Anchovy Oil Thermal Polymerization Kinetics

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ABSTRACT: The thermal polymerization reaction kinetics of anchovy oil was investigated with and without catalyst. In order to make a comparison, linseed oil was included in the study. Reactions were carried out 260, 270, and 280°C, and a kinetic model was determined for each case. The reactions for linseed oil with and without catalyst at all temperatures followed the first-order kinetics. In the case of anchovy oil, the best-fitted straight line is obtained by plotting viscosity values against time, and the reaction proceeds in two stages at 280°C without catalyst. The use of catalyst lowered the temperature to 270°C for the appearance of two different rates. Additionally, some mathematical equations were derived between iodine value, refractive index, viscosity, and reaction time.

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KEY WORDS: Anchovy oil, kinetics, linseed oil, thermal polymerization.

Drying oils, such as linseed, soybean, dehydrated castor, and fish oil, are used in making paints, varnishes, enamels, printing inks, and other protective and decorative coatings of an oil-based type. Since raw and refined oils have low viscosity, and give easy brushing, poor leveling, slow drying, and relatively low gloss, various methods have been used for their modification. One of the well-known modification methods is heat polymerization. Heat-polymerized, bodied, or stand oils generally have better drying, wetting, and color retention properties than the unbodied oils (1,2).

The mechanism of the thermal polymerization of some vegetable oils, their fatty acids, and methyl esters is well-documented in the literature (3–13). However, only a few investigations document the reaction kinetics (8,10,14,15). Erhan and Bagby (15) studied the catalyzed and uncatalyzed thermal polymerization of sunflower, soybean, safflower, cottonseed, and canola oils at temperatures from 280 to 320°C. The reaction was first-order (15). Sims (8) also studied the polymerization kinetics of linseed, safflower, oiticica, and tung oils at 240 to 310°C.

During the heat-bodying process, polymerization is controlled by determining viscosity of the oil. As viscosity increases, iodine value is decreased due to saturation of carbon-carbon double bonds, and growth in molecular size is reflected by increases in refractive index (16). The most common catalysts are sulfur dioxide, hydrogen chloride, boron trifluoride, metallic nickel, and rubber accelerators (2, 17–19). In the heat-bodying process, formation of free acid and dark color is due mostly to oxidative decomposition during heating in an open kettle when bodying takes place under an inert atmosphere or reduced pressure.

In the present study, reaction kinetics of heat polymerization of anchovy oil was investigated with and without catalyst. Linseed oil was included as a control treatment. Reactions were carried out at 260, 270, and 280°C. A kinetic model was determined for each case. In addition, mathematical equations were derived between some properties and reaction temperature.

EXPERIMENTAL PROCEDURES

Materials. Linseed oil purchased from Garanti Bezir Co. (Istanbul, Turkey) and anchovy oil obtained from Ar Kimya Co. (Istanbul, Turkey) were used. Table 1 presents the main characteristics and fatty acid compositions of these oils. Anthraquinone was analytical grade from Merck (Darmstadt, Germany).

For the determination of fatty acids, methyl esters of anchovy and linseed oils were subjected to capillary gas chromatographic analysis with apparatus of Hewlett-Packard 6890 Series 2 (Hewlett-Packard, Waldron, Germany) fitted with a flame-ionization detector and a data processor, under the following conditions: column, Ultra 2 (25 m × 0.32 mm) with 0.52 µm film thickness, 5% diphenyl, 95% dimethyl polysiloxane; nitrogen carrier gas at 1.72 mL/min; air flow of 450 mL/min; hydrogen flow 69 mL/min; injection, split 50:1, 0.5 µL; injection temperature, 225°C; oven temperature program, 150°C (5 min), 150 to 225°C (5°C/min), 225°C (30 min); flame-ionization detector temperature, 250°C.

Experimental setup. Thermal polymerization reactions were carried out in a four-necked flask equipped with a stirrer, a thermometer, an inert gas inlet tube, and an inclined air condenser.

Polymerization of the oil. In the reaction, 150 g refined oil was placed into the 250-mL reaction flask and heated, by using a heating mantle, to the reaction temperature. In the case of catalyzed reactions, 1% by weight of anthraquinone was added to the reaction flask. The stirring rate was adjusted to 200 rpm, and nitrogen was passed over the surface of the reaction mixture to provide an inert atmosphere. Samples were withdrawn at predetermined time intervals and cooled immediately by immersion into a cold-water bath.

The refractive indexes (20) and iodine values (21) of the samples were obtained by using standard methods. The viscosities of the samples were determined with a Gardner-Holdt Bubble Viscometer (Gardner Lab., Silver Spring, MD) by following the American Society for Testing and Materials Method ASTM D-1545-63 (22).

RESULTS AND DISCUSSION

The change of viscosity with time for the polymerization reaction of linseed and anchovy oils is shown in Figures 1 and 2, the extent of the changes in viscosity for linseed and anchovy oils is sharply different from each other. Rates of the polymerization reaction were estimated from changes in viscosity. For this purpose, the integral method was used to correlate the experimental data. The first-order rate equation showed the best fit to the experimental data for linseed oil with and without catalyst at all temperatures (Fig. 3). However, in the case of anchovy oil, the best-fitted straight line is obtained by plotting viscosity values against time (Fig. 4). As can be seen from Figure 4, the course of the reaction without catalyst at 280°C may be resolved into two stages. The reaction proceeds rapidly in the initial 2-h reaction period, and after this period it progresses at a smaller rate. The use of catalyst lowered the temperature to 270°C for the appearance of two different rates. Below 270°C, the experimental data belonging to both catalyzed and uncatalyzed reactions were fitted well to only one straight line in the whole reaction period of 10 h. This observation can be explained by fatty acid composition of anchovy oil. It is well known that the heat bodying (thermal polymerization) is mainly due to the Diels-Alder reaction of the double bonds present in the fatty acid chains. For this reaction, first, isolated double bonds migrate to the conjugated position, and then remaining isolated double bonds on the other molecules are added to this conjugated system. The amount and position of the double bonds cause the oil to behave in a different manner in thermal polymerization. As seen in Table 1, anchovy oil contains about 25% fatty

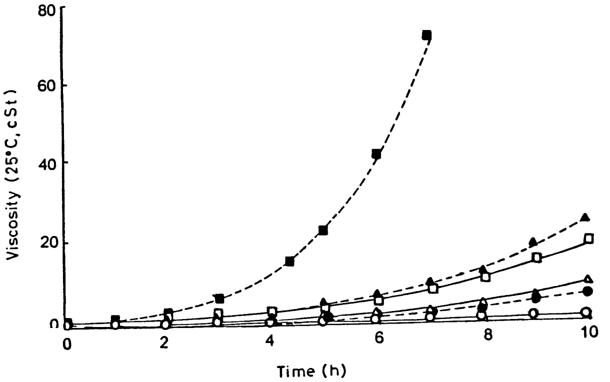

FIG. 1. The change of viscosity for the thermal polymerization reaction of linseed oil at: ○, 260°C without catalyst; △, 270°C without catalyst; □, 280°C without catalyst; ●, 260°C with catalyst; ▲, 270°C with catalyst; ■, 280°C with catalyst.

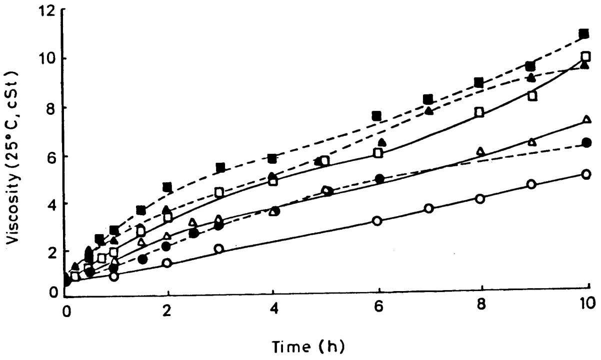

FIG. 2. The change of viscosity for the thermal polymerization reaction of anchovy oil at: ○, 260°C without catalyst; △, 270°C without catalyst; □, 280°C without catalyst; ●, 260°C with catalyst; ▲, 270°C with catalyst; ■, 280°C with catalyst.

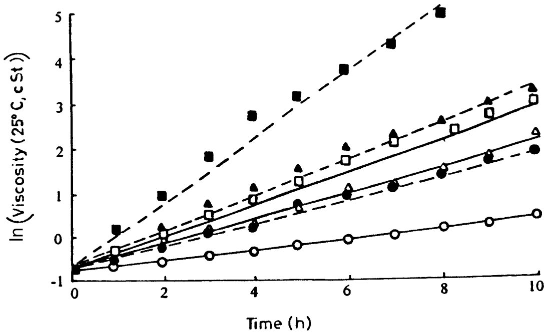

FIG. 3. Rate of thermal polymerization reaction of linseed oil at: ○, 260°C without catalyst, r^2 (coefficient of determination) = 0.9918; △, 270°C without catalyst, r^2 = 0.9930; □, 280°C without catalyst, r^2 = 0.9956; ●, 260°C with catalyst, r^2 = 0.9963; ▲, 270°C with catalyst, r^2 = 0.9832; ■, 280°C with catalyst, r^2 = 0.9931.

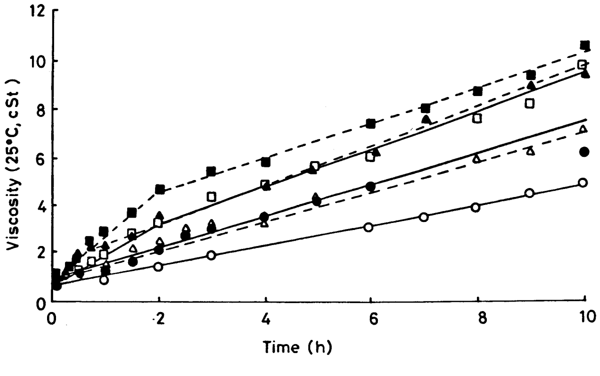

FIG. 4. Rate of thermal polymerization reaction of anchovy oil at: ○, 260°C without catalyst, r^2 (coefficient of determination) = 0.9967; △, 270°C without catalyst, r^2 = 0.9850; □, 280°C without catalyst (for initial stage) r^2 = 0.9927, (for final stage) r^2 = 0.9798; ●, 260°C with catalyst, r^2 = 0.9644; ▲, 270°C with catalyst (for initial stage) r^2 = 0.9653, (for final stage) r^2 = 0.9929; ■, 280°C with catalyst, (for initial stage) r^2 = 0.9967, (for final stage), r^2 = 0.9930.

TABLE 1
Characteristics and Composition of Oil Specimens

Property	Anchovy oil	Linseed oil
Refractive index[a] (n_D^{25})	1.4768	1.4786
Acid value[a]	2.7	1.1
Saponification value[a]	196.7	195.5
Iodine value[b]	147.7	172.7
Viscosity (25°C) (cSt)	0.65	0.5
Fatty acid composition (%)		
$C_{14:0}$	6.5	—
$C_{15:0}$	0.3	—
$C_{16:0}$	19.4	3.5
$C_{16:1}$	9.0	—
$C_{16:2}$	0.7	—
$C_{16:3}$	0.2	—
$C_{16:4}$	0.9	—
$C_{17:0}$	0.8	—
$C_{18:0}$	4.2	2.5
$C_{18:1}$	22.0	31.0
$C_{18:2}$	2.8	23.0
$C_{18:3}$	1.3	—
$C_{18:4}$	1.3	—
$C_{20:0}$	0.2	0.4
$C_{20:1}$	0.9	—
$C_{20:2}$	2.0	—
$C_{20:4}$	1.4	—
$C_{20:5}$	7.6	—
$C_{22:1}$	2.1	—
$C_{22:4}$	1.6	—
$C_{22:5}$	1.6	—
$C_{22:6}$	12.7	—
Fatty acid composition (%)		
Saturated acids	31.4	6.4
Monounsaturated acids	34.0	31.0
Diunsaturated acids	5.5	23.0
Triunsaturated acids	2.1	35.0
More than triunsaturated acids	27.1	—

[a] Reference 20.
[b] Reference 21.

acids of more than 20 carbon atoms, some of which have more than four double bonds. As explained previously, at the initial stage of the reaction, conjugation occurs and the Diels-Alder reaction takes place. There is no doubt that, after addition of double bonds to the conjugated system at a given fatty acid chain, the remaining double bonds cannot readily go into subsequent reaction owing to steric hindrance.

The other fact is that anchovy oil contains about 30% saturated fatty acids whereas linseed oil has 6.4% saturated fatty acids. In the light of these facts, it may be possible to explain the different behavior of anchovy oil in thermal polymerization. At higher temperatures, most of the double bonds are forced to participate in the reaction within 2 h, and the remaining less reactive double bonds are consumed with a slower reaction rate owing to steric hindrance compared to initial reaction rate. However, at lower temperatures, consumption of readily reactable double bonds continues within all reaction periods of 10 h, and only one straight line is fitted to all experimental data.

The viscosity increase in linseed oil is higher than that in anchovy oil. As stated above, in comparison with linseed oil, the saturated portion of anchovy oil is larger and may show a plasticizer effect in the heat-bodied oil and decrease the viscosity.

As can be seen in Table 2, in the anthraquinone-catalyzed reaction, the viscosity increase is greater in comparison with the case of uncatalyzed reaction. Hydrogen atom from the methylene groups between two double bonds is abstracted by the anthraquinone, and free radical is formed on the fatty acid chain (10,11,17). The double bonds are shifted to the conjugated position to provide a more stable structure, and two kinds of polymerization may occur, i.e., Diels-Alder addition and free radical polymerization. Even in the presence of anthraquinone catalyst, the viscosity increase in anchovy oil is lower than that in linseed oil for the same reason explained above. For linseed oil, gelation occurred at 280°C with catalyst.

From the slopes of the straight lines, the rate constants (k) were calculated, and the results are presented in Table 3. The activation energies given in the same table were determined from the slopes of the lines obtained by plotting ln k against $1/T$, where I is the reaction temperature (K). Comparing the k belonging to the same ordered reactions, thermal polymerization reaction was accelerated by using anthraquinone and by increasing the temperature. The initial stages of the reactions represented by two straight lines at Figure 4 are approximately two times faster than those of the final stages.

To follow the reaction course with easily measurable properties, some additional work was carried out. For this purpose,

TABLE 2
Some Properties of the Final Products[a]

Reaction temperature (°C)	Catalyst used in the reaction	Properties			
		Iodine value of LO	Viscosity of LO (cSt)	Iodine value of AO	Viscosity of AO (cSt)
260	None	136.0	1.6	103.2	5.0
	Anthraquinone	137.4	6.3	86.5	6.1
170	None	125.3	9.8	82.6	7.1
	Anthraquinone	125.8	24.9	90.6	9.3
280	None	115.6	19.3	88.7	9.8
	Anthraquinone	122.7[b]	138.1[b]	87.0	10.7

[a] Properties of the product after 10 h.
[b] Properties of the product after 8 h (gelation occurred after 10 h); LO, linseed oil; AO, anchovy oil.

TABLE 3
Rate Constants and Activation Energies for the Thermal Polymerization Reactions

Oil	Catalyst used in the reaction	Rate constant (k) (cSt/h) 260°C	270°C	280°C	Activation energy (E) (kcal/mole)
Linseed oil	None	0.1196[a]	0.2849[a]	0.3818[a]	34.1
Linseed oil	Anthraquinone	0.2664[a]	0.4046[a]	0.6975[a]	28.2
Anchovy oil	None	0.4386	0.5927	1.4048[b], 0.7297[c]	34[d], 15[e]
Anchovy oil	Anthraquinone	0.6896	1.6984[b], 0.7843[c]	1.9446[b], 0.1[a,c]	30.5[d], 7.4[e]

[a] The unit of the rate constant is h^{-1}.
[b] The k corresponding to the initial stage.
[c] The k corresponding to the final stage.
[d] E corresponding to the initial stage.
[e] E corresponding to the final stage.

TABLE 4
Relations for the Changes of Iodine Value and Refractive Index with Time[a]

Property	Oil	Reaction temperature (°C)	Equation for the reaction: Without catalyst	r^2	With catalyst	r^2
Iodine value	Linseed oil	260	$IV = 0.1329t^2 - 5.4722t + 176.34$	0.9629	$IV = 0.1565t^2 - 4.8784t + 173.64$	0.9785
		270	$IV = 0.0303t^2 - 5.2889t + 173.57$	0.9919	$IV = 0.143t^2 - 5.8679t + 171.93$	0.9909
		280	$IV = 0.1812t^2 - 7.3824t + 172.16$	0.9979	$IV = 0.6646t^2 - 11.853t + 172.95$	0.9971
	Anchovy oil	260	$IV = 0.8375t^2 - 11.522t + 138.58$	0.9310	$IV = -10.344\ln(t) + 123.04$	0.9692
		270	$IV = 0.5628t^2 - 10.687t + 135.98$	0.9115	$IV = -11.12\ln(t) + 114.25$	0.9861
		280	$IV = -12.82\ln(t) + 116.3$	0.9713	$IV = -10.919\ln(t) + 110.58$	0.9913
Refractive index (n_D^{25})	Linseed oil	260	$RI = -2 \times 10^{-5}t^2 + 10^{-5}t + 1.4796$	0.9669	$RI = -3 \times 10^{-5}t^2 + 10^{-3}t + 1.4789$	0.9919
		270	$RI = -3 \times 10^{-6}t^2 + 7 \times 10^{-4}t + 1.4785$	0.9961	$RI = -8 \times 10^{-6}t^2 + 17 \times 10^{-4}t + 1.4788$	0.9962
		280	$RI = -3 \times 10^{-5}t^2 + 12 \times 10^{-4}t + 1.4784$	0.9930	$RI = -2 \times 10^{-4}t^2 + 25 \times 10^{-4}t + 1.4792$	0.9851
	Anchovy oil	260	$RI = 0.0015\ln(t) + 1.4780$	0.9806	$RI = 0.0011\ln(t) + 1.4797$	0.9480
		270	$RI = 0.0012\ln(t) + 1.4794$	0.9333	$RI = 0.0012\ln(t) + 1.4807$	0.9837
		280	$RI = 0.0012\ln(t) + 1.4794$	0.9883	$RI = 0.0013\ln(t) + 1.4810$	0.9813

[a] t, time (h); IV, iodine value; RI, refractive index (n_D^{25}); r^2, coefficient of determination.

TABLE 5
Relations for the Changes of Iodine Value, Refractive Index, and Viscosity During the Thermal Polymerization Reaction[a]

Oil	Reaction temperature (°C)	Equation for the reaction: Without catalyst	r^2	With catalyst	r^2
Linseed oil	260	$IV = -9303.3\ (RI) + 13880$	0.8413	$IV = -5219.8\ (RI) + 7893.2$	0.9661
		$IV = 147.18\ (V)^{-0.2234}$	0.9573	$IV = 161.97\ (V)^{-0.0803}$	0.9761
		$RI = 0.0021 \ln(V) + 1.4806$	0.9596	$RI = 0.0023 \ln(V) + 1.4811$	0.9699
	270	$IV = -7646.5(R)I + 11479$	0.9888	$IV = -4896.7\ (RI) + 7416.2$	0.9699
		$IV = 160.67\ (V)^{-0.1174}$	0.9767	$IV = 162.95\ (V)^{-0.0735}$	0.9876
		$RI = 0.0023 \ln(V) + 1.4802$	0.9804	$RI = 0.0022 \ln(V) + 1.4813$	0.9691
	280	$IV = -6391.7\ (RI) + 9622.1$	0.9898	$IV = -5131.3\ (RI) + 7763.8$	0.9816
		$IV = 159.06\ (V)^{-0.1026}$	0.9932	$IV = 162.27\ (V)^{-0.065}$	0.9755
		$RI = 0.0023 \ln(V) + 1.4805$	0.9926	$RI = 0.0018 \ln(V) + 1.4815$	0.9309
Anchovy oil	260	$IV = 2349450(RI)^2 - 6960740(RI) + 5155770$	0.9667	$IV = -341380(RI)^2 + 1000870(RI) - 733370$	0.9759
		$IV = 127.99(V)^{-0.1714}$	0.8446	$IV = 134.03\ (V)^{-0.1712}$	0.9694
		$RI = 0.0022 \ln(V) + 1.4781$	0.9596	$RI = 0.0022 \ln(V) + 1.4785$	0.9707
	270	$IV = -827130(RI)^2 + 2436020(RI) - 1793450$	0.9561	$IV = -72649\ (RI)^2 + 205604\ (RI) - 145042$	0.9948
		$IV = 130.82\ (V)^{-0.2485}$	0.9154	$IV = 138.37\ (V)^{-0.2025}$	0.9709
		$RI = 0.0022 \ln(V) + 1.4786$	0.9206	$RI = 0.0023 \ln(V) + 1.4783$	0.9552
	280	$IV = -63682\ (RI)^2 + 177317\ (RI) - 122831$	0.9854	$IV = -253042\ (RI)^2 + 741047\ (RI) - 542367$	0.9899
		$IV = 129.98\ (V)^{-0.1939}$	0.9516	$IV = 133.14\ (V)^{-0.1862}$	0.9861
		$RI = 0.0019 \ln(V) + 1.4782$	0.9773	$RI = 0.0023 \ln(V) + 1.4786$	0.9775

[a] IV, iodine value; RI, refractive index (n_D^{25}); V, viscosity (25°C, cSt); r^2, coefficient of determination.

the relations of viscosity, refractive index, and iodine value with time and with one another were derived by applying the least-squares curve-fitting method. The best fit for the experimental data was decided by considering the coefficients of determination (r^2). The obtained relations are given in Tables 4 and 5 together with the corresponding r^2.

REFERENCES

1. Swern, D., *Bailey's Industrial Oil and Fat Products*, 4th edn., John Wiley & Sons, New York, 1982, Vol. 1, pp. 687–816.
2. Cowan, C.J., Drying Oils, in *Kirk-Othmer Encyclopedia of Chemical Technology,* 3rd edn., edited by H.F. Mark, D.F. Othmer, C.G. Overberger, and G.T. Seaborg, John Wiley & Sons, New York, 1979, Vol. 8, pp. 130–150.
3. Bradley, T.F., and W.B. Johnston, Drying Oils and Resins. Reactions Involving the Carbon-to-Carbon Unsaturation During the Thermal of Some Esters of Unsaturated C_{18} Fat Acids, *Ind. Eng. Chem. 32*:802–809 (1940).
4. Powers, P.O., Mechanism of the Heat Bodying of Linseed Oil, *J. Polymer Sci. 5*:741–743 (1950).
5. Maschka, A., and A. Mendl, Investigation by Means of Ultraviolet Spectroscopy of the Catalytic Bodying of Linseed Oil, *Ibid. 5*:429–441 (1950).
6. Joubert, F.J., and D.A. Sutton, The Chemistry of Polymerized Oils, *J. Am. Oil Chem. Soc. 29*:287–291 (1952).
7. Paschke, R.F., J.E. Jackson, and D.H. Wheeler, Thermal Polymerization of Drying Oils, *Ind. Eng. Chem. 44*:1113–1118 (1952).
8. Sims, R.P.A., Possible Mechanisms in Thermal Polymerization of Drying Oils. I. Catalysis and Inhibition Studies, *J. Am. Oil Chem. Soc. 32*:94–98 (1955).
9. Sims, R.P.A., Possible Mechanisms in Thermal Polymerization of Drying Oils. II. Polymer Formation, *Ibid. 34*:466–469 (1957).
10. Rushman, D.F., and E.M.G. Simpson, The Thermal Polymerization of Methyl Linoleate. Part 1. The Uncatalyzed Reaction, *Trans. Faraday Soc. 51*:230–236 (1955).
11. Rushman, D.F., and E.M.G. Simpson, The Thermal Polymerization of Methyl Linoleate. Part 2. The Catalyzed Reaction, *Ibid. 51*:237–241.
12. Boelhouwer, C., J. T. Knegtel, and M. Tels, On the Mechanism of the Thermal Polymerization of Linseed Oil, *Fette-Seifen Anstrichm. 69*:432–436 (1967).
13. Koley, S.N., Mechanism of Oil Polymerization. I. Thermal Polymerization, *Indian Oil Soap J. 36*:212–216 (1971).
14. Paschke, R.F., and D.H. Wheeler, Thermal Polymerization of Methyl Linolenate, Alpha- and Beta-Eleostearates, *J. Am. Oil Chem. Soc. 32*:469–473 (1955).
15. Erhan, S.Z., and M.O. Bagby, Polymerization of Vegetable Oils and Their Uses in Printing Inks, *Ibid. 71*:1223–1226 (1994).
16. Mattiello, J.J., *Protective and Decorative Coatings, Vols. 1–5*, John Wiley & Sons, New York, pp. 1941–1945.
17. Croston, C.B., I.L. Tubb, J.C. Cowan, and H.M. Teeter, Polymerization of Drying Oils. VI. Catalytic Polymerization of Fatty Acids and Esters with Boron Trifluoride and Hydrogen Fluoride, *J. Am. Oil Chem. Soc. 29*:331–333 (1952).
18. Waterman, H.I., C. van Vlodrop, and M.J. Pfauth, The Activation of Linseed Oil by Sulfur Dioxide, *Verf-kroniek 13*:130–136 (1940). *C.A. 34*:8305^8 (1940).
19. Waterman, H.I., C. van Vlodrop, and J. Hannewijk, Catalytic Action of Sulfur Dioxide of Fatty Oils, *Ibid. 13*:180–182 (1940). *C.A. 34*:8305^9 (1940).
20. Cocks, L.V., and C. van Rede, *Laboratory Handbook of Oil and Fat Analysts*, American Press, London and New York, 1966.
21. Kaufman, H.P., *Analyse der Fette u. Fettprodukte*, Vol. 1, Springer-Verlag, Berlin, 1958, p. 571.
22. *American Society for Testing and Materials, Book of ASTM Standards,* American Society for Testing and Materials, Philadelphia, 1963, ASTM D-1545-63.

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