5. Krzeminski, L. F., and Quackenbush, F. W., submitted to Arch. Biochem. Biophys.
6. Lein, J., Puglisi, T., and Lein, P. S., Arch. Biochem. Biophys., *45*, 434 (1953).
7. Ottke, R. C., Arch. Biochem., *23*, 49 (1949).
8. Ottke, R. C., Tatum, E. L., Zabin, I., and Bloch, K., J. Biol. Chem., *189*, 429 (1951).
9. Schlenk, H., Gellerman, J. L., Tillotson, J. A., and Mangold, H. K., J. Am. Oil Chemists' Soc., *34*, 377 (1957).
10. Todd, D., Stone, D., Hechter, O., and Nussbaum, A., J. Biol. Chem., *229*, 527 (1957).
11. Zalokar, M., Arch. Biochem. Biophys., *50*, 71 (1954).

[Received January 11, 1960]

Polymerization of Linseed Oil in an Electric Discharge

C. BOELHOUWER, T. HOEKSTRA,[1] H. I. WATERMAN, and J. B. WESTERDIJK, with the collaboration of J. VAN DAM and A. J. KRUIDENIER, Laboratory of Chemical Engineering, Technological University, Delft, Holland

WHEN MINERAL OILS or fatty oils are subjected to the action of glow discharges in a hydrogen or a nitrogen atmosphere at low pressure a considerable increase in viscosity is effected, probably because of polymerization of the starting material. In the "Elektrion" process of De Hemptinne (1), also known as "Voltol" process (2), this reaction was applied, especially during the first World War, on a commercial scale for the preparation of high-grade lubricating oils.

The phenomena in an electric discharge are very complicated. In a low-pressure hydrogen atmosphere the action of hydrogen atoms, in all probability, is of primary importance (3). Polymerization of unsaturated as well as saturated compounds takes place by the combination of radicals which have been formed primarily by the action of the hydrogen atoms; in addition, hydrogenation and dehydrogenation reactions have been reported (4).

Several authors (5, 6) investigated the applicability of the Voltol-process for the preparation of polymerized oils in the paint industry. According to Goldenstein (6), the properties of voltolized linseed oils are better in several respects than thermally polymerized oils, especially in regard to the hardness and resistance of the films after drying. This might be due to the completely different chemical structure of the polymerized oils. The thermal polymerization, which can be considered as a Diels-Alder condensation of conjugated double bonds in the fatty acid chains, results in the formation of six-membered rings in the polymerized oils (7, 8); polymerization in a glow discharge at low temperature, *e.g.*, 70°C., is a result of a combination of radicals into compounds in which the occurrence of cyclic structures is questionable (9).

In 1952 Boelhouwer, Jol, and Waterman (8) published a general scheme for analysis of polymerized fatty oils, which allows for a reliable determination of the contribution of intramolecular reactions (combination of fatty acid chains in the original glyceride molecules) and intermolecular reactions (combination of fatty acid chains of different glyceride molecules), also for a proper study of the coupling of the fatty acid chains in the polymerization process, particularly in regard to the occurrence of rings in the polymerized oils.

According to this scheme the polymerized oil to be investigated is first stabilized by hydrogenation (150°C., 100 atm. hydrogen, 5% of a nickel on kieselguhr catalyst) to saturate the olefinic double bonds, then separated quantitatively into monomeric and polymeric glycerides by repeated molecular distillation in a falling film still (10). Both the monomeric and the polymeric glycerides are saponified and the fatty acids, after transformation into their methyl esters, are submitted to ordinary vacuum fractionation. Monomeric esters distill at 150°–200°C. at 1 mm. Hg and dimeric esters remain as a residue (boiling point >250°C. at 1 mm. Hg). The degree of intramolecular polymerization is indicated directly by the amount of residual methyl esters obtained from the monomeric glycerides. To investigate the presence of rings, the methyl ester fractions are transformed into saturated hydrocarbon mixtures, *e.g.*, by direct hydrogenation (11) (300°–350°C., 300 atm. hydrogen, and 20% of a nickel copper on kieselguhr catalyst). The average number of rings per molecule in the hydrocarbon mixtures follows from their physical properties according to ring analysis methods (13) and can also be calculated directly from ultimate analysis and molecular weight.

This scheme was applied in earlier work to the study of thermally polymerized linseed oils (8) and tung oils (12). For comparison the analysis of some voltolized linseed oils is described in this paper.

Description of Apparatus

For the treatment of linseed oil a laboratory "Voltol" reactor was constructed (Figure 1) which resembles commercial equipment described in the literature (1, 2) and allows voltolization of oils under corresponding conditions.

The experiments are conducted in a rotating cylindrical Pyrex tube (500 × 90 mm.) composed of two parts, which are held together by glass flanges, tightened with oil-resistant rubber rings. The narrow ends of the rotating reactor are connected with fixed inlet and outlet tubes with spherical joints, lubricated with Apiezon grease.

Two concentric aluminum cylinders serve as electrodes. They are separated by a glass cylinder, protruding 60 mm. on both ends of the electrodes. The contact wires, which connect the electrodes with sliding contacts on both ends of the reactor, are laid on in such a way that there is no danger of sparks. Tungsten wires connect with the outside of the reactor.

In the reactor approximately 600 ml. of oil can be treated. The surfaces of the electrodes and the separating glass cylinder are wetted continuously by an

---

[1] Compare T. Hoekstra, Thesis, Delft 1958 (in Dutch).

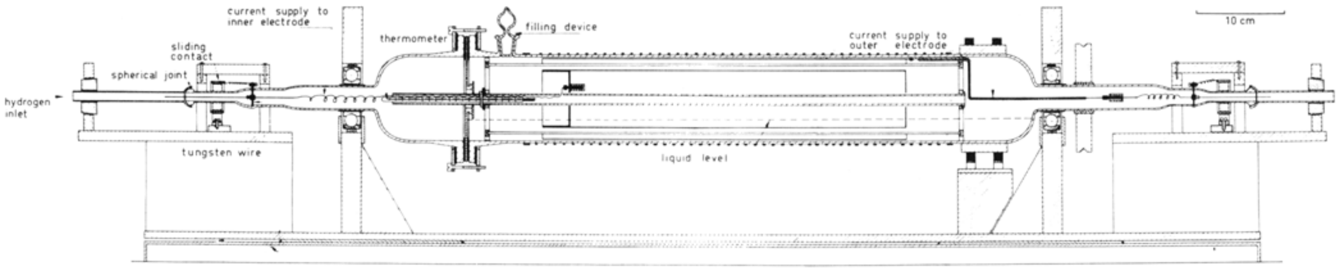

FIG. 1. Laboratory Voltol apparatus.

oil film which is maintained by the rotation of the system.

A thermometer is placed in a small central glass tube and a heating spiral is wound around the outside of the reactor. Current supply is provided by a sliding contact.

Experimental

In the laboratory Voltol apparatus, linseed oil was submitted to electrical discharges in a hydrogen atmosphere at a pressure of 8 cm. Hg and a temperature of 70°C. The reactor was rotated 10 times per minute. The effective potential difference between the electrodes amounted to 6,000 V, the effective discharge current was 24 mA, and the applied frequency 500 Herz.

To maintain a constant hydrogen pressure in the apparatus, hydrogen had to be supplied during the experiments because some hydrogenation of the oil occurred.

It is a well known fact that the reaction time of voltolization processes of fatty oils is limited by the formation of high molecular products, which are insoluble in the oil and may give rise to inhomogeneities in the reaction products even when the viscosity increase is still small. In our experiments the voltolization was finished before these phenomena set in; therefore the obtained voltolized oils possessed a limited viscosity only.

In Table I the reaction conditions for two experiments are given, and some physical data of the reaction products are presented.

The voltolized linseed oils were analyzed according to the scheme mentioned above, and each was transformed into four hydrocarbon fractions, representing the monomeric and polymeric fatty acid groups of both the monomeric and polymeric glyceride molecules of the reaction products. The results are shown in Table II in which, for comparison, are also given analytical data of a thermally polymerized linseed oil (9).

Discussion of Results

1. Table I shows that considerable polymerization occurs during the voltolization process of linseed oil. The molecular weight and the viscosity of the oil show a remarkable increase. The consumption of hydrogen points to a distinct hydrogenation of olefinic double bonds. The carboxylic groups are not attacked; the saponification value remains constant during the process.

2. Reaction of fatty acid chains during the voltolization process is nearly exclusively intermolecular (Table II). The amount of glyceride molecules in which an intramolecular combination of fatty acid chains occurs can be ignored. There is an obvious difference with thermal polymerization, where a fair, though not predominant, intramolecular polymerization is effected.

When it is assumed that during voltolization intramolecular reactions can be ignored, also in the polymeric glycerides, the ratio of monomeric and polymeric methyl esters obtained from the polymeric glycerides (which amounts to $14.5:7.5 \simeq 2:1$ in oil I) indicates that in the beginning only dimeric glycerides are formed. In later stages of the process formation of trimeric glycerides also occurs; the decreased ratio of the methyl esters in oil II ($36:25 \simeq 3:2$) might indicate that approximately one-half of the polymeric glyceride molecules is dimeric, the other half is trimeric. The molecular weights of the voltolized oils (Table I) are in reasonable accordance with these considerations.

3. The results of the structural analyses of the hydrocarbon fractions, obtained from the voltolized oils (Table II), show that the products are poor in cyclic structures. The monomeric fatty acid chains are not at all cyclic; the polymeric groups contain only 0.8 rings on the average. This indicates a sharp contrast with the structure of thermally polymerized linseed oils. The polymeric fatty acid chains contain more than two rings per average molecule, and even the monomeric fatty acid chains themselves show a distinct cyclization (0.5 rings per average molecule).

4. The completely different chemical structure of voltolized and thermally polymerized linseed oils finds expression also in their completely different physical properties and particularly in their viscosities.

TABLE I
Voltolization of Linseed Oil

Product	Consumption of hydrogen liters H_2 (0°C. 1 at.) per kg. of oil	Consumption of energy kWh per kg. of oil	Properties of reaction products									
			n^{20}/D	$d^{20}/4$	Mol weight	Specific refraction	Acid value	Saponification value	Iodine value (Wijs)	Kinematic viscosity centistokes		
										20°C.	40°C.	70°C.
Original linseed oil	....	....	1.4810	0.9318	900	0.3054	5.8	192	182	64	30	14
Id. 500 g. voltolized 4.4 hrs.	0.2	0.3	1.4828	0.9354	1050	0.3052	4.4	190	167	112	50	21
Id. 540 g. voltolized 17.8 hrs.	5.7	1.0	1.4861	0.9433	1490	0.3044	4.1	189	143	776	281	93

TABLE II

Structural Analysis of Polymerized Linseed Oils

Product	Results of molecular distillation wt. % of original oil	Distillation of methanolized glycerides wt. % of original oil	Percentage of original glycerides that reacted		Hydrocarbons, prepared from methyl esters				
			Only intramolecular[b]	Intermolecular	n_D	d	Specific refraction $r^{20/D}$	Average mol weight	Average number of rings per molecule (n, d, M-method)
I Voltolized linseed oil I.V. 167, viscosity 1, 12 st. at 20°C.	78% Monomeric glycerides	77.0% Monomers	1.5	22	1.4215 (70°)	0.7522 (70°)	0.3362	272	—0.1
		1.0% Polymers			....	....	....	....	....
	22% Polymeric glycerides	14.5% Monomers			1.4194 (70°)	0.7486 (70°)	0.3363	272	—0.1
		7.5% Polymers			1.4403[a] (70°)	0.7967[a] (70°)	0.3297	423	0.8
II Voltolized linseed oil I.V. 143, viscosity 7, 76 st. at 20°C.	39% Monomeric glycerides	38.5% Monomers	1	61	1.4178 (70°)	0.7460 (70°)	0.3364	255	—0.1
		0.5% Polymers			....	....	....	....	....
	61% Polymeric glycerides	36.0% Monomers			1.4172 (70°)	0.7446 (70°)	0.3366	258	—0.1
		25.0% Polymers			1.4454[a] (70°)	0.8039[a] (70°)	0.3300	520	0.8
III Thermally polymerized linseed oil I.V. 116, viscosity 76 st. at 20°C.	(5% free fatty acids) 38% Monomeric glycerides	27.0% Monomers	16.5	57	1.4495 (20°)	0.8069 (20°)	0.3327	305	0.5
		11.0% Polymers			1.4644 (50°)	0.8453 (50°)	0.3259	560	2.3
	57% Polymeric glycerides	26.0% Monomers			1.4488 (20°)	0.8053 (20°)	0.3329	295	0.5
		31.0% Polymers			1.4772 (20°)	0.8675 (20°)	0.3258	625	2.6

[a] Extrapolated.

[b] Calculated by multiplying the percentages of polymeric methyl esters from the monomeric glycerides by 3/2.

Voltolization of linseed oil under these conditions does not allow production of "stand oils" of reasonable viscosity. Even when approximately 60% of the oil is polymerized, the viscosity does not exceed 8 stokes. Prolonged reaction results in the formation of undesired high molecular solid material. On the other hand, it has been stated (5, 6) that voltolized oils possess highly desirable drying properties, particularly in regard to the hardness and resistance of the film.

Thermal polymerization of linseed oil results in viscous stand oils, *e.g.*, when only 60% of the original glycerides are polymerized, viscosity already amounts to 76 stokes. The process can be continued until a high polymerization degree is obtained (90% and more); the viscosity of the oil can be increased to any desired value (Table II).

Perhaps a combination of the two processes would open new possibilities for the preparation of high viscosity stand oils of completely different properties. The relatively low energy-consumption during the voltolization of linseed oil (approximately 1.0 kWh per kg. of oil to polymerize 60% of the glycerides) certainly will not hamper such development.

5. The number of charged particles which plays a part in the voltolization process can be easily calculated from the discharge current and the reaction time. Thus it follows that in the case of Oil II (discharge current 24 mA, reaction time 17.8 hrs.) $6.4 \times 10^{-2} \times N_{Av}$ collisions have happened between electrons and positive ions and the oil film (N_{Av} = Avogadro number, oil films are present both on the glass tube and on the electrodes).

The number of carbon-carbon linkages formed during the voltolization can be calculated from the analytical data of Tables I and II. In the case of Oil II 60% by weight of the glyceride molecules polymerized into equal numbers of dimeric and trimeric glycerides (compare sub. 2). This means that per 100 molecules of the original oil at least $12 + 24 = 36$ new carbon-carbon linkages have been formed (or more when the cyclization is also taken into consideration). With 540 g. (= 0.6 mol.) of the starting material thus at least $0.6 \times 0.36 \times N_{Av} = 22 \times 10^{-2} \times N_{Av}$ new carbon-carbon linkages occurred; this is approximately 3 to 4 per collision.

Although the initiation of 3 to 4 reactions by only one charged particle has not been proved impossible, it can be concluded from the above calculations that in all probability other active particles, particularly hydrogen atoms, will have played a predominant part in the polymerization phenomena.

Summary

The treatment of linseed oil by the action of electric discharges (voltolization) in a hydrogen atmosphere (80 mm. Hg, 70°C.) is described.

It has been known for a long time that voltolization of linseed oil brings about a polymerization of the oil. Now it has been proven that the nature of the polymerization product thus obtained is absolutely different from that of thermally or catalytically polymerized linseed oils.

In contrast to the latter, voltolized linseed oils contain only small amounts of cyclic compounds. Their viscosity is relatively low, even at a high polymerization degree, and considerably less than that of thermally polymerized oils of a corresponding degree of polymerization.

Atomic hydrogen seems to play an important part in the voltolization process. Coupling of fatty acid chains is made possible by combining radicals, formed primarily by the action of hydrogen atoms. Coupling reaction occurs almost exclusively intermolecularly.

The possibility of transforming linseed oil and other drying oils into polymerization products of a completely different chemical structure, depending on the applied polymerization process, opens new possibilities for their manufacture.

REFERENCES

1. De Hemptinne, A., Bull. Sci. Acad. Roy. Belg., 550 (1904); 161 (1919); 146, 458, 590 (1921).
2. Friedrich, V., Z. Ver. Deut. Ing., *65*, 1171 (1921).
   Eichwald, E., Z. Angew. Chem., *35*, 505 (1922); *36*, 611 (1923).
   Hock, L., Z. Elektrochemie, *29*, 111 (1923).
   Becher, H., Wiss. Veröff. Siemens, *5*, 160 (1926).
   Roogiers and Decavel, Compt. Rend. X Congr. Chim. Ind. (1931).
   Hock, L., and Nottebohm, C. L., Kolloidchem. Beih., *31*, 185 (1930).
   Fussteig, R., Petr. Eng., *11*, (5), 58 (1940).
   Whiteley, R. S., Kimberlin, C. N., Matheson, G. L., and Richardson, R. W., Ind. Eng. Chem., *42*, 2471 (1950).
3. Van Steenis, J., thesis, Delft, 1951.
   Boelhouwer, C., thesis, Delft, 1952.
4. Nikuradse, A., and Berger, A., Physik. Z., *45*, 71 (1944).
   Menzel, W. Berger, A., and Nikuradse, A., Ber. *82*, 418 (1949).
5. Slansky, P., Farben-Ztg., *37*. 1419 (1932).
6. Goldenstein, J. J., Chem. Zentr., *112*, 1357 (1941).
7. Kappelmeier, C. P. A., Farben-Ztg., *38*, 1018, 1077 (1933); Paint, Oil Chem. Rev., Nos. 1, 2, 4, 100 (1938); Verfkroniek, *11*, 71 (1938).
8. Boelhouwer, C., Jol, A. C., and Waterman, H. I., Research, *5*, 337 (1952).
9. Boelhouwer, thesis, Delft, 1952.
10. Waterman, H. I., and Oosterhof, D., Rec. Trav. Chim., *52*, 895 (1933).
11. Hosman, B. B. A., Van Steenis, J., and Waterman, H. I., Rec. Trav. Chim., *68*, 939 (1949).
12. Boelhouwer, C., Klaassen, W. A., and Waterman, H. I., Research 7. 62 S (1954).
13. Waterman, H. I., "Correlation Between Physical Constants and Chemical Structure," Elsevier, Amsterdam, 1958.

[Received January 8, 1960]

• *Letter to the Editor*

The Calculation of Restricted Random Glyceride Distribution[1]

KARTHA (1) has proposed that the fatty acyl groups in triglycerides are distributed at random except that in certain cases a restriction may be placed on the amount of trisaturated glyceride that can be formed. He has given the following equations for calculating the glyceride distribution of fats from random distribution and the amount of trisaturated glyceride found experimentally:

$$(GS_3)_r - GS_3 = F$$

$$GS_2U = (GS_2U)_r + F + \frac{(2/3)(F)(GSU_2)_r}{(2/3)(GSU_2)_r + (GU_3)_r}$$

$$GSU_2 = (GSU_2)_r - \frac{(2/3)(F)(GSU_2)_r}{(2/3)(GSU_2)_r + (GU_3)_r} + \frac{F(GU_3)_r}{(2/3)(GSU_2)_r + (GU_3)_r}$$

$$GU_3 = (GU_3)_r - \frac{F(GU_3)_r}{(2/3)(GSU_2)_r + (GU_3)_r}$$

where the subscript r refers to the values calculated by random distribution and GS_3, GS_2U, GSU_2, and GU_3 are the actual amounts of the four glyceride types.

However it is not correct to calculate from one equilibrium state to another by proportions. This is best demonstrated by the fact that the above equations give negative values for GU_3 in cases where the saturated acids exceed 61.8% and the amount of trisaturated glyceride is reduced to its smallest possible value. The other three glyceride types add up to more than 100% in these cases.

A correct equation for the conditions that Kartha has proposed can be derived in the following way. Let the real proportions of GS_3, GS_2U, GSU_2, and GU_3 be a, b, c, and d, respectively. Let the mol proportion of saturated acids be S, then

$$a + b + c + d = 1$$
$$3a + c + 2b = 3S$$

An equilibrium condition may be considered to exist such that

$$GU_3 + GS_2U \rightleftharpoons 2GSU_2$$

and thus

$$db/c^2 = K$$

where K is the equilibrium constant. Since there is no restriction on this equilibrium $K = 1/3$, for in a random distribution there are three ways to form GSU_2 and GS_2U for each way that leads to GU_3. Using these equations to solve for b in terms of S and a,

$$GS_2U = b = (3/2)(1 + S - 2a) - (3/2)(1 - 3S^2 + 2S - 4a + 4Sa)^{1/2}$$

Also

$$GSU_2 = c = 3S - 2b - 3a$$
$$GU_3 = d = 1 + 2a + b - 3S$$

A comparison of the results obtained by Kartha's equation with our equation for various values of S and for the least amount of GS_3 possible indicates that his values may deviate from the correct values by 2% in many places and by 4.5% in one place. These are extreme conditions, and, in general, Kartha's solution will lie closer to the correct value.

The amount of the individual glycerides may be calculated, as Kartha indicated, by multiplying the random value by the proportion in which the glyceride type to which it belongs has changed.

The present method of calculating glyceride distributions from equilibrium considerations is by no means limited to the conditions that Kartha has proposed. It may be used for calculating the glyceride structure when the distribution is believed to be basically a random one which is limited in some specific way, *e.g.*, the type of distribution proposed by Vander Wal (2). However the algebra involved in solving the equations can become complex, and this method may not be the simplest approach.

EARL G. HAMMOND AND GARY V. JONES,
Department of Dairy and Food Industry, Iowa State University of Science and Technology, Ames

REFERENCES

1. Kartha, A. R. S., "Studies on the Natural Fats," Vol. 1, p. 103, published privately by author at Ernakulam, India, 1949; also J. Am. Oil Chemists' Soc., *30*, 326 (1953).
2. Vander Wal, R. J., J. Am. Oil Chemists' Soc., *37*, 18 (1960).

[Received April 4, 1960]

---

[1] Journal Paper No. J-3837, Iowa Agricultural and Home Economics Experiment Station, Ames, Ia.