilization of soybean oil as a drying oil has continued to grow since domestic oil was first offered to the industry. This growth has been slow because certain inherent properties limited its use. However, during and since World War II, the shortage of other drying oils has forced chemists and technologists to learn how to use it. At present, the paint and varnish industry is using soybean oil at the rate of nearly 150 million pounds per year.

The utilization of large percentages of soybean oil in outside white paints and many other protective coatings has resulted usually in a tacky film. This film collects dust and dirt which adheres to the surface until removal by chalking or self-cleaning. Another objectionable feature of soybean oil in paints is that the coatings tend to soften and re-liquefy when exposed to the high temperatures and humidities of the summer months. These softened coatings retain dust and dirt which becomes imbedded in the film so deeply that it cannot be washed out. This results in coatings that are unsightly in appearance and difficult to repaint. Also, the durability of the coatings is impaired by the stresses and strains set up by internal movements caused by repeated softening and hardening.

There are a number of ways in which the effect of these disadvantages can be reduced, in part or entirely; by proper pigmentation (7, 9); the use of soybean oil reacted with maleic anhydride (4); the use of soybean oil converted to pentaerythritol esters (2); the use of long-oil resins containing phthalic anhydride and glycerol (3); the use of oil modified with other dibasic acids and polyalcohols in small amounts to form molecules of higher functionality (13); the use of oils modified by copolymerization with styrene (8, 10), by copolymerization with tung oil (11), by blending with linseed and other unsaturated oils (7, 9); and other methods.

In connection with studies at the Northern Regional Research Laboratory on the catalytic isomerization of soybean oil, a conjugated oil was produced that dried rapidly to a tack-free coating when used as the oil vehicle in a basic lead carbonate paint (12). But these coatings, after an outdoor exposure of a week at 45° south in hot, humid weather, softened badly and collected a large amount of dirt which could not be removed by washing, and the coatings remained soft for a long time. This condition was particularly true of coatings prepared from oil isomerized at 200° to 220°C. and was probably

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