seems that the closely related gossypol-like pigments present in crude screw-pressed oils and included in the values determined for total gossypol (14) in the present investigation are responsible for the increase in bleach color of the crude oils on storage. This relationship is illustrated by the data shown in Figure 1, where the initial content of total gossypol pigments in the crude oils is plotted against the increase in bleach color after storage of the crude oils for 40 days at 95-100°F.

Summary

Processing conditions, particularly cooking procedures, have a marked influence on the chemical properties of screw-pressed meal and oil. Cooking prepared meats at 240-250°F., as in normal mill practice, produced meals with low free gossypol content but at the expense of considerable protein damage. The resultant crude oils showed some color reversion upon storage at 95°F. Dry cooking (7% moisture) at temperatures not exceeding 200°F. gave meals of improved chemical properties, but the crude oils exhibited considerable color reversion on storage.

Wet low-temperature cooking (200-210°F.), followed by evaporative cooling, yielded a meal intermediate in quality between that for normal mill practice and dry low-temperature cooking. The crude oils, which corresponded to hydraulic-pressed oil, did not exhibit any appreciable color reversion upon storage at elevated temperatures.

The selection of processing conditions, notably cooking, enables wide variations in the distribution of gossypol between meal and oil.

The increase in the bleach color of crude oils stored at 95-100°F. was found to be directly related to the initial gossypol content of the crude oils.

Acknowledgments

The mill scale tests were made possible by the interest and cooperation of the South Texas Cotton Oil Company, Harlingen, Tex., and the Central Oil and Milling Company, Clayton, N. C.

The authors are indebted to Vidabelle O. Cirino, Alva F. Cucullu, and Julian F. Jurgens for many of the chemical analyses reported in this paper.

The assistance of Aaron M. Altschul, E. A. Gastrock, T. H. Hopper, and P. A. Williams in the planing of this investigation is gratefully acknowledged.

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[Received January 11, 1954]

Aqueous Vapor Pressure of Soybean Meal and Its Fractions[1]

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THE role of water in the maturing and storage of soybeans and its effects on the changes in the proteins, carbohydrates, and other constituents of the bean have never been adequately evaluated. These water-colloid relationships are of primary importance in understanding processing operations involving desolventizing, toasting, and dehydration of soybean products as well as changes that occur during storage of the beans or meal.

Beckel, Bull, and Hopper (1) have published data showing the progressive denaturation of protein in soybean meal by the application of increasing amounts of moisture and heat. The moisture conditions imposed on the meals were defined in terms of the relative humidity maintained in the system during heating and as such cannot be directly translated into moisture content. Data have been reported on the hygroscopicity of soybeans and soybean oil meals by Ramstad and Geddes (11) and by Larmour, Sallans, and Craig (6). However in each case the information was obtained by equilibrating the samples in a series of desiccators, each containing a solution of constant humidity, maintaining the temperature at 25°C., and subsequently determining moisture contents. Such information is adequate for low temperature investigations. However processing conditions are seldom at this temperature level, and in the present investigations it was deemed necessary to include temperature as a variable. It is interesting to note that because of the empirical nature of the results obtained by existing procedures for determining moisture of biological materials, it has been advocated by Makower and Myers (8) that aqueous vapor pressure replace the moisture determination as an indication of the extent of hydration.

The present investigation was undertaken to establish the moisture adsorbing capacity of soybean oil meal and its fractions at various temperatures by a manometric method. Such data will be applicable to many practical soybean production problems as well as to the storage of these materials.

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[1] Presented at fall meeting of American Oil Chemists' Society, November 2-4, 1953, in Chicago, Ill.

[2] Formerly with the Northern Utilization Research Branch.

[3] One of the branches of the Agricultural Research Service, U. S. Department of Agriculture.

Materials and Methods

The materials investigated were a) undenatured soybean oil meal, b) denatured soybean oil meal, c) the water-soluble fraction (pH = 7.4) of the meal, and d) the solubles at pH 4.6 or the so-called "soybean whey" fraction. Materials a) and b) were prepared from 1948 Hawkeye beans. The beans were cracked and flaked by methods simulating commercial practice, and the oil was removed to less that 1% with hexane, b.p. 30°-60°C. The hexane was removed by room temperature evaporation to give the undenatured meal having an analysis of nitrogen 8.56% and ash 6.58% on a moisture-free basis. The nitrogen solubility in water was 74.0% as determined by the procedure of Smith and Circle (12). Two denatured meals were prepared by heating the undenatured material in an autoclave a) for 30 minutes at atmospheric pressure, and b) for 45 minutes at 15 p.s.i.g. (121°C.). Nitrogen solubilities in water for these were 15.7 and 5.2%, respectively.

The water-soluble and whey fractions were prepared from a composite of equal quantities of Lincoln, Hawkeye, Adams, Wabash, and Blackhawk beans from the 1950 crop. The water-soluble fraction was prepared by extracting the undenatured hexane-extracted flakes with water adjusted to pH 7.4 with sodium hydroxide. The solution was clarified by screening, followed by centrifuging; and the dissolved solids were recovered by spray drying. The water solubles contained 10.18% nitrogen, 1.0% reducing sugar determined as glucose, 10.1% non-reducing sugar determined as sucrose, and 7.18% ash. The whey solubles were prepared from the oil-free meal of the composited flakes by extracting with water adjusted to the pH 4.6 with hydrochloric acid, clarifying the solution in a centrifuge, and recovering the solubles in a spray dryer. This fraction analyzed 3.61% nitrogen, 3.4% reducing sugar determined as glucose, 27.5% non-reducing sugar determined as sucrose, and 17.18% ash.

Sample Preparation. The meal samples were ground in a hammer mill so that substantially all passed a 100-mesh screen whereas the spray-dried materials were used in their powdered form. The samples were adjusted to various moisture levels in the range of 5 to 25% by conditioning in constant humidity desiccators containing sulfuric acid solutions of 20, 30, 45, 65, and 70%. Conditioning to higher moisture levels was accomplished over distilled water in which case it was necessary to limit the conditioning period to a few days to prevent mold growth. A moisture determination was made on each sample prior to its vapor pressure determination by the A.O.C.S. Official Method BA-2-38, which employs an oven temperature of 130°C. for 2 hours. Calculations showed that the loss in moisture content of the sample under vapor pressure measurement was negligible because of the small volume of the system over the sample, and consequently the determination of the original moisture was a satisfactory means of correlating the results.

Vapor Pressure Measurements. The aqueous vapor pressure measurements were conducted in a manometric system similar to that described by Makower and Myers (8) and also used by Vincent and Bristol (13) and Fischbach (4). The apparatus is shown in Figure 1. The measuring system consisted of a small sample container connected on one side to a moisture trap and on the other side to a closed-end, U-tube manometer. Two vacuum-type stopcocks were inserted in the apparatus, one at the outlet of the moisture trap so the entire system could be evacuated and closed to atmospheric conditions and the other so that the sample could be isolated from the remainder of the system. The sequence of their operation will be explained in a description of the procedure. The sample container was fabricated of approximately 2½ in. of 7 mm. tubing (to insure rapid heat transfer to the sample) connected to a 24/40 standard taper ground glass joint. The moisture trap and the manometer, 80 cm. long, were constructed of 10 mm. combustion tubing. Mercury was used as the manometric fluid throughout this investigation. The sample container, its ground glass joint, the stopcocks, and the moisture trap were fabricated in one piece, which was connected to the manometer by means of a short length of Tygon tubing wired to the glass tubing. The assembled apparatus was securely fastened to a frame so that the entire unit could be immersed in a large constant temperature bath. The Tygon connection gave the apparatus sufficient flexibility to minimize strain during the testing period in the bath and permitted the removal of the manometer for degassing operations. The manometer was frequently checked against a standard barometer to indicate the condition of the Torricellian seal. The bath was thermostatically controlled to ±0.1°C. at the desired temperature levels of 30, 40, 50, 60, and 80°C. Only a few determinations were conducted at 80°C. to establish the validity of extrapolating the straight lines of the isosteric plots beyond the range of the experimental data.

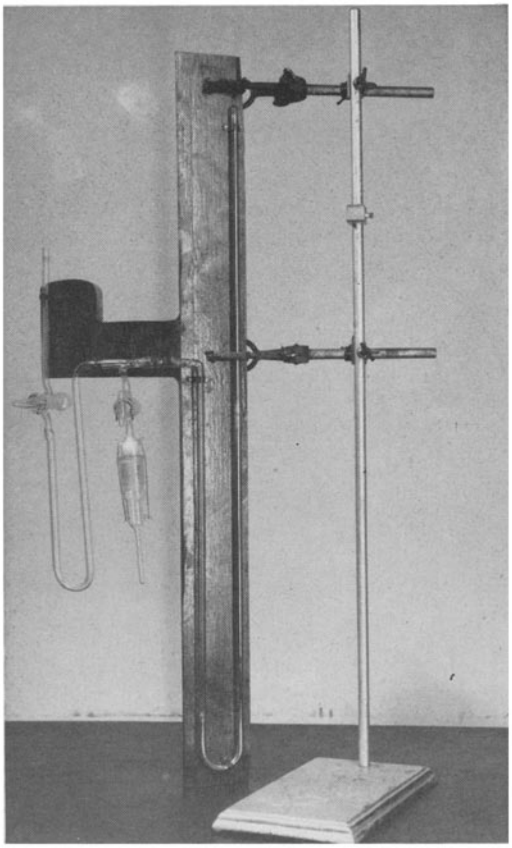

Fig. 1. Apparatus for measuring the aqueous vapor pressure of soybean oil meal and its fractions.

The procedure for determining the aqueous pressure of a sample was as follows. The bath was regulated to the desired temperature, usually the lowest one to be used. Approximately 0.25 g. of the sample was placed in the containing tube and attached to the rest of the system. The sample tube and the moisture trap were immersed in dry ice-acetone baths, and the system was evacuated by means of an oil pump. At the end of the evacuation period, 15 minutes, the stopcock on the moisture trap was closed, the cooling baths were removed, and the entire assembly was placed in a constant temperature bath. The system remained in the bath until pressure and temperature equilibrium had been approached as indicated by a constant reading of the manometer over a period of 20-30 minutes. The mercury levels were measured by a cathetometer with an accuracy of ±0.05 mm. of mercury. Readings were taken every 5 minutes during the test period. It was necessary gently to tap the manometer between readings to prevent erroneous values. Depending on the temperature level of the determination, ½ to 2 hrs. were required for reaching equilibrium.

After equilibrium had been established, the stopcock above the sample container was closed and the system was removed from the bath. A dry ice-acetone bath was placed around the moisture trap, and the vaporized moisture was condensed from the system. Any residual pressure reading caused by inadequate initial evacuation or entrapped inert gases, originally present in the sample which were released during the test, was determined by this procedure. The difference between the initial and final values was taken as the aqueous vapor pressure of the sample. Density values for mercury from the International Critical Tables (5) were used to adjust the values to standard temperature of 0°C.

The system was returned to the bath for measurement at another temperature level, and the cycle described was repeated.

Results and Discussion

The results of this investigation, although reported as aqueous vapor pressures, may be readily changed to relative humidity. The experimental data for the different temperature levels were smoothed by plotting the measured vapor pressures *versus* moisture content using logarithmic graph paper to cover the entire range. These plots are reproduced in Figure 2 for the undenatured and denatured meal samples and in Figure 3 for the water and whey solubles.

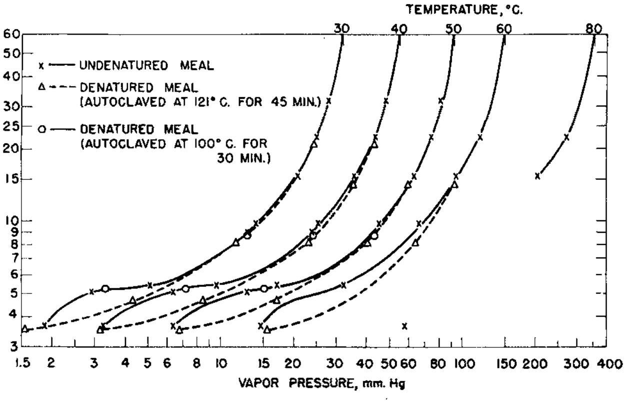

Fig. 2. Isotherms for denatured (O,Δ) and undenatured (X) soybean oil meals. The O is for meal autoclaved at atmospheric steam pressure for 30 minutes and the Δ for meal autoclaved at 15 p.s.i.g. for 15 minutes.

The isothermal curves shown in Figures 2 and 3 have the sigmoid shape typical of adsorption phenomena. They are characterized by an inflection point considered by previous investigators (2, 3, 9) to represent the limit of monolayer adsorption and the beginning of "multilayer adsorption" or "capillary condensation." Examination of these isotherms indicates that this limit exists at a moisture content between 4 and 5% for undenatured soybean meal and the water-soluble fraction while the inflection point is nearer 10% moisture for the whey solubles fraction. However the severe heat treatment received by the denatured meal has altered the colloidal system so that no inflection point was apparent at a value as low as 3½% moisture. As will be shown later, substances which influence the water adsorbing capacity of soybean materials are present in the whey soluble carbohydrate fraction, and they apparently decompose or associate with other constituents of the meal on exposure to extreme temperature. The partial destruction of the hydrophilic properties of soybean meal with heat confirms a conclusion previously reached by Ramstad and Geddes (11).

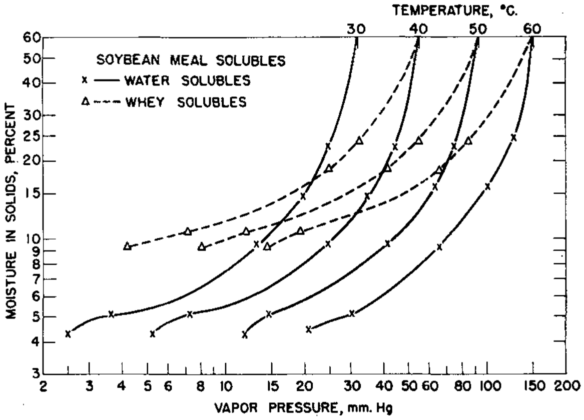

Fig. 3. Isotherms for water solubles (X) and whey solubles (Δ).

It is interesting to note that all of the isotherms approach the vapor pressure of pure water at approximately a moisture content of 60%. All moisture below this value must be classified as "bound" which does not exert its full vapor pressure at the temperature imposed on the sample. Difficulty of conditioning samples at high moisture contents eliminates any further precision in determining this value.

From Figures 2 and 3 values of aqueous vapor pressure for given moisture contents were obtained by graphical interpolation and plotted by a method proposed by Othmer (10). The vapor pressure is plotted *versus* temperature; the scale is established by the vapor pressure of a reference material, in this instance the vapor pressure of water. The advantage of this method of plotting is that a linear relationship exists between the aqueous vapor pressure of soybean products and the vapor pressure of water over a wide range of temperatures. The isosteric lines so obtained may be interpolated or extrapolated with more assurance than can a plot of the logarithm of vapor pressure *versus* the reciprocal of the absolute temperature as indicated by the Clausius-Clapeyron equation. Furthermore the slope of the straight line is numerically equal to the ratio of the isosteric heat of desorption to the latent heat of vaporization of water at that temperature. This graphical presentation of the data is given in Figure 4 for undenatured meal, Figure 5 for the water-soluble fraction, Figure 6 for denatured meal, and Figure 7 for the whey solubles.

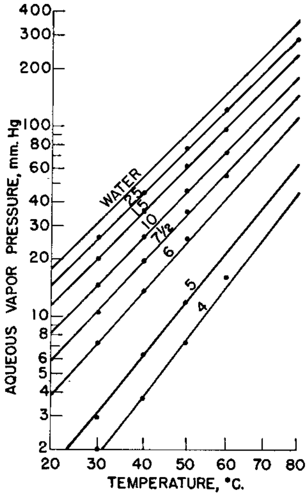

FIG. 4. Isosteres for undenatured soybean oil meal showing the relationship of aqueous vapor pressure to temperature in the moisture range from 4 to 25%.

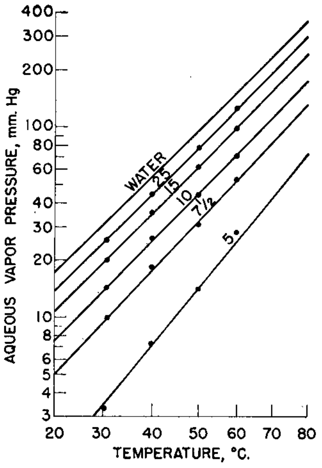

FIG. 5. Isosteres for water-soluble fraction of soybean oil meal showing the relationship of the aqueous vapor pressure to temperature at moisture levels from 5 to 25%.

In order that a comparison might be made between the results of this study and the results of other investigators reported in the literature for a temperature of 25°C., values of the aqueous vapor pressure of undenatured soybean meal were obtained by graphical extrapolation to this temperature of the isosteres of Figure 4 and converted into values of relative humidity or saturation. These values and those published by other authors are plotted in Figure 8. It appears that the data from different sources and by different methods give results which agree within the experimental error of the measurements below a relative humidity of 50% (or a moisture content of 9%). Above this value the manometric procedure used in this investigation resulted in a higher moisture content for any given humidity. Because of the uncertainty of the moisture measurements and the possible effect of physical dimensions in this region of "capillary condensation," it is not evident at this time whether this difference is inherent in the manometric technique or is a result of physical differences in the solid material used by the various investigators. Such physical differences could be varietal in nature or the result of the preparation procedures.

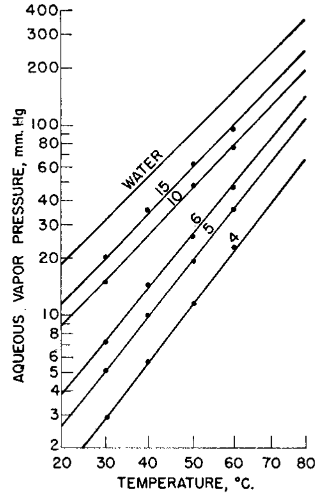

FIG. 6. Isosteres for denatured soybean oil meal showing the relationship of aqueous vapor pressure to temperature in the moisture range of 4 to 15%.

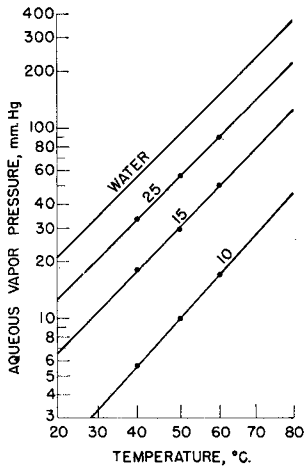

FIG. 7. Isosteres for whey soluble fraction of soybean oil meal showing the relationship of aqueous vapor pressure to temperature at 10, 15, and 25% moisture.

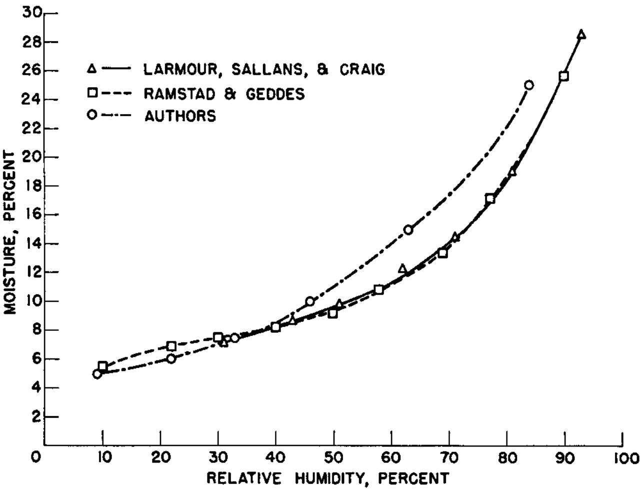

FIG. 8. Comparison of results with those of Ramstad and Geddes and Lamour, Sallans and Craig at 25°C. Our results were obtained by graphical extrapolation of data shown in Figure 4 and these values converted to relative saturation.

As previously stated, the slope of the isosteric lines for any given moisture content is equal to the ratio of the heat of desorption to the latent heat of vaporization of water at that temperature. These ratios have been determined for each of the materials and plotted in Figure 9. It is apparent for all materials studied, with the exception of the whey solubles, that this ratio has a value of essentially 1.0 until a moisture content of approximately 7% is reached. In the region where this slope is essentially unity, the amount of moisture adsorbed by the material is independent of temperature and becomes a function of only one variable, the relative humidity imposed on the sample. It is also apparent that the state of denaturation of the protein has been essentially eliminated as a variable

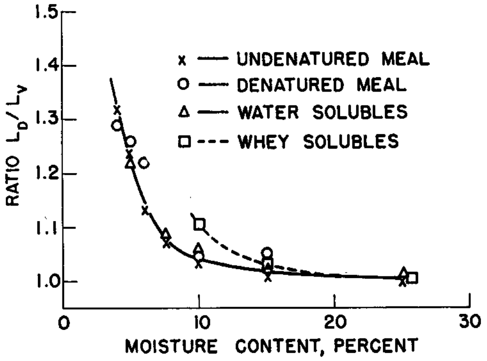

FIG. 9. Variation of the ratio of heat desorption of water, L_D, to latent heat of vaporization, L_V, with moisture content for materials studied.

at moisture contents above the critical value of 7%. The importance of the relationship presented in Figure 8 becomes evident in that it is applicable to all soybean oil meals irrespective of their history at moisture contents above 7%. The limitations on the relationship between relative humidity and moisture content shown in Figure 8 have been previously discussed. Below this moisture level the ratio rises sharply and the water-adsorbing capacity becomes temperature dependent. However the increase for the whey solubles starts at a higher moisture content, 12%, and the change appears to be more gradual. It is interesting to note that the sharp rise obtained by Makower (7) in the study of whole eggs and attributed by him to be due to the proteins involved does not occur until a moisture content of 5% is reached.

In general, the data obtained in this study corroborate visual observations that the materials increase in hygroscopicity in the following order: denatured meal, undenatured meal, water solubles, and whey solubles. It might be expected that a lyophilized product would give slightly different results from those of the spray-dried materials. Such a conclusion is improbable in view of the extreme heat treatment required to alter the adsorbing characteristics of the meal. Although proteins are known to be strongly hydrophilic, comparison of the data and observations from this investigation on soybean meals and fractions indicate that there is a component or components present in the complex system identified as the whey solubles which exerts considerable influence on the water-adsorbing capacity of these materials. The chemical nature of these materials, whether carbohydrates, phosphatides, or inorganic salts, is unknown at present, but visual observations following additional fractionation of the whey solubles indicate that the controlling substance or substances is present in the dialyzable portion. No material commonly defined as protein would occur in this fraction, and it must be concluded that the protein is not the component having the major influence on the hygroscopicity of the soybean oil meal and its fractions. The significance of this observation is the subject of another investigation.

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[Received January 21, 1954]

Tall Oil Studies. V. Detergency Evaluation of Some Nonionic Derivatives

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IN a previous publication (1) the condensation of tall oil with ethylene oxide to form nonionic detergents was described. For optimum detergency, approximately 13 moles of ethylene oxide was required per mole of tall oil. In such a molecule the hydrophobic radical consists of rosin and fatty acids containing unsaturated linkages, and the polyethenoxy radical possesses a hydroxyl group at the end of the hydrophilic chain.

$$\text{R-(CH}=\text{CH)—COO-(CH}_2\text{-CH}_2\text{O)}_{12}\text{-CH}_2\text{-CH}_2\text{-OH}$$

Both of these functional groups provide means of attaching other substituents, in the former case to the hydrophobic portion of the molecule, and in the latter to the hydrophilic group. The present study involves the preparation of derivatives such as the chloro-, bromo-, hydroxy-formoxy-, etc., of the hydrophobic unsaturated and various urethanes and esters of the hydrophilic hydroxyl group. In several additional experiments the hydrophilic chain was extended with ethylene oxide to 33, 43, and 57 moles of ethylene oxide. Detergency values of all the derivatives synthesized from the polyethenoxy tallate were determined on built mixtures.

Preparation of Derivatives

For these experiments a polyethenoxy tallate (I) was prepared by accurately condensing 13 moles of ethylene oxide with each mole of triple distilled Indusoil[1] (1, 2). The ethenoxy content of I was checked by a saponification equivalent.

The *chlorinated* (II) and *brominated* (III) derivatives were prepared by completely saturating the hydrophobic groups in one case with chlorine in carbon tetrachloride solution and in the other with bromine in ether. The *ozonide* (IV) was prepared by direct combination of 20 g. of I with 2 g. of ozone (4). The *hydroxy-formoxy* (V) and *hydroxy-acetoxy* (VI) derivatives were synthesized by the previously described (5) method by use of hydrogen peroxide and formic and acetic acids, respectively. The *maleic anhydride adduct* (VII) was prepared by maintaining 9.8 g. of maleic anhydride with 86.2 g. of I at 80°C. for two hours. An *excessively chlorinated* (VIII) polyethenoxy tallate was prepared by bubbling chlorine gas into 500 ml. of aqueous solution containing 86.2 g. of I for 16 hours. From the gain in weight it was noted that approximately 20% of chlorine had been introduced into the molecule; therefore it is quite possible that along with addition to the double bonds some chlorine may have been substituted along the hydrophilic chain. Sulfation with sulfur trioxide gas, using perchloroethylene as a solvent, followed by

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[1] West Virginia Paper and Pulp Company analyses indicate approximately 30 parts of rosin acid to 70 parts of fatty acids and approximately 1.7 unsaturated groups for each tall oil unit. See Ref. 3 for the proportions of different acids in tall oil.