Possible Mechanisms in Thermal Polymerization of Drying Oils.
I. Catalysis and Inhibition Studies[1,2]

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BEFORE a detailed study of the kinetics of thermal polymerization of drying oils could be attempted, further knowledge of the mechanisms operating at polymerization temperatures was considered essential. Although polymerization is generally considered to proceed by a Diels-Alder mechanism, there are a number of reasons for suspecting that the reaction may be more complex. The high temperatures used in bodying an oil suggest that the mechanism is not simple. Moreover the decomposition that accompanies thermal polymerization and the high over-all activation energies for the bodying of non-conjugated oils (3) indicate complexity. The present work was undertaken to determine whether, by a study of the catalysis and inhibition of thermal polymerization and by a comparison of the reaction at high and low temperatures, some indication of the mechanism of thermal polymerization could be obtained.

Materials and Methods

Linseed, safflower, oiticica, and tung oils were polymerized in this study. The linseed and safflower oils were alkali-refined and bleached at 110°C. to a light shade with 2% Superfiltrol whereas the tung and oiticica oils were used as received. Oil from the same batch was used throughout the investigation, and the oils were kept under nitrogen at 7°C. between experiments. The tung oil, analyzed by the method of O'Connor *et al.* (11), contained 75% α- and 5% β-elaeostearic acid on a glyceride basis. One sample of tung oil was isomerized in the presence of a trace of iodine to 80% β-isomer.

The catalysts and inhibitors were reagent quality products except for the primary and secondary products of the oxidation of linseed oil. These oxidation products were obtained by oxidizing linseed fatty acids at 5°C. to 1.0 mole O_2/kg. and at 60°C. to 1.2 moles O_2/kg., respectively. The primary oxidation products were separated from the unreacted material by extraction with 80% ethanol (21). The secondary products were obtained by the method of Chang and Kummerow (4) and had the same ultimate analysis as those obtained by these authors. The products were then reduced by stannous chloride from a peroxide value of 1850 to 5 m. mole/kg.

The nitrogen used in these experiments, "prepurified" grade, was supplied by the Matheson Company Inc., East Rutherford, N. J. Its freedom from oxygen was shown by an inability to oxidize ammoniacal cuprous chloride solution.

Two experimental techniques were used, polymerization in a nitrogen-swept reactor with provision for removal of samples without disturbing the reaction (17) and polymerization in sealed tubes. The reactor and tubes were heated in a thermostat controlled to ± 0.3°C. The temperature was measured by a thermocouple and recording potentiometer that had been calibrated against a platinum resistance thermometer.

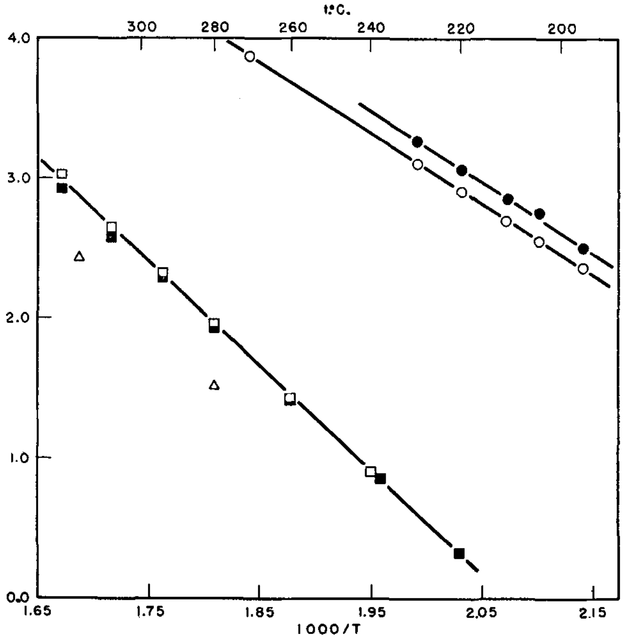

FIG. 1. Logarithm of viscosity rate constant *vs.* reciprocal absolute temperature

- ● 80% β-tung oil; ○ 5% β-tung oil
- □ linseed oil in nitrogen-swept reactor
- ■ linseed oil in sealed tubes
- △ safflower oil in nitrogen-swept reactor.

Samples of oil were taken at appropriate intervals, and the extent of polymerization was determined by measuring the viscosity of the oil at 30 ± 0.1°C., using Ostwald-Fenske viscosity pipettes (18). The time required for the oil in a tube to reach reaction temperature was determined, and the cooling of the samples was adjusted to coincide. When tung oil was heated at 270°C. however, the tubes were quenched in ice water with vigorous shaking. In this experiment, reaction time was obtained by subtracting heat-up time from total time in the thermostat. For polymerization in the gas-swept reactor, zero time was calculated to the nearest minute from the individual heating curves, using the over-all activation energy obtained by Cannegieter (3).

The efficiency of the addends was expressed as the ratio of extent of polymerization with the addend to that of a blank. The error in efficiency factor was found to be ± 3%. Gaseous addends were metered into the gas stream whereas solid and liquid addends were used in sealed tubes on a mole % basis. In these calculations the mean molecular weight was taken as 880. At any one temperature all of the tubes were heated for the same length of time.

The infrared spectrum of selected samples was determined by using a 2% by weight solution of the oil in carbon tetrachloride. The spectra were recorded by a Perkin-Elmer double beam spectrophotometer, Model 21, using a sodium chloride prism.

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[2] Part of this paper presented at the Fall Meeting of the American Oil Chemists' Society, Chicago, Ill., November, 1953.

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Experimental and Results

Rate of polymerization was estimated by means of the semi-logarithmic relation between the viscosity of a bodied oil and heating time. Linear plots were obtained with linseed oil up to viscosities of about 4 stokes and up to 20 stokes with safflower oil. Above these viscosities the plots were non-linear. With tung oil the relation held until a viscosity of 30 stokes was reached. Polymerization rate constants were obtained from the linear portions of these plots.

When the logarithms of the rate constant were plotted against reciprocal absolute temperature, straight lines resulted (Figure 1). From the slopes of the lines the following apparent over-all activation energies were obtained: linseed 34.4, safflower 35.0, native tung 23.2, and isomerized tung oil (80% β-form) 23.2 K cal. per mole.

With oiticica oil, rate constants were calculated by determining the power to which the viscosity must be raised to produce a linear plot (1). However the rate constants obtained in this investigation for oiticica oil, like those of Berger (1), did not give a straight Arrhenius plot.

Linseed Oil. To test whether the decomposition products of thermal polymerization inhibited the reaction, polymerization studies were made in duplicate. At the same time as the nitrogen-swept reaction was proceeding, sealed tubes were also being heated in the same bath. Sampling and tube removal were made to coincide on an elapsed time basis. Up to temperatures of 260°C. (Figure 1) no difference in rate could be measured. Above 260°C. and markedly at 310°C. the rate of polymerization in the sealed tubes was slower than that in the swept reaction vessel.

TABLE I

Catalysis and Inhibition of Linseed Oil Polymerization

Addend	Efficiency Factor[a]			
	1 mole %			6.25 mole %
	240°C.	270°C.	310°C.	310°C.
Catalysts				
Trichloroacetic acid	1.5	1.41	1.17	1.26
Naphthalene-β-sulphonic acid	21.1	4.90	4.20	2.6[b]
Iodine	23.2	16.7	4.04	1.2[b]
Bromine	......	......	1.14	2.83
Anthraquinone	30.0	8.21	2.61	......
p-Methoxybenzylamine	......	......	1.11	1.63
Agerite Resin D	......	......	1.06	1.61
Primary oxidation products	2.32	1.94	......	......
Secondary oxidation products (reduced)	1.20	1.27	2.04	......
Cumene hydroperoxide	1.07	1.40	1.00	0.97
Benzoyl peroxide	1.32	1.17	1.08	1.46
Ditertiarybutyl peroxide	1.10	1.09	1.10	1.46
Azobisisobutyronitrile	1.01	1.02	1.11	......
Diazoaminobenzene	1.00	1.06	1.10	......
Diphenyl disulphide	......	......	3.15	2.85
Inhibitors				
Ditertiarybutylhydroquinone	1.01	1.03	1.08	......
Tricresyl phosphate	......	......	0.97	0.97
Octadecyl Mercaptan	......	......	1.31	3.34
Mercaptobenzimidazole	......	......	1.10	1.36
Hydrogen sulphide (10%)	......	......	1.14	......
Dinitrochlorobenzene	1.42	2.23	1.55	4.55
Cetyl trimethylammonium bromide	......	......	0.98	1.00
Dimethylaniline	1.01	1.02	0.97	0.93
Propylene (10%)	......	......	1.00	......
Nitric oxide (10%)	......	......	2.11	......

[a] Values >1.0 represent catalysis, <1.0 inhibition.
[b] Part of addend surrounded by gel.

The effect of certain catalysts on the polymerization of linseed oil is shown in Table I. Four types of catalysts were tried: acids, bases, oxygen-containing radicals, and oxygen-free radicals. Most oxygen-free radicals were generated readily at low temperatures and had insignificant catalytic power over thermal polymerization in the temperature range of 240 to 310°C. However the phenyl radicals generated from benzoyl peroxide and the sulphide radicals from diphenyldisulphide were more efficient. In contrast, oxygen-containing radicals, from the primary and secondary oxidation products of linseed oil, were reasonably good catalysts.

Materials such as sulphonic acids, chloroacetic acids, iodine, bromine, iodine monochloride, provisionally classified here as ionic catalysts, have certain features in common. These compounds increased the rate of polymerization 20-fold at 240°C. and 3- to 4-fold at 310°C.

Agerite Resin D, a polyquinoline, p-methoxybenzylamine, and anthraquinone all catalyzed the polymerization. At 240°C. the quinone provisionally classified here as a base, was the most effective catalyst used. At higher temperatures however the acid catalysts tended to be more efficient.

The extent of radical participation was estimated by means of inhibition studies. The inhibitory effect of the reaction products is shown in Figure 2, where the rate of polymerization decreased when the nitrogen sweep was interrupted and increased when the sweep was restored. Propylene, when present at 10% of the gas sweep, and nitric oxide, at 0.1 and 1% of the sweep, had no appreciable effect on the rate of polymerization. However, at 10% concentration, nitric oxide catalyzed the reaction (Figure 2). The effect of solid and liquid addends usually classified as polymerization inhibitors is shown in Table I. Tri-

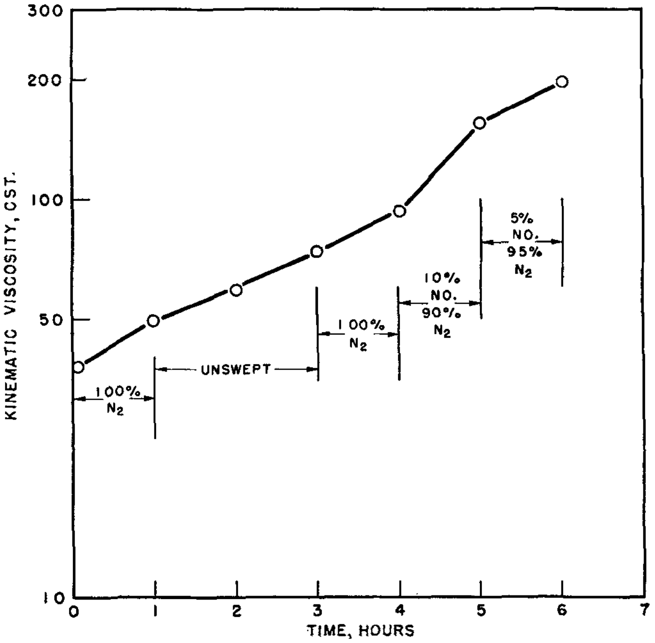

Fig. 2. Kinematic viscosity *vs.* heating time, showing effect of various atmospheres.

cresyl phosphate and cetyl trimethylammonium bromide were without effect whereas hydrogen sulphide and mercaptans catalyzed the reaction, as did dinitrochlorobenzene. Dimethylaniline, an inhibitor of ionic reactions, reduced extent of polymerization only when present at the 6.25 mole % level. Ditertiarybutylhydroquinone did not inhibit the reaction at 240°C. or at 270°C. and appeared to catalyze the reaction slightly at 310°C.

Tung Oil. The effect of catalysts and inhibitors on the polymerization of tung oil is shown in Table II. After heating native tung oil (75% α, 5% β) at 270°C. for 0.17 hr. in the presence of 1 mole % of the addends mentioned above, catalysis was observed in all cases except with dimethylaniline, which caused a 13% reduction in rate.

TABLE II
Catalysis and Inhibition of Tung Oil Polymerization

Addend	Efficiency Factor [a]		
1 mole % concentration	270°C. 10% β	195°C.	
		10% β	80% β
Trichloroacetic acid	1.82	1.29	1.30
Naphthalene-β-sulphonic acid	3.16	3.41	2.00
Iodine	1.22	1.25	1.03
Bromine	......	......	3.91
Anthraquinone	1.22	1.10	1.03
Primary oxidation products	1.11	......	......
Secondary oxidation products (reduced)	1.00	......	1.13
Cumene hydroperoxide	1.88	1.00	1.03
Benzoyl peroxide	1.19	1.06	1.07
Ditertiarybutyl peroxide	2.51	1.29	1.03
Azobisisobutyronitrile	1.76	1.07	1.02
Diazoaminobenzene	1.19	1.12	1.00
Ditertiarybutylhydroquinone	1.71	1.10	1.02
Dinitrochlorobenzene	2.48	1.27	1.21
Dimethylaniline	0.87	0.64	0.92

[a] Values >1.0 represent catalysis, <1.0, inhibition.

The experiment was repeated at 195°C. with 3.0-hr. heating. Except for naphthalene-β-sulphonic acid the same concentration of catalyst produced, at this lower temperature, much less acceleration. In contrast, the inhibitory efficiency of dimethylaniline increased to 36%.

To determine whether the catalysts operated by converting *cis* triene to the *trans* form, an additional experiment was performed. The *trans* double bond content of native tung oil was increased by isomerization from 68.7 to 100%. The isomerized oils were then heated for 3.0 hr. at 195°C. in the presence of addends. The all *trans* tung oil was even less sensitive to addends.

Properties of the Addends. If the Diels-Alder reaction is considered to proceed through an initial lining up of polar and polarized groups, the dielectric constant of the medium could influence the strength of the preliminary union between the diene and dienophile. Accordingly the dielectric constant of linseed oil, plain and with addends, was measured at 25°C. and at 275°C. The maximum increase in dielectric constant was only 17%, increasing the value from 1.8 to 2.1.

In media of such low dielectric constant it is improbable that the ionic addends, *e.g.*, sulphonic acids, would ionize. However, at high temperatures, thermal agitation might be sufficient to break up the original ion pairs. Therefore the conductivity of linseed oil and its solutions of addends was measured at 25°C. and 275°C. with the results shown in Table III. At 25°C. the specific conductances were very low. Of the addends tested, only iodine monochloride increased the conductivity markedly. At 275°C. most of the addends distilled out of the cell, making the measurements of little value. Iodine monochloride was again the most effective addend.

TABLE III
Specific Conductance of Linseed Oil Solutions [a]

Addend	25°C. $K \times 10^{10}$	275°C. $K \times 10^{7}$
Iodine monochloride	25.0	5.9
Dinitrochlorobenzene	3.3	3.6
Naphthalene-β-sulphonic acid	2.0	3.3
Dimethylanaline	1.4	3.9
Anthraquinone	0.5	3.1
No addend	0.0	2.9

[a] To convert to molar conductance, multiply by 10^5.

To determine whether the infrared spectra of linseed oil polymerized in the presence and absence of addends would show significant differences, the spectra of three samples of oil heated for 5 hr. at 280°C. were compared. They showed that in the absence of catalyst, the content of *trans* double bonds was higher.

Catalyst	k(968 cm.$^{-1}$)
None, N_2 sweep	0.176
10% nitric oxide in sweep	0.155
1 mole% diphenyldisulphide	0.142

The samples also differed in absorption at 690 and and 3100 cm.$^{-1}$ The oil polymerized in the presence of diphenyldisulphide showed no absorption at 3100 cm.$^{-1}$ whereas the others had a shoulder on the C-H stretching band.

Discussion

Rates of polymerization and catalyst efficiency were estimated from changes in kinematic viscosity. Concurrent studies in this laboratory have established relations between kinematic and dynamic viscosity and between kinematic viscosity and percentage polymeric glyceride and polymeric acyl groups in a sample of heated oil (18). Therefore the viscosity rate constant can be related directly to polymerization and the over-all activation energies to the union of monomeric acyl groups and triglycerides. Since, in the present investigation, oil from one batch was heated with adequate temperature control and protection from oxidation, the values reported for the over-all activation energies can be considered reliable.

The lines in Figure 1 for α- and β-tung oil are essentially parallel, indicating that the increased reactivity of the all-*trans* β-form is due to increased probability of reaction and not to further reduction in energy of activation. The lower △E of the conjugated acyl groups (23.2 K. cal. per mole) and the larger PZ factor connected with the all-*trans* form suggests that the thermal polymerization of β-tung oil might be considered a limiting process approached in varying degrees by the other oils.

Linseed and tung oils behaved differently in the presence of addends. Linseed oil was more sensitive to acidic and basic catalysis than tung oil, and tung oil containing 80% β-isomer was unaffected by most of the addends. This might be considered further indication that conjugated trienoic material in the *trans* configuration represents the limiting state in thermal polymerization. From the slower rate of polymerization in sealed tubes it might be concluded that, at temperatures greater than 260°C., satellite reactions begin to occur. Bradley (2) has summarized the reactions of simple olefins to show analogy between them and drying oils. Inspection of the reactions shows that, in general, these simple analogues behave differently at 300°C. than they do at temperatures around 250°C. or lower.

Some of the data obtained from the catalysis and inhibition studies appear anomalous. Perhaps the most surprising observation is that of catalysis by recognized inhibitors. However, at the high temperatures employed in thermal polymerization, the radicals formed by union of inhibitor and monomer, which are normally stable, can propagate further. Catalysis by mercaptans and hydrogen sulphide suggests that hydrogen abstraction produces reactive sulphide radicals. Catalysis by 2,4-dinitrochlorobenzene can possibly be explained by the susceptibility of thermal polymerization to polarity of medium. The molar conductances (Table III) are of the same order of magnitude as those encountered in ionic polymerization (12).

Catalysis of the polymerization of tung oil by acidic material is not surprising since the Diels-Alder reaction is mildly subject to general acid catalysis (9). Its inhibition by dimethylaniline is likewise conventional. However the slight but definite catalysis of the polymerization of tung oil by anthraquinone was unexpected as this addend is reputed to act as a conjugation catalyst. Moreover the magnitude of the effect of acidic addends would seem to be greater than might be expected for a Diels-Alder reaction. However, at lower temperatures and with β-tung oil, the effect of addends was less.

The behavior of anthraquinone has been likened to that of potassium hydroxide in glycol (6). The acceleration of the polymerization of linseed oil by p-methoxybenzylamine and Agerite Resin D lends some support to this hypothesis. Moreover, when the data of Falkenburg *et al.* (6) on the effect of anthraquinone on polymerization rate were treated kinetically, the following over-all activation energies for the polymerization of soybean and linseed oils were obtained:

Concentration of anthraquinone		Over-all activation energy	
% by wt.	Mole %	Soybean oil	Linseed oil
2	8.4	20.5	......
5	21.0	26.5	28.4
10	42.0	29.5	......

These values suggest that, at low concentrations, anthraquinone may behave as a true catalyst. At the very high molar ratios employed by these workers however it would seem reasonable to suspect that anthraquinone reacts with the oil.

Iodine has been said to catalyze conversion of *cis* polyolefins to the *trans* form (20) and also their conjugation (10). Iodine compounds also cause conjugation (14). Therefore either mode of action would be possible. However, in this investigation, the halogens, iodine, iodine monochloride, or bromine, are absorbed by the oil shortly after mixing. Consequently the catalyst would seem to be the halogen that is released after absorption. Moreover the polymerization of β-tung oil is catalyzed by halogen. Therefore the halogens have been provisionally included with the acidic catalysts.

Nitric oxide has been shown to cause oleic acid to change to elaidic acid at room temperature (7). Hence it is possible that catalysis by nitric oxide may have been due to this effect. However nitric oxide is a free radical and could possibly have initiated vinyl polymerization. Moreover Gourlay (8) has shown that linseed oil bodying is a slower reaction than the formation of *trans* double bonds and the data obtained from infrared spectra show a lower concentration of *trans* material in the oil heated in the presence of nitric oxide. Diphenyldisulphide does not cause conjugation in oils (6) and does not cause accelerated conversion of *cis* double bonds to the *trans* configuration. Therefore, as suggested by Radlove (13), vinyl polymerization may occur in oils catalyzed by radical sources.

The question of whether the "volatile" material formed during a polymerization reduces the viscosity of a bodied oil by acting as a low molecular weight diluent or by inhibiting the polymerization process has been raised by Seavell and Sleightholme (15). In a concurrent publication (18) samples of linseed oil heated at 310°C. in sealed tubes were shown by molecular distillation to contain 3% less polymer, after correction for volatile material, than corresponding samples taken from a swept reactor. This information, coupled to that given in Figure 2 suggests that the volatile decomposition products do inhibit the thermal polymerization of linseed oil at temperatures greater than 260°C.

The alternative possibility, that the nitrogen used in the sweep might contain sufficient oxygen to catalyze the polymerization, is ruled out by a negative test for oxygen in the gas, using ammoniacal cuprous chloride. Moreover, in the sealed tubes, cetyl trimethyl-ammonium bromide, which inhibits the peroxide catalyzed polymerization of styrene (16), did not affect the rate of polymerization and Agerite Resin D, a polyquinoline antioxidant stable at high temperatures, acted as a basic catalyst and not as an inhibitor.

The magnitude of the acid catalysis and the experimentally determined over-all activation energy of the polymerization of non-conjugated oils are not in keeping with a Diels-Alder reaction (9). If a corresponding large PZ value is used, as is usual with a Diels-Alder reaction (19), the P term becomes too great. In addition, the activation energy for the reverse Diels-Alder reaction is also 35 K. cal. per mole (9). This reaction is characterized by a large PZ factor and would therefore take place readily at temperatures of 300°C. On the other hand, the activation energy for the thermal polymerization of tung oil is near the upper limit for Diels-Alder reactions, and if the over-all polymerization of linseed oil includes conjugation, the large activation energy for non-conjugated oils could be accounted for.

Thermal polymerization of drying oils has many of the characteristics of a polycondensation and the Diels-Alder reaction appears to be a suitable explanation for the growth in molecular size. In the absence of polarizing substituents on the diene and dienophile and ionic catalysis, it is likely that the Diels-Alder reaction proceeds homolytically. Therefore the initial reaction in thermal polymerization of drying oils is probably the opening up of double bonds to form diradicals. If the chain stops at dimerization, the reaction is essentially a Diels-Alder condensation.

However even in the presence of a large concentration of radicals, such as pyrolysis would produce, the chain could propagate further.

In summary, it would appear that the polymerization of β-tung oil might be considered as the limiting case in thermal polymerization. With non-conjugated oils this basic reaction seems to be accompanied by other reactions: some necessary, such as conjugation; and others, purely satellite. The basic reaction has many of the characteristics of a Diels-Alder reaction, and Clingman's recent proof of the presence of six-membered rings in the reaction products (5) is additional supporting evidence for this hypothesis. Of the alternative reactions, only those involving radicals are likely to occur in the absence of deliberate catalysis and then only at relatively high temperatures. The high activation energy of the reaction involving non-conjugated acyl groups might be considered to be the sum of the energy of conjugation and the energy of polymerization. However no rate equation describing these conditions has yet been developed.

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Prepress-Solvent Extraction of Cottonseed, Processing Conditions and Characteristics of Products[1]

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THE use of screw-pressing prior to solvent-extraction is a growing development in the cottonseed processing industry. This process, commonly termed prepress-solvent extraction, comprised some 12% of the crush in 1951-1952 (6) and probably 20-25% at the present time. Since this indicates widespread availability of prepress-solvent extracted cottonseed meals and oils, the quality of these relatively new products is of considerable interest in current research on improving the value of cottonseed products (1, 2, 3, 9, 10). Accordingly a survey of this process was undertaken with the cooperation of 11 mills located throughout the cottonseed processing area. The survey was designed to yield information concerning the influence of processing conditions normally used by the cooperating mills both on the chemical properties of meals and oils and on the nutritive value of the meals.

Samples and Methods of Analysis

Samples, representative of the materials at various stages of processing, were obtained by appropriately compositing individual samples taken at regular intervals during a period of eight hours of normal operation by each mill. Where possible three complete sets of samples, taken at intervals of about six weeks, were obtained for each mill. Data on processing conditions are summarized in Tables I and II.

Moisture, oil, total nitrogen, free fatty acids, and free gossypol were determined by use of Official Methods of the American Oil Chemists' Society (4). Methods proposed by Pons *et al.* (14, 15) were employed for the determination of total gossypol in meats and meals and in crude oils. Nitrogen solubility was determined by dispersion in 0.5 M sodium chloride as proposed by Olcott and Fontaine (13), and in 0.02 N sodium hydroxide as suggested by Lyman *et al.* (11).

The crude oils were refined in accordance with Official Method Ca 9a-52 of the American Oil Chemists' Society; prepressed oils were treated as directed for expeller oils and solvent-extracted oil as indicated for hydraulic oils. These procedures were employed since no official refining methods are available for prepressed oils and for solvent-extracted oils from prepressed cake. The refined oils were bleached as directed by Official Method Cc 8a-52, and oil color was determined by use of the photometric method Cc 13c-50 of the American Oil Chemists' Society (4). The values reported for refining loss and oil color were selected in accordance with the settlement rules of the National Cottonseed Products Association (12).

Discussion of Results

It is generally recognized that, during the processing of cottonseed, the pigment glands which are dis-

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