Isomerization of Drying and Semi-Drying Oils: The Use of Anthraquinone as a Conjugation Catalyst

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NO general explanation for the activity of polymerization catalysts used for heat-bodying drying and semi-drying oils seems to have been given. However, Terrill (11) proposed the hypothesis that anthraquinone (9) and similar compounds (8) increase the rate of polymerization of oils because they actually isomerize the polyunsaturated fat acid radicals to conjugated configurations prior to polymerization and do not have a catalytic effect on the polymerization mechanism since it is well known that conjugated oils heatbody much more rapidly than non-conjugated oils. While no direct experimental proof was offered, some evidence for the hypothesis does exist. In 1936 Waterman and Van Vlodrop (12) discovered that sulfur dioxide was a catalyst for the thermal polymerization of linseed oil. Later they demonstrated that sulfur dioxide induces a shift of the isolated double bonds in linseed oil to conjugated positions (14). This method for the isomerization of oils is the subject of a recent patent (2).

Recently two of the authors (6) advanced the idea that drying oils might polymerize according to more than one mechanism, depending on the kind or type of oil (conjugated or non-conjugated), and that at least two types of polymerization catalysts exist. One group of catalysts, represented by sulfur dioxide, is effective because they isomerize the oil prior to polymerization. The materials in this group should not be considered to be actual polymerization catalysts. The other group, represented by diphenyl disulfide, does not conjugate the oil so far as is known. Members of this group can be considered to be true polymerization catalysts.

During a study on the rates of polymerization of oils with various catalysts it was noted that soybean oil when heated for one hour at 305-310°C. in the presence of 0.5% anthraquinone contained 7.3% conjugation. This amount of conjugation is an unusually high percentage for such a treatment and was strong evidence that anthraquinone induces a shift of the double bonds in oils during thermal treatment. It was therefore of interest to determine whether conditions could be found whereby anthraquinone or other similar polymerization catalysts would induce high percentages of conjugation without undue polymerization.

Isomerization Activity of Polymerization Catalysts

Alkali-refined soybean oil containing 2% of the polymerization catalyst was prepared by dissolving the requisite amount of material in 20 grams of oil with the aid of heat. Approximately 15 grams of the oil catalyst solution in a sealed, glass ampoule was heated in an oil bath at 280° ± 2°C. for two hours. After heating, the solution was rapidly cooled to room temperature. The refractive index of the oil before and after treatment was compared as an indication of conjugation (13). Samples exhibiting an unusual amount of exhaltation were analyzed for percentage conjugation by means of ultraviolet absorption with a Beckman Spectrophotometer (1, 4). Results are shown in Table I.

It is apparent from Table I that the quinones were the only class of compounds tested which readily induced conjugation with the exception of quinone itself. Quinone possibly does induce isomerization but may react immediately with the conjugated system by means of the Diels-Alder reaction, thus destroying its catalytic activity. On the other hand, the polycyclic quinoid compounds do not react possibly because of stearic factors.

Anthraquinone was chosen from the active compounds for further study because it appeared to be

TABLE 1

Comparative Isomerization Activity of Various Polymerization Catalysts in Soybean Oil[1]
2 Hours at 280°C.

Compound[2]	n_d^{25} Before Treatment[3]	n_d^{25} After Treatment[4]	Viscosity (Gardner-Holt)	Color	Per Cent Conjugation Nil	Catalyst Recovery
Anthracene	1.4761	1.4772	B	Yellow	Nil	Catalyst does not precipitate
Anthraquinone	1.4725	1.4765	D-E	Yellow	14.0	97%+ recovery
β-Amino Anthraquinone	1.4729	1.4782	D	Yellow	9.0	Fair recovery
Benzidine	1.4768	....	Gelled	Dark Brown	......	....
Benzil	1.4751	1.4767	C	Yellow	Nil	Catalyst does not precipitate
β-Chloroanthraquinone	1.4730	1.4780	G	Yellow	17.2	Fair recovery
Dihydroxyanthraquinone[5]	1.4739	1.4797	F	Dark Brown	16.6	Catalyst does not precipitate
Diphenyl disulfide	1.4752	1.4762	C	Yellow	Nil	Catalyst does not precipitate
8-Hydroxy Quinoline Sulfate[6]	1.4729	1.4740	B	Yellow	Nil	
β-Methyl Anthraquinone	1.4747	1.4782	D	Yellow	12.6	Fair recovery
1,2-Naphthaquinone	1.4757	1.4813	K	Dark Brown	10.8	Catalyst does not precipitate
Phenanthrene	1.4761	1.4772	B	Yellow	Nil	Catalyst does not precipitate
Quinone	1.4730	1.4771	D	Orange	3.6	Catalyst does not precipitate
Resorcinol	1.4740	1.4745	B	Yellow	Nil	Catalyst does not precipitate

[1] Alkali-refined oil; $n_d^{25} = 1.4724$.

[2] 2% based on weight of oil. Eastman Technical Grade used.

[3] *Compound dissolved in hot oil, solution cooled to room temperature and any precipitate filtered off.*

[4] Treated oil was cooled to room temperature and filtered from the catalyst if it precipitated.

[5] Mixture of 65% 1,5- and 35% 1,8-dihydroxyanthraquinone.

[6] Not completely soluble in the hot oil.

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[1] Present Address: Standard Oil of Ohio, Cleveland, Ohio.

[2] Present Address: Glidden Company, Chicago, Illinois.

[3] Present Address: A. E. Staley Mfg. Co., Decatur, Illinois.

TABLE 2

Isomerization of Soybean Oil

Alkali-refined grade (Acid value = 0.1; n_d^{25} = 1.4728)

2% Anthraquinone (Based on weight of oil)

Time (Minutes)	Per Cent Conjugation	n_d^{25}	Viscosity (Poises)	Acid Value
Temperature—260°C.				
0	1.2	1.4732	0.45	
20	2.7	1.4735		
40	4.5	1.4740	0.6	
60	5.4	1.4743		0.60
80	6.9	1.4747	0.7	
100	7.9	1.4750		
120	9.0	1.4751	0.8	
140	9.7	1.4753		
160	10.9	1.4757	1.0	
180	11.0	1.4760		
200	11.8	1.4761		
220	12.4	1.4762	1.1	
240	13.0	1.4765		
260	13.1	1.4768		
280	13.3	1.4769	1.3	1.5
Temperature—270°C.				
0	1.0	1.4738	0.4	
20	4.2	1.4740		
40	6.7	1.4745		1.5
60	8.3	1.4750	0.6	
80	8.6	1.4753		
100	11.1	1.4758		
120	11.5	1.4762		
140	12.4	1.4768	1.0	1.6
160	13.2	1.4770		
180	14.3	1.4775	1.2	
200	14.9	1.4779		
220	15.2	1.4781	1.6	
240	15.5	1.4782		
260	15.6	1.4783		2.4
280	16.1	1.4788	2.3	
Temperature—280°C.				
0	2.3	1.4734	0.5	
20	4.9	1.4740		
40	7.5	1.4747		
60	10.4	1.4754	0.8	1.4
80	12.1	1.4759		
100	13.1	1.4763		
120	13.9	1.4770	1.2	
140	14.8	1.4775		
160	15.3	1.4778		
180	15.4	1.4780	1.9	
200	15.5	1.4785		
220	15.8	1.4790		2.5
240	15.6	1.4793	2.8	
260	15.4	1.4796		
280	15.1	1.4800	4.0	3.4
Temperature—290°C.				
0	1.8	1.4740	0.5	
15	5.0	1.4747		
30	7.2	1.4751		1.4
45	9.7	1.4759	0.8	
60	11.0	1.4765		
75	12.8	1.4770		
90	13.1	1.4775	1.3	
105	13.4	1.4779		
120	13.8	1.4780		3.2
135	13.9	1.4782	2.1	
150	14.1	1.4790		
165	14.3	1.4792		
180	13.7	1.4795	3.4	
195	13.6	1.4798		
210	13.5	1.4800	4.7	4.6
Temperature—300°C.				
0	2.4	1.4739	0.7	
15		1.4750		1.6
30	11.9	1.4760	1.0	
45	14.0	1.4770		
60	15.0	1.4779	1.4	
75	15.7	1.4784		
90	15.6	1.4792	2.5	4.1
105	15.5	1.4800		
120	15.4	1.4803	3.7	
135	15.0	1.4809		
150	14.4	1.4811	6.2	
165	13.8	1.4813		
180	13.3	1.4818	10.7	
195	12.9	1.4820		
210	12.6	1.4821	15.6	6.9

the most suitable for commercial application. It is readily available and relatively inexpensive and produces an oil of good color. Even more important, it precipitates almost completely when its oil solution is cooled and can easily be recovered by filtration.

Isomerization Studies with Anthraquinone

Alkali-refined soybean and linseed oils (1700 gms.) containing various percentages of anthraquinone were heated at various temperatures in a closed 3-liter, three-necked flask fitted with a mechanical stirrer and thermometer. A closed system was necessary due to the volatility of the anthraquinone. A slight error in the per cent catalyst was introduced in this work as some of the anthraquinone sublimed from the hot oil solution and condensed on the uppermost part of the flask. No attempt was made to conduct the experiments under an inert atmosphere for preliminary work demonstrated that the presence of air had no deleterious effect.

The flask containing the oil was heated at a uniform rate by means of a Glas-Col mantle; after the desired temperature was reached the anthraquinone (commercial grade) was introduced and the temperature was controlled within ± 2°C. Samples were withdrawn at regular intervals for determination of the various constants. Each sample was allowed to remain at room temperature 16 hours before filtering off the catalyst which had precipitated on cooling. Similar experiments were also carried out with both the fat acids and methyl esters of linseed and soybean oils. The data obtained from these runs are presented in Tables 2 to 7 inclusive and Figures 1 to 7 inclusive.

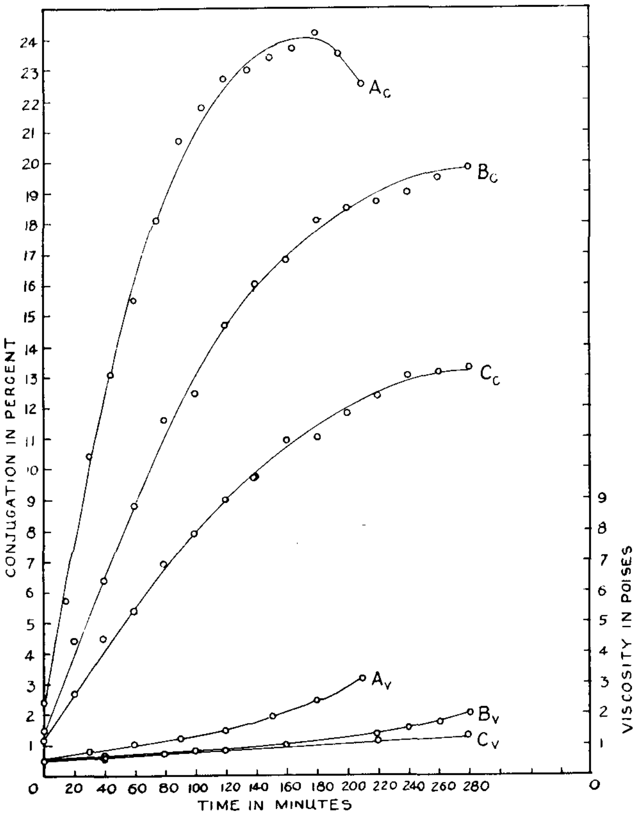

FIG. 1. Alkali-Refined Soybean Oil. Temperature 260°C.
A. 10% Anthraquinone
B. 5% Anthraquinone
C. 2% Anthraquinone

In order to compare the effectiveness of the treatment on the various grades of oil, crude, non-break, and alkali-refined soybean oils were heated with 5% anthraquinone at 290°C. for 70 minutes. Likewise the analogous grades of linseed oils were treated with 5% of the catalyst at 285°C. for 30 minutes. Table 8 lists the results obtained.

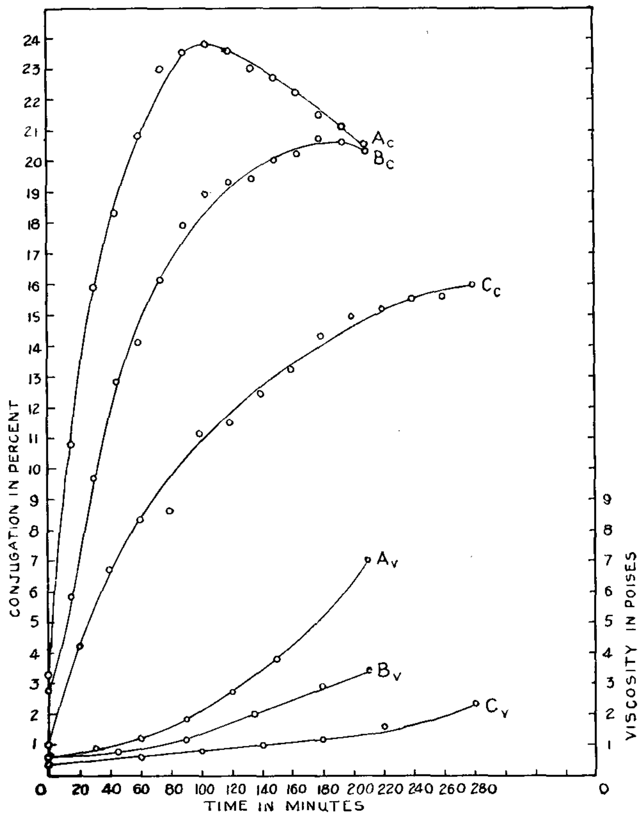

Fig. 2. Alkali-Refined Soybean Oil. Temperature 270°C.

A. 10% Anthraquinone
B. 5% Anthraquinone
C. 2% Anthraquinone

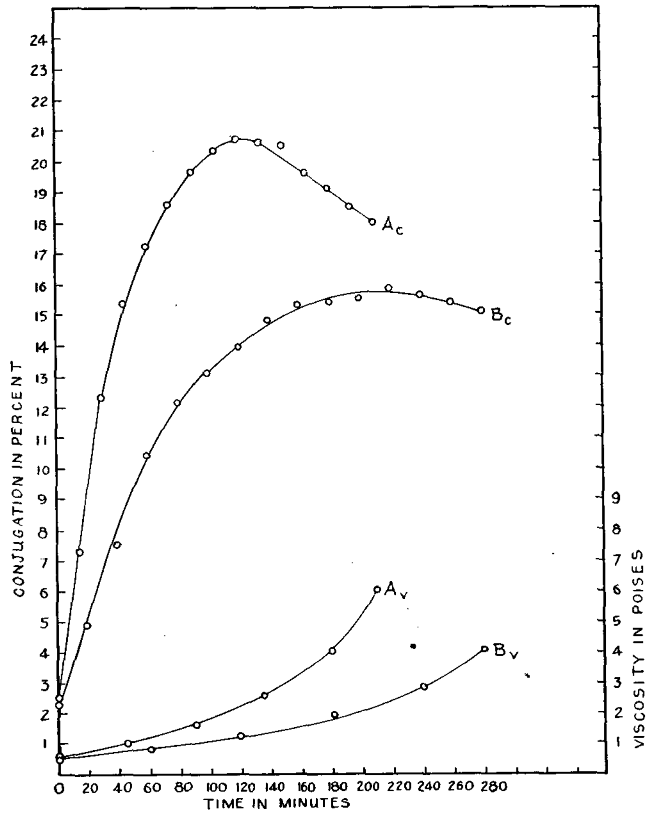

Fig. 3. Alkali-Refined Soybean Oil. Temperature 280°C.

A. 5% Anthraquinone
B. 2% Anthraquinone

TABLE 3

Isomerization of Soybean Oil

Alkali-refined grade (Acid value = 0.1; n_d^{25} = 1.4728)

5% Anthraquinone (Based on weight of oil)

Time (Minutes)	Per Cent Conjuga-tion	n_d^{25}	Viscosity (Poises)	Acid Value
Temperature—260°C.				
0	1.5	1.4733	0.5	
20	4.4	1.4740		
40	6.4	1.4745	0.7	
80	11.6	1.4755		
100	12.5	1.4760	0.8	
120	14.7	1.4765		
140	16.0	1.4766		
160	16.8	1.4768	1.0	
180	18.1	1.4772		
200	18.5	1.4777	1.1	
220	18.7	1.4780	1.3	
240	19.0	1.4782	1.5	
260	19.5	1.4787	1.7	
280	19.8	1.4789	2.0	1.4
Temperature—270°C.				
0	2.8	1.4734	0.6	
15	5.8	1.4741		
30	9.7	1.4750		0.9
45	12.8	1.4759	0.8	
60	14.1	1.4761		
75	16.1	1.4768		
90	17.9	1.4772	1.2	
105	18.9	1.4776		
120	19.3	1.4781		1.8
135	19.4	1.4785	2.0	
150	20.0	1.4789		
165	20.2	1.4793		
180	20.7	1.4796	2.9	
195	20.6	1.4800		
210	20.3	1.4801	3.4	2.3
Temperature—280°C.				
0	2.5	1.4740	0.6	
15	7.3	1.4750		
30	12.3	1.4759		1.1
45	15.3	1.4764	1.0	
60	17.2	1.4770		
75	18.6	1.4778		
90	19.6	1.4783	1.6	
105	20.3	1.4788		
120	20.7	1.4793		2.3
135	20.6	1.4799	2.5	
150	20.5	1.4802		
165	19.6	1.4807		
180	19.1	1.4808	4.0	
195	18.5	1.4809		
210	18.0	1.4812	6.0	2.9
Temperature—290°C.				
0	3.8	1.4732	0.6	
10	10.1	1.4745		1.7
20	14.1	1.4753		
30	16.4	1.4767	1.0	
40	18.4	1.4771		
50	19.3	1.4780		
60	19.6	1.4786	2.0	
70	20.0	1.4790		2.8
80	19.6	1.4793		
90	19.1	1.4798	3.5	
100	19.0	1.4801		
110	18.5	1.4805		
120	18.2	1.4806	5.5	
130	17.7	1.4809		
140	17.5	1.4810	7.0	3.9
Temperature—300°C.				
0	5.1	1.4739	0.7	
10	12.6	1.4753		1.6
20	17.5	1.4770	1.0	
30	17.7	1.4780		
40	19.9	1.4790	2.0	
50	20.0	1.4799		
60	20.2	1.4802	3.2	3.5
70	19.7	1.4807		
80	19.6	1.4810	5.4	
90	18.5	1.4812		
100	17.7	1.4813	8.8	
110	16.4	1.4814		
120	16.0	1.4818	12.9	
130	12.6	1.4820		
140	10.0	1.4822	19.5	5.7

The percentages of conjugation were determined by means of a Beckman Spectrophotometer, using carefully purified Skellysolve F as the solvent (1, 4). $E_{1cm.}^{1\%}$ values were taken as 1150 and 1850 at 2320 Å and at 2705 Å, respectively, for 100% diene and 100% triene conjugation. Viscosities were determined at 25° ± 0.1°C. with a Gardner-Holt bubble viscosimeter. Colors were obtained by comparison with Gardner Color Standards and acid values were determined by titration with 0.1 N potassium hydroxide using phenolphthalein as the indicator.

Discussion of Results

The data illustrate the fact that considerable amounts of conjugation can be induced in linseed and soybean oils without appreciable polymerization by heating the oils at 260°-300°C. in the presence of anthraquinone or related compounds. As might be expected, the amount of conjugation reaches a maximum, the value depending on the concentration of catalyst and the temperature, and then drops off due to polymerization. These facts prove that isomerization followed by condensation occurs when heat bodying oils in the presence of quinoid type catalysts.

The mechanism by which the quinoid type catalysts operate may be analogous to that proposed by Kass and Skell (5) for the alkali isomerization of oils. They postulated that isomerization occurred by means of a prototropic shift and this can be represented in the case of anthraquinone and linoleic acid as shown below.

Similar equations can be written for the formation of 10,12-linoleic acid and the various possible linolenic acid isomers.

Possible Commercial Application

It should be relatively simple and economical to isomerize vegetable oils on a large scale by means of the anthraquinone treatment. The reaction is capable of being carried out in any closed reaction vessel which can be heated to the required temperatures.

TABLE 4

Isomerization of Soybean Oil

Alkali-refined grade (Acid value = 0.1; n_d^{25} = 1.4728)

10% Anthraquinone (Based on weight of oil)

Time (Minutes)	Per Cent Conjugation	n_d^{25}	Viscosity (Poises)	Acid Value
Temperature—260°C.				
0	2.4	1.4738	0.5	
15	5.7	1.4748		0.7
30	10.4	1.4752	0.8	
45	13.1	1.4759		
60	15.5	1.4763	1.0	
75	18.1	1.4770		
90	20.7	1.4777	1.2	
105	21.8	1.4780		
120	22.7	1.4789	1.4	
135	23.0	1.4792		1.5
165	23.7	1.4798		
180	24.2	1.4800	2.4	
195	23.5	1.4802		
210	22.5	1.4805	3.1	2.0
Temperature—270°C.				
0	3.2	1.4739	0.6	
15	10.8	1.4751		1.6
30	15.9	1.4764	0.9	
45	18.3	1.4771		
60	20.8	1.4779	1.2	
75	23.0	1.4788		
90	23.5	1.4794	1.8	3.5
105	23.8	1.4799		
120	23.6	1.4801	2.7	
135	23.0	1.4805		
150	22.7	1.4808	3.8	
165	22.2	1.4811		
180	21.5	1.4815	5.5	
195	21.1	1.4818		
210	20.5	1.4820	7.0	5.7

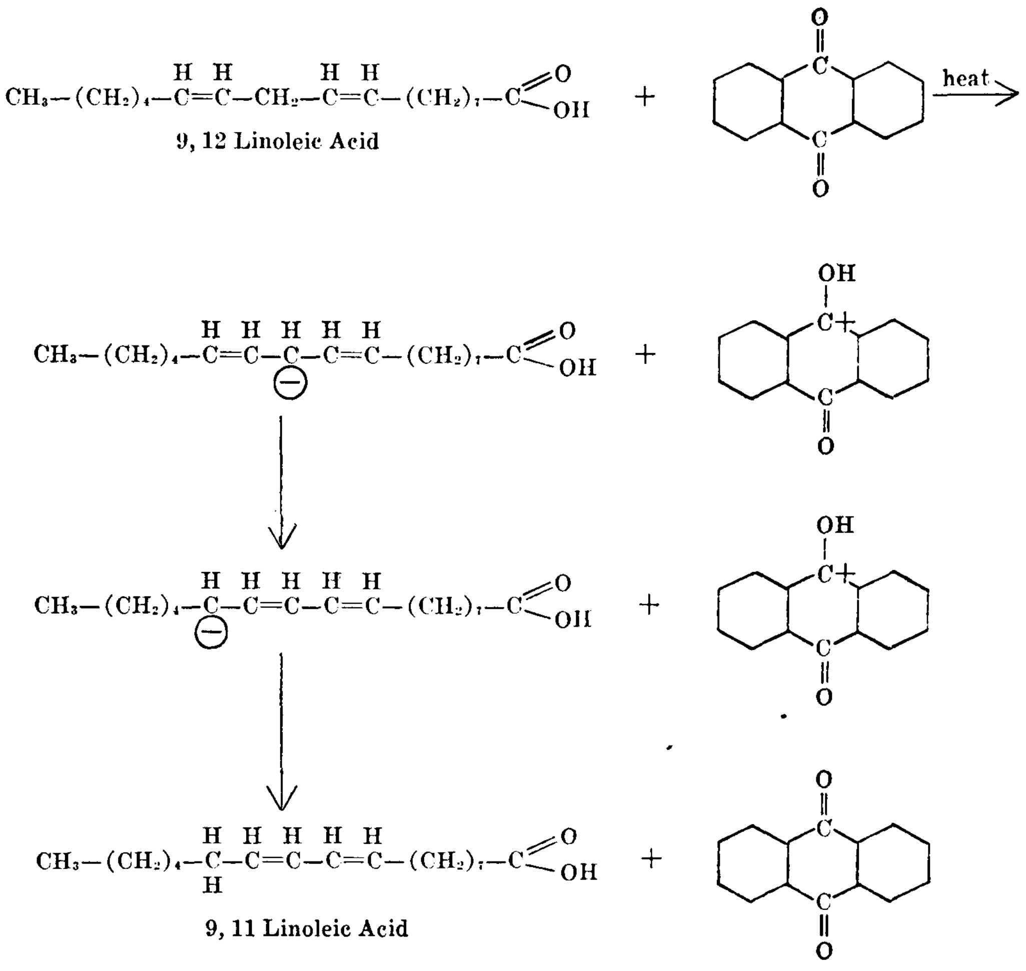

TABLE 5

Isomerization of Linseed Oil

Alkali-refined oil (Acid value = 0.2; n_d^{25} = 1.4788)

5% Anthraquinone (Based on weight of oil)

Time (Minutes)	Per Cent Conjugation			Viscosity (Poises)	n_d^{25}	Acid Value
	Diene	Triene	Total			
Temperature—280°C.						
0	4.5	.6	5.1	1.5	1.4795	1.0
10	9.3	1.9	11.2		1.4815	
20	12.0	2.5	14.5	2.0	1.4835	
30	15.0	2.7	17.7		1.4845	1.9
40	16.3	2.7	19.0	2.8	1.4855	
50	16.7	2.4	19.1		1.4865	
60	16.9	2.3	19.2	6.0	1.4870	2.4
70	17.4	2.2	19.6		1.4878	
80	16.1	2.0	18.1	12.0	1.4884	
90	15.6	1.8	17.4		1.4889	
100	15.3	1.6	16.9	20.5	1.4891	
110	14.2	1.4	15.6		1.4898	
120	12.9	1.2	14.1	36.0	1.4907	3.2
Temperature—260°C.						
0	2.4	.2	2.6	1.2	1.4791	0.5
15	4.8	.9	5.7		1.4800	
30	7.5	1.8	9.3		1.4811	
45	10.5	2.5	13.0	1.7	1.4820	1.5
60	12.4	2.8	15.2		1.4832	
75	14.0	2.8	16.8	2.0	1.4846	
90	15.1	2.8	17.9		1.4848	
105	16.1	2.8	18.9	3.0	1.4851	
120	16.7	2.7	19.4		1.4859	
135	17.2	2.6	19.8	4.2	1.4864	2.4
150	17.0	2.4	19.4		1.4866	
165	16.9	2.4	19.3	5.5	1.4872	
180	16.9	2.2	19.1		1.4877	
195	16.8	2.1	18.9		1.4879	
210	16.6	2.1	18.7	9.9	1.4881	2.8

After the reaction mixture is cooled, the anthraquinone is easily separated from the oil by filtration. The needle-like anthraquinone crystals readily lend themselves to filtration, and the recovered catalyst can be reused indefinitely.* Over 95% recovery of the anthraquinone can be realized if the reaction mixture is allowed to stand at room temperature for at least 15 to 20 hours. This "aging" of the oil-catalyst mixture may constitute a serious drawback to the process.

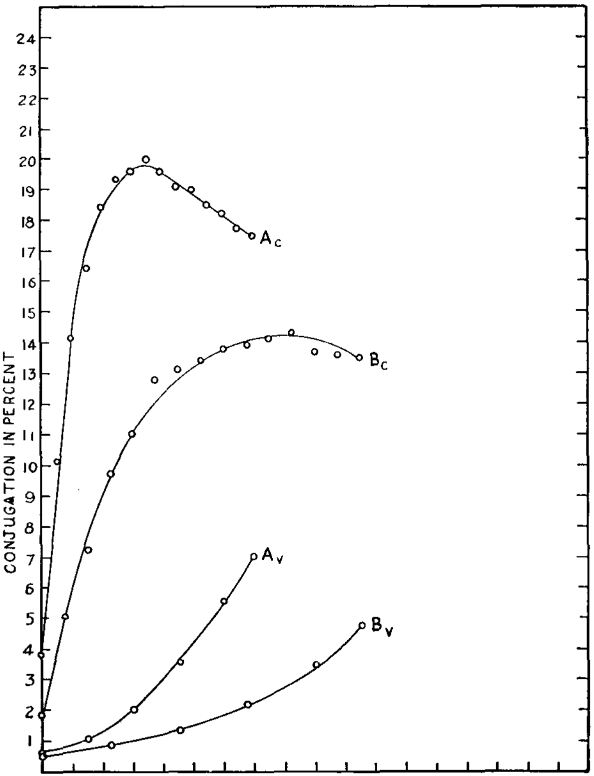

FIG. 4. Alkali-Refined Soybean Oil. Temperature 290°C.

A. 5% Anthraquinone
B. 2% Anthraquinone

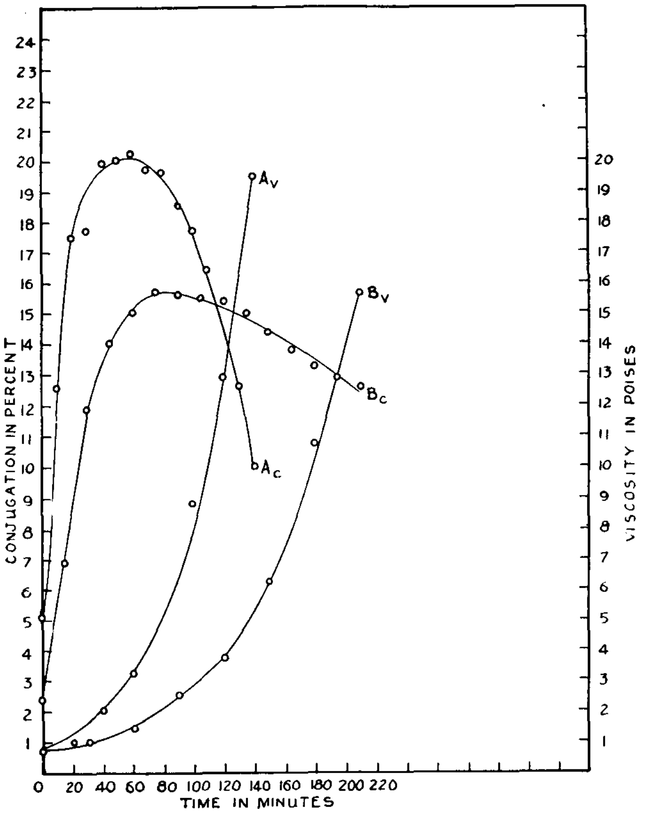

FIG. 5. Alkali-Refined Soybean Oil. Temperature 300°C.

A. 5% Anthraquinone
B. 2% Anthraquinone

It should be noted that the above isomerization treatment is operable on all grades of linseed and soybean oils and can be used to isomerize the fat acids or methyl esters of these oils. However, even though raw oils can be isomerized with anthraquinone, such would not be practical because the break material will cause difficulty in filtering the catalyst besides contaminating it for further use.

Preliminary investigations were conducted on the possible utilization of the isomerized oils. The results

TABLE 6

Isomerization of Fat Acids

5% Anthraquinone — T = 285°C.

Soybean F. A.			Linseed F. A.				
Time (Minutes)	Per Cent Conjugation	Acid Value	Time (Minutes)	Per Cent Conjugation			Acid Value
				Diene	Triene	Total	
0	3.3	204	0	5.1	0.8	5.9	200.2
15	10.3		15	13.0	2.2	15.2	
30	14.1		30	15.6	2.1	17.7	
45	17.5	203.8	45	16.6	2.0	18.6	197.0
60	19.3		60	17.4	1.8	19.2	
75	19.5		75	17.6	1.7	19.3	
90	20.7		90	15.8	1.5	17.3	
105	19.5	201.2	105	14.7	1.4	16.1	
120	18.8		120	13.2	1.3	14.5	195.5
135	18.5		135	12.1	1.2	13.3	
150	18.3		150	11.8	1.0	12.8	
165	17.3	200.8	165	11.0	.8	11.8	
180	16.6		180	10.2		10.2	
195	15.6		195	9.9		9.9	
210	15.4	199.5	210	9.4		9.4	
			235	8.8		8.8	195.1

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* The recovered catalyst has been reused as many as 10 times. The precipitated material was shown to be identical with the original anthraquinone by the method of mixed melting points.

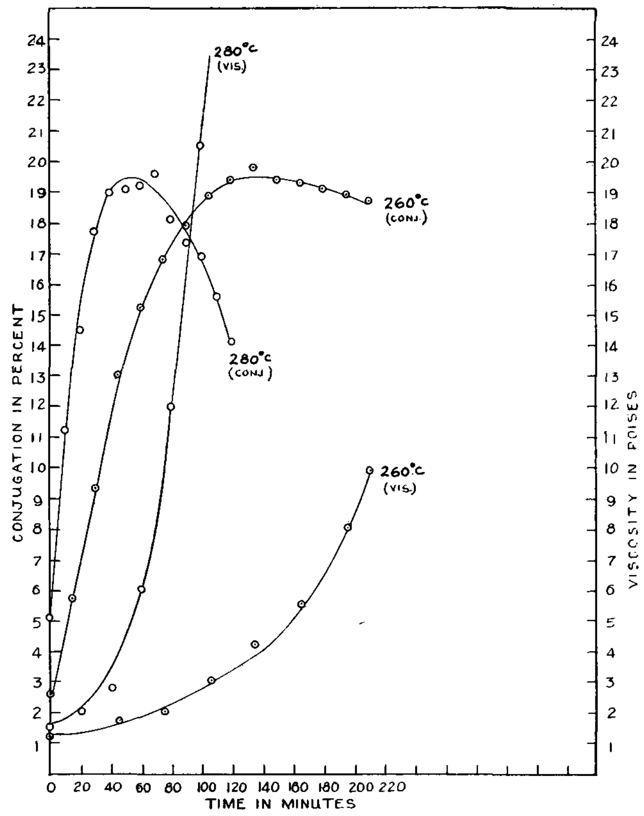

FIG. 6. Alkali-Refined Linseed Oil. 5% Anthraquinone.

obtained were in general similar to those obtained from utilization studies on isomerized oils prepared by other means (3, 7, 10). However, the anthra-

TABLE 7

Isomerization of Methyl Esters
5% Anthraquinone T = 285°C.

Soybean Methyl Esters

Time (Minutes)	Per Cent Conjugation	n^{25}_{d}	Acid Value
0	3.4	1.4561	0.21
15	7.9	1.4563	
30	12.3	1.4570	
45	15.7	1.4579	
60	18.1	1.4590	
75	19.8	1.4597	
90	20.6	1.4601	
105	21.0	1.4609	
120	21.7	1.4610	
135	21.5	1.4613	0.25
150	21.2	1.4616	
165	21.1	1.4621	
180	20.3	1.4623	
195	19.3	1.4626	
210	18.5	1.4629	0.32

Linseed Methyl Esters

Time (Minutes)	Per Cent Conjugation			n^{25}_{d}	Acid Value
	Diene	Triene	Total		
0	1.9	0.4	2.3	1.4613	0.27
10	8.9	1.2	10.1	1.4630	
20	12.5	2.6	15.1	1.4640	
30	14.7	2.7	17.4	1.4650	
40	16.0	2.7	18.7	1.4662	
50	17.2	2.7	19.9	1.4670	
60	17.9	2.7	20.6	1.4680	
70	17.8	2.5	20.3	1.4685	
80	17.7	2.3	20.0	1.4690	0.65
90	17.2	2.1	19.3	1.4692	
100	16.9	2.0	18.9	1.4697	
110	16.4	1.8	18.2	1.4699	0.77
120	15.8	1.7	17.5	1.4701	
130	15.5	1.6	17.1	1.4702	
140	14.2	1.4	15.6	1.4703	
150	14.1	1.4	15.5	1.4705	0.88

TABLE 8

Comparative Isomerization of Anthraquinone on Different Grades of Oil—5% Catalyst

	Physical Constants	Before Treatment	After Treatment
	A. Soybean Oils—290°C.—70 minutes		
Crude Oil	% Conjugation	....	19.9
	Viscosity	A	K—
	Color	11	off color—Brown
	n^{25}_{d}	1.4732	1.4800
	Acid Value	0.9	6.8
Non-Break Oil	% Conjugation	....	20.3
	Viscosity	A	K—
	Color	10	7
	n^{25}_{d}	1.4729	1.4800
	Acid Value	1.7	4.9
Alkali-Refined Oil	% Conjugation	....	19.9
	Viscosity	A	L—
	Color	3	7
	n^{25}_{d}	1.4729	1.4802
	Acid Value	0.1	3.9
	B. Linseed Oils—285°C.—30 minutes		
Raw Oil	% Conjugation	....	16.9
	Viscosity	A—	I
	Color	11	9
	n^{25}_{d}	1.4790	1.4858
	Acid Value	1.8	4.3
Non-Break Oil	% Conjugation	....	19.0
	Viscosity	A—	L
	Color	11	10
	n^{25}_{d}	1.4788	1.4859
	Acid Value	3.3	5.9
Alkali-Refined Oil	% Conjugation	....	18.7
	Viscosity	A—	J
	Color	5	6
	n^{25}_{d}	1.4788	1.4857
	Acid Value	0.3	2.3

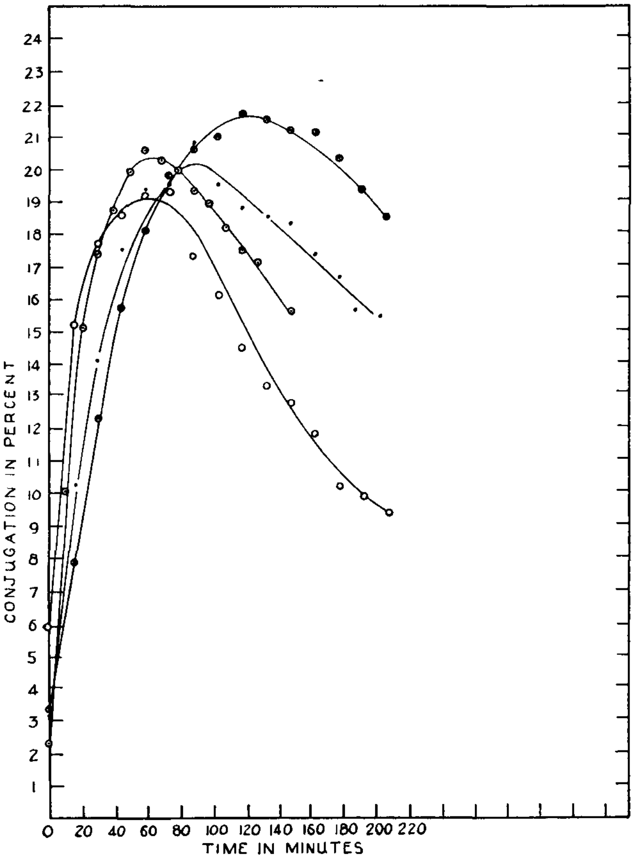

FIG. 7. 5% Anthraquinone. Temperature 285°C.
⊗—Soybean Methyl Esters
⊙—Linseed Methyl Esters
●—Soybean Fat Acids
○—Linseed Fat Acids

quinone isomerized oils exhibited much less after-tack than did the Nickel-Carbon isomerized oils.

Summary

Anthraquinone and its derivatives have been found to be effective catalysts for the isomerization of drying and semi-drying oils to conjugated forms. A possible mechanism to account for the catalytic activity of these materials has been proposed. Possible commercial application of the isomerization of oils with anthraquinone was briefly discussed.

Acknowledgment

Grateful acknowledgment is made to Mrs. R. E. Brown for the many spectroscopic analyses performed during this research.

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Bromination of Methyl Esters of Soybean Fat Acids and Methyl Linoleate With N-Bromosuccinimide[1]

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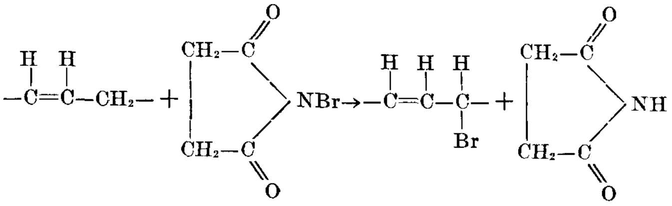
ZIEGLER, *et al.* (5), have shown that a hydrogen atom on a methylene group adjacent to an ethylenic double bond may easily be replaced by bromine by means of N-bromosuccinimide. The reaction may be formulated as follows:



The reaction is of quite general applicability, but in the field of fats and oils apparently the only instance of its use is Ziegler's bromination of methyl oleate. Beyond the statement that the bromine in methyl bromoleate is loosely bound, Ziegler gave no further description of the product and its reactions.

Since the double bonds in unsaturated fatty acids are located near the center of the carbon chain, this reaction is of great interest as a possible means of introducing a reactive center without undesirable side reactions such as polymerization or loss of unsaturation. This reactive center might serve for the preparation of new derivatives of unsaturated fatty acids through replacement of bromine by other groups, such as hydroxyl or cyano groups, or through coupling reactions.

The reaction of methyl esters of soybean fat acids with N-bromosuccinimide was therefore studied, and the reactions of the brominated esters with sodium methoxide, cuprous cyanide, and sodium cyanide were investigated. The reaction was also applied to methyl linoleate.

Although it became necessary to discontinue this investigation before more than preliminary data had been obtained on the replacement of halogen in the brominated methyl esters, the data are, nevertheless, presented because they may be of interest to others.

Discussion of Results

The reaction of methyl esters of soybean fat acids with N-bromosuccinimide proceeded rapidly and almost quantitatively (Tables I and II). The conditions specified by Ziegler (5), i.e., refluxing the reaction mixture which contained a small amount of carbon tetrachloride, were too vigorous and resulted in marked decomposition of the product. Excellent results were obtained, however, at temperatures of 70°C. or lower.

TABLE I

Bromination of Methyl Esters of Soybean Fat Acids and Methyl Linoleate
(40-Minute Reaction Time)

Substance	Halogen transfer	Succinimide recovered
	Per cent	*Per cent*
Methyl esters of soybean fat acids	97 99 92 99	86 91 96 96
Methyl linoleate	76 72	107 111

A solvent was not necessary to insure complete reaction (Table III) although a small amount facilitated stirring and filtration of the reaction mixture. When the volume of carbon tetrachloride or mixed heptanes was increased, the extent of reaction was substantially decreased (Tables III and IV), but this effect could be overcome by prolonging somewhat the time of reaction (Table II). Other solvents used included benzene and halogenated aliphatic and aromatic hydrocarbons (Table IV). Increasing the volume of these solvents had little effect on the extent of reaction. From the standpoint of color of product, benzene and mixed heptanes were outstanding.

Besides causing bromination, N-bromosuccinimide may also add to the ethylenic bond. The addition product with methyl esters of soybean fat acids would contain approximately 3% nitrogen. Nitrogen analy-

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