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Reactions of Tertiary Butyl Hypochlorite With Vegetable Oils and Their Derivatives. VII. Partial Chlorination of Soybean Oil[1]

H. M. TEETER, E. W. BELL, and L. C. WOODS, Northern Regional Research Laboratory,[2] Peoria, Illinois

THE major problem in the preparation of fast drying oils by dechlorination of chlorinated soybean oil is that of removal of halogen to an extent such that residual traces of halogen are unobjectionable. One approach to the solution of this problem is the investigation of various dechlorinating agents, some of which might effect more complete dechlorination whereas others might react selectively with the most active halogen.

Results of our study of this approach have been given in a previous paper (2) in which it was shown that aqueous solutions of salts, such as sodium acetate or disodium hydrogen phosphate, were effective dechlorinating reagents for chlorinated soybean oil. It was also concluded from the effects of these reagents on methyl chlorooleate that allylic and non-allylic monochloride types of halogen were attacked to a greater degree than was the dichloride type.

A second approach to the problem is partial chlorination of the oil. In this case preferential formation of products containing more reactive types of halogen might be expected. Furthermore oils containing unobjectionable amounts of residual chlorine might be obtained even if dechlorination was no more effective than in the case of the chlorinated oils previously studied.

The purpose of this paper is to report the results obtained by partial chlorination of soybean oil with *t*-butyl hypochlorite, dechlorination of the products with aqueous sodium acetate solution, and determination of the thermal stability of the residual halogen.

Partial Chlorination. Several chlorinations were run in which the amount of *t*-butyl hypochlorite was varied from 0.1 to 1.0 equivalent per equivalent of soybean oil (i.e., 0.1 to 1.0 mole per fatty acid chain in the oil). The results of these experiments are shown in Figure 1, in which refractive index and percentage of conjugation are plotted against the percentage of chlorine in the product. The conjugation present in the samples was of the diene type. Only traces of triene and tetraene conjugation were observed. Colors of the products varied from 4 to 8 (Gardner), and viscosities varied from B to N (Gardner). The lower viscosities and lighter colors were associated with oils containing smaller amounts of chlorine.

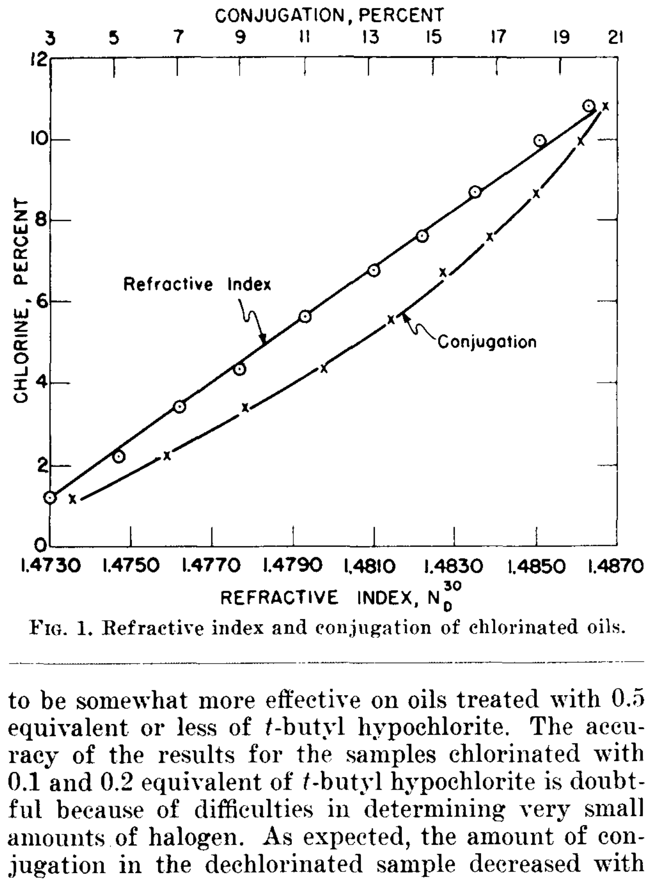

FIG. 1. Refractive index and conjugation of chlorinated oils.

Dechlorination. The samples of partially chlorinated soybean oil were dechlorinated by autoclaving with aqueous sodium acetate solution. The results obtained are given in Table I. Dechlorination appeared to be somewhat more effective on oils treated with 0.5 equivalent or less of *t*-butyl hypochlorite. The accuracy of the results for the samples chlorinated with 0.1 and 0.2 equivalent of *t*-butyl hypochlorite is doubtful because of difficulties in determining very small amounts of halogen. As expected, the amount of conjugation in the dechlorinated sample decreased with the chlorine content of the original oil. For this reason oils chlorinated with less than 0.4 to 0.5 equivalent of *t*-butyl hypochlorite would not be suitable for the production of fast drying oils.

Thermal Stability of Residual Halogen. Each dechlorinated oil was heated for 5 hours at 250° in a current of nitrogen, and the remaining halogen was determined. The results are shown in Table II. For samples originating from oils chlorinated with 0.5 equivalent or less of hypochlorite, these data appear to indicate a substantial increase in stability of the residual halogen. However we have found that the experimental error of determination of chlorine at levels less than 1% is about ±0.2%. This error is large enough to obscure the relationship, if any, between chlorine content and stability in samples containing small percentages of chlorine. Nevertheless, since no loss in halogen was detected in four out of five samples containing 1% or less of residual halogen, it seems reasonable to conclude that residual

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[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE I

Dechlorination of Partially Chlorinated Soybean Oil With Sodium Acetate

TOCl (equivalents)[a]	Cl removed	Cl remaining % absolute	Viscosity (Gardner)	Color (Gardner)	Conjugation			
					Diene	Triene	Tetraene	Total
	%				%	%	%	%
1	78	2.36	V-W	18+	9.99	8.89	1.11	19.99
0.9	76	2.38	R-S	16-17	10.93	12.93	1.89	31.75
0.8	74	2.27	L-M	15-16	10.56	13.84	1.84	26.24
0.7	74	1.98	J-K	11-12	8.09	13.42	1.87	23.38
0.6	71	1.95	H-I	11-12	7.31	11.21	1.38	19.00
0.5	86	0.85	H	10-11	7.76	9.98	1.08	18.82
0.4	90	0.42	E	11-12	5.13	12.10	1.08	18.31
0.3	84	0.60	C-D	10-11	3.77	6.29	0.65	10.71
0.2	100	0.00	D-E	18+	6.83	0.40	......	7.23
0.1	74	0.31	A-B	8-9	2.10	2.30	0.20	4.60

[a] Per equivalent of soybean oil; TOCl = *t*-butyl hypochlorite.

halogen is comparatively stable in products obtained by dechlorination of oils treated with 0.5 equivalent or less of hypochlorite.

Preliminary tests indicate that the dechlorinated oils obtained from soybean oil chlorinated with 0.5 equivalent of *t*-butyl hypochlorite have substantially improved drying properties as compared with nonbreak soybean oil. These oils have also been used successfully in the preparation of ester-gum varnishes. More extensive evaluative tests are under way, and the results will be reported in a subsequent paper.

TABLE II

Thermal Stability of Dechlorinated Soybean Oil

TOCl (equivalents)[a]	Cl removed %[b]	Cl remaining % absolute
1	69	0.72
0.9	33	1.59
0.8	31	1.57
0.7	32	1.34
0.6	33	1.30
0.5	0	1.10
0.4	0	0.67
0.3	42	0.35
0.2	0	0.0
0.1	0	0.42

[a] Per equivalent of soybean oil.

[b] See Table I for original chlorine content.

Experimental

Chlorination. The general procedure followed was that previously described (1) with one modification as follows. When chlorination was complete, the reaction flask was chilled at —10° until the by-product *t*-butyl alcohol had crystallized out. The crystals were then removed by filtration through sintered glass or cheesecloth. About 70% of the by-product alcohol was recovered in this way. The time required to strip out the remaining alcohol at 60-70° and 1.0 mm. pressure was thus substantially reduced, resulting in products having improved colors.

Five-hundred-gram batches of soybean oil were chlorinated at each level of chlorination studied. The products were examined for chlorine content, refractive index, and conjugation; results are shown graphically in Figure 1.

Dechlorination. Dechlorinations were conducted by a method similar to that described in an earlier publication (2). A 250-gram sample of chlorinated oil was charged into a 2-liter stainless steel autoclave. A volume of 12% aqueous sodium acetate solution containing a weight of sodium acetate equivalent to the chlorine in the oil was added. (Samples chlorinated with 0.1 and 0.2 equivalent of hypochlorite were treated with 2.5% and 5% solutions of sodium acetate, respectively, in order to maintain a suitable total volume of reactants). The autoclave was sealed and heated with stirring over a period of about 1 hour to a maximum pressure of 460 p.s.i. The contents were then immediately discharged from the autoclave, and the product was isolated by usual means. Analyses and physical constants for the products are given in Table I.

Stability of Residual Halogen. Each dechlorinated oil was heated for 5 hours at 250° and atmospheric pressure in a current of nitrogen. Chlorine analyses on the products are given in Table II.

Summary

Soybean oil has been partially chlorinated by treatment with from 0.1 to 1.0 equivalent of *t*-butyl hypochlorite per equivalent of oil. The products were dechlorinated by autoclaving with aqueous sodium acetate solution, and the stability of the residual halogen in the dechlorinated oils was determined by a heat test.

It was found that oils halogenated with 0.5 equivalent or less of hypochlorite were more completely dechlorinated than those halogenated with larger amounts of hypochlorite and that the residual halogen in the dechlorinated oils produced was more stable.

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