

# Allylic Bromination of Soybean Oil and Subsequent Dehydrobromination

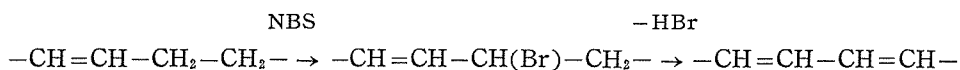
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## Introduction

Several methods have been used to convert non-drying and semi-drying oils into drying oils. Among them may be mentioned isomerization of non-conjugated fatty acids in oil to conjugated acids<sup>1,2</sup>; "solvent segregation" which involves heat-bodying of oils followed by liquid-liquid extraction with ketones, higher alcohols or other polar solvents<sup>3,4</sup>, etc.; displacement of combined glycerol in oil by another polyhydric alcohol, such as pentaerythritol<sup>5,6</sup>, sorbitol<sup>6,7</sup>, etc.; chlorination of oils with tert.-butyl hypochlorite followed by dechlorination<sup>8,9,10,11,12,13</sup>. Probably the most interesting method is one based on increasing the degree of unsaturation of fatty acids themselves in oil.

In previous papers<sup>14,15</sup>, it was shown that when a mixture of methyl oleate and linoleate was treated with N-bromosuccinimide (NBS), the esters were brominated almost exclusively in the "allyl position", and the resulting bromo-esters were thermally dehydrobrominated to produce a mixture of conjugated polyunsaturated acid esters.



In the present study, as an attempt to improve the drying properties of semi-drying oils, the above allylic bromination followed by dehydrobromination was applied to soybean oil consisting largely of oleic and linoleic acids and a small amount of linolenic and saturated acids, and it was found that under controlled conditions the allylic bromination proceeded satisfactorily, and that although the subsequent dehydrobromination was somewhat incomplete and complex because of the occurrence of polymerization, under suitable conditions a considerable amount of conjugated polyunsaturated acids was produced and the drying property of the resulting oil was considerably improved. The details of the experimental results are given below.

## Experimental

### I. Allylic Bromination

*Materials.* - The analytical data of the soybean oil used in this investigation were as follows: acid value, 3.33; iodine value, 129.3; saponification value, 195.5; unsaponifiable matter, 0.92%.

N-Bromosuccinimide (NBS) was freshly prepared according to the procedure described in the literatures<sup>16,17</sup>, and the purity of the product was determined iodometrically.

*Procedure.* - To a solution of soybean oil (10.0 g.) in carbon tetrachloride an equivalent amount of NBS was added gradually under constant stirring. The mixture was kept at a given temperature for a given length of time. After the resulting succinimide had been filtered off, the filtrate was washed with cold water, dried over anhydrous sodium sulfate, and the solvent was completely removed by distillation under reduced pressure. The bromo-oil thus obtained in each experiment was analyzed.

### Results and Discussion

In Table I are tabulated some typical experiments illustrative of allylic bromination conditions, together with product characterizations.

Table I  
Allylic Bromination of Soybean Oil (I.V., 129.3) with NBS  
(Oil, 10 g.; NBS (97.9%), 9.25 g.; NBS/F<sub>1</sub>=1/1)

Exp. No.	Conc. (Oil/CCl <sub>4</sub> ), %	Temp., °C.	Time, hr.	Yield, g.	Observ. I.V. <sup>a)</sup>	Calc. I.V. <sup>b)</sup>	Br, % <sup>c)</sup>
1	40	60	1	8.7	106.6	130.1	18.1
2	40	80	1	9.6	94.3	128.2	26.5
3	40	95	1	8.0	93.7	123.0	23.9
4	20	80	1	10.0	98.8	128.3	23.1
5	40	80	1	9.6	94.3	128.2	26.5
6	60	80	1	11.8	87.9	118.0	25.5
7	80	80	1	11.0	88.6	116.7	24.1
8	100	80	1	7.8	88.7	116.8	24.1
9	40	80	1	9.6	94.3	128.2	26.5
10	40	80	2	11.4	92.7	126.3	26.6
11	40	80	4	11.5	89.5	120.1	25.5

<sup>a)</sup> Determined by Klee-Beham's method (J. Am. Oil Chemists' Soc., **27**, 130)

<sup>b)</sup> Converted into the value for Br-free compound, the following equation being used :

$$\text{Calc. I. V.} = \{ \text{Observ. I. V.} / (100 - \text{Br}\%) \} \times 100$$

<sup>c)</sup> Determined by the procedure of Kimura (J. Soc. Chem. Ind., Japan, **37**, 1310)  
The maximum value for monosubstitution is 28.9%.

The important variables in the products are iodine value and content of bromine. It is desirable that the bromination should be accomplished without decrease in unsaturation of the oil.

As can be seen from the results of the first three experiments listed in Table

I, the temperature at which the reaction is carried out has a marked influence upon the bromine content and the iodine value of the product : at 80°C., the reaction proceeds most satisfactorily to give a product having the highest bromine content (26.5%) and a degree of unsaturation (I.V., 128.2) similar to that of the original oil (I.V., 129.3); at 60°C., it proceeds without appreciable decrease in iodine value, but to a lesser extent (Br, 18.8%); at 95°C., it gives a product having a somewhat lower bromine content (23.9%) and a lower iodine value (123.0). These decreases in bromine content and in iodine value are presumably due to the occurrence of dehydrobromination and polymerization during the reaction.

The data of the experiments 4, 5, 6, 7 and 8 in Table I illustrate the effect of a concentration of the oil in carbon tetrachloride on the characteristics of the product: under the conditions employed in these experiments a concentration of 40% is most favorable, and increase in concentration has the same influence as increase in temperature.

From the data of the experiments 9, 10 and 11 in Table I, it can be seen that the bromination is complete after an hour under the conditions employed in these experiments, and that prolonged heating results in lowering both the bromine content and the iodine value of the product.

From the above results so far obtained, it may be concluded that the allylic bromination of soybean oil proceeds most satisfactorily under the conditions of a heating temperature of 80°C., a concentration of 40% in carbon tetrachloride and of a heating time of one hour.

## II. Thermal Dehydrobromination of the Brominated Oil

*Materials.* - Two brominated soybean oils of different bromine contents were used in this investigation, and their characteristics were as follows:

Bromo-oil A: calc. iodine value, 120.9; bromine content, 27.2% (approximately one bromine atom per one double bond)

Bromo-oil B: calc. iodine value, 133.6; bromine content, 12.8% (approximately one bromine atom per three double bonds)

*Procedure.* - In each experiment, 2.0 g. of the brominated oil was placed in a 100-ml. round-bottom flask immersed in an oil-bath held at a given temperature. After being heated for a given time, the oil remaining in the flask was tested directly for iodine value, bromine content, and for drying time. Heating was conducted at three selected temperatures, namely 150°C., 210°C. and 270°C., and continued for 1, 3, 5, 10, 25 and 60 minutes at each temperature. These experiments were carried out in vacuum, nitrogen and/or in air to examine influence of the atmosphere in the reaction system. In heating in vacuum and in nitrogen, the flask was evacuated to 4-5 mm. pressure and flushed with oxygen-free nitrogen, respectively.

## Results and Discussion

In Table II and III are tabulated a number of experiments illustrative of dehydrobromination conditions, together with product characterizations.

Table II. Thermal Dehydrobromination of Highly Brominated Soybean Oil  
(calc. iodine value, 129.9; bromine content, 27.2%)

Exp. No.	Temp., °C.	Time, min.	Observ. I.V. <sup>a)</sup>	Calc. I.V. <sup>b)</sup>	Br, %	Drop in I.V. <sup>c)</sup>	Drying time, hr. <sup>d)</sup> (set-to-touch time)
1		1	89.2	121.2	26.4	4.4	over 200
2		3	90.9	123.2	26.2	3.6	100
3	150	5	92.9	124.9	25.6	5.4	100
4	(in air)	10	98.3	129.9	24.3	7.7	38
5		25	99.4	125.7	20.9	29.9	23
6		60	111.2	134.0	17.0	60.4	14
7		1	88.1	121.0	27.2	-0.1	144
8		3	90.1	123.3	26.9	-1.2	66
9	150	5	98.2	133.6	26.5	-8.5	44
10	(in N <sub>2</sub> )	10	101.2	135.8	25.5	-4.9	44
11		25	109.8	139.3	21.2	14.8	2
12		60	111.4	137.4	18.9	28.1	2
13		1	89.2	121.2	26.4	4.4	over 100
14		3	90.5	122.6	26.2	4.2	100
15	150	5	93.9	126.2	25.6	4.1	100
16	(in vacuum)	10	105.7	139.4	24.2	1.2	38
17		25	117.2	141.9	17.4	30.7	2
18		60	115.7	140.8	17.8	30.0	16
19		1	106.3	125.2	15.1	57.9	19
20		3	108.6	127.6	14.9	56.3	19
21	210	5	113.4	131.4	13.7	57.7	15
22	(in air)	10	103.4	118.3	12.6	75.5	over 240
23		25	103.4	116.6	11.3	82.5	"
24		60	102.9	114.3	10.0	90.0	"
25		1	102.8	134.2	23.4	8.3	23
26		3	106.5	131.2	18.8	34.8	38
27	210	5	116.1	137.7	15.7	42.7	24
28	(in N <sub>2</sub> )	10	113.9	135.0	15.6	45.8	48
29		25	109.5	129.0	15.1	54.1	48
30		60	113.4	129.6	12.5	64.6	240
31		1	125.3	139.1	9.9	65.5	21
32		3	130.3	142.4	8.5	67.6	36
33	210	5	130.3	140.6	7.3	83.9	40
34	(in vacuum)	10	132.2	140.5	5.9	89.1	190
35		25	125.2	131.1	4.5	93.5	"
36		60	116.5	121.2	3.9	105.4	over 240
37		1	113.3	128.3	11.7	69.2	over 240
38		3	114.3	128.4	11.0	71.9	"
39	270	5	114.3	128.4	11.0	71.9	"
40	(in air)	10	112.1	122.9	8.8	86.0	"
41		25	111.8	113.4	1.4	121.6	-
42		60	97.9	99.0	1.2	136.7	-
43		1	116.1	138.2	16.0	40.9	over 240
44		3	122.7	141.7	13.4	48.7	"
45	270	5	126.4	143.8	12.1	52.0	"
46	(in N <sub>2</sub> )	10	126.7	141.9	10.7	59.6	"
47		25	125.6	139.7	10.1	74.2	"
48		60	129.2	132.0	2.1	103.3	-
49		1	121.3	132.3	8.3	78.5	over 240
50		3	128.1	135.1	5.2	87.2	"
51	270	5	126.2	132.4	4.7	91.5	"
52	(in vacuum)	10	125.9	131.1	4.0	95.2	"
53		25	107.9	113.1	4.6	111.1	"
54		60	110.0	112.7	2.4	119.0	"

<sup>a)</sup> Measured by Klee-Benham's method

<sup>b)</sup> Calculated from the same equation as shown at foot-note in Table I.

<sup>c)</sup> Calculated from the following equation:

$$\text{Drop in I. V.} = \{B_b/(100 - B_b) - D_b/(100 - D_b)\} \times (127 \times 2 \times 100/80) \\ - (D_i - B_i)$$

where,  $B_b$  = Br% for brominated oil;  $D_b$  = Br% for debrominated oil;  $B_i$  = calc. I. V. for brominated oil;  $D_i$  = calc. I. V. for debrominated oil. This value is a difference between an increase in iodine value calculated on the basis of an amount of bromine removed and an observed increase.

<sup>d)</sup> This test was carried out without dryer.

Table III

Thermal Dehydrobromination of Partly Brominated Soybean Oil  
(calc. iodine value, 133.6; bromine content, 12.8%)

Exp. No.	Temp., °C.	Time, min.	Observ. I.V. <sup>a)</sup>	Calc. I.V. <sup>b)</sup>	Br, %	Drop in I.V. <sup>c)</sup>	Drying time, hr. (set-to-touch time) <sup>d)</sup>
1		1	116.4	132.7	12.3	3.0	20
2		3	129.3	145.9	11.4	-6.5	20
3	150	5	130.7	146.7	10.9	-5.3	20
4	(in N <sub>2</sub> )	10	135.3	150.0	9.8	-4.3	7
5		25	139.7	150.7	7.3	4.5	2
6		60	141.2	150.4	6.1	9.2	2
7		1	119.2	135.0	11.7	-0.9	29
8		3	122.2	136.5	10.5	-2.0	24
9	150	5	128.4	141.6	9.3	6.1	14
10	(in vacuum)	10	128.5	141.1	8.9	8.1	7
11		25	137.3	148.1	7.3	7.1	2
12		60	141.3	149.8	5.7	11.1	2
13		1	120.5	132.6	9.1	15.8	6
14		3	128.8	138.1	6.7	19.3	3
15	210	5	131.5	141.4	7.0	14.9	17
16	(in N <sub>2</sub> )	10	132.9	140.8	5.6	20.4	28
17		25	123.0	130.6	5.8	30.1	44
18		60	121.7	127.6	4.6	27.3	44
19		1	132.6	141.5	6.3	17.4	2
20		3	137.5	146.8	6.3	12.1	4
21	210	5	139.7	147.7	5.4	14.4	18
22	(in vacuum)	10	136.5	143.5	4.9	20.4	43
23		25	136.0	142.3	4.4	23.3	54
24		60	121.9	127.5	4.4	38.1	60
25		1	128.9	139.1	7.3	16.1	150
26		3	123.4	128.7	6.3	20.4	150
27	270	5	120.8	128.6	6.1	21.0	over 240
28	(in N <sub>2</sub> )	10	120.9	127.4	5.1	23.3	"
29		25	114.1	120.6	5.4	15.5	"
30		60	113.0	118.0	4.1	17.5	"

<sup>a)</sup>, <sup>b)</sup>, <sup>c)</sup> and <sup>d)</sup> See foot-note in Table II.

Moreover, the effect of the heating time on the residual bromine content or iodine value of the products is graphically shown in Figs. 1 - 2.

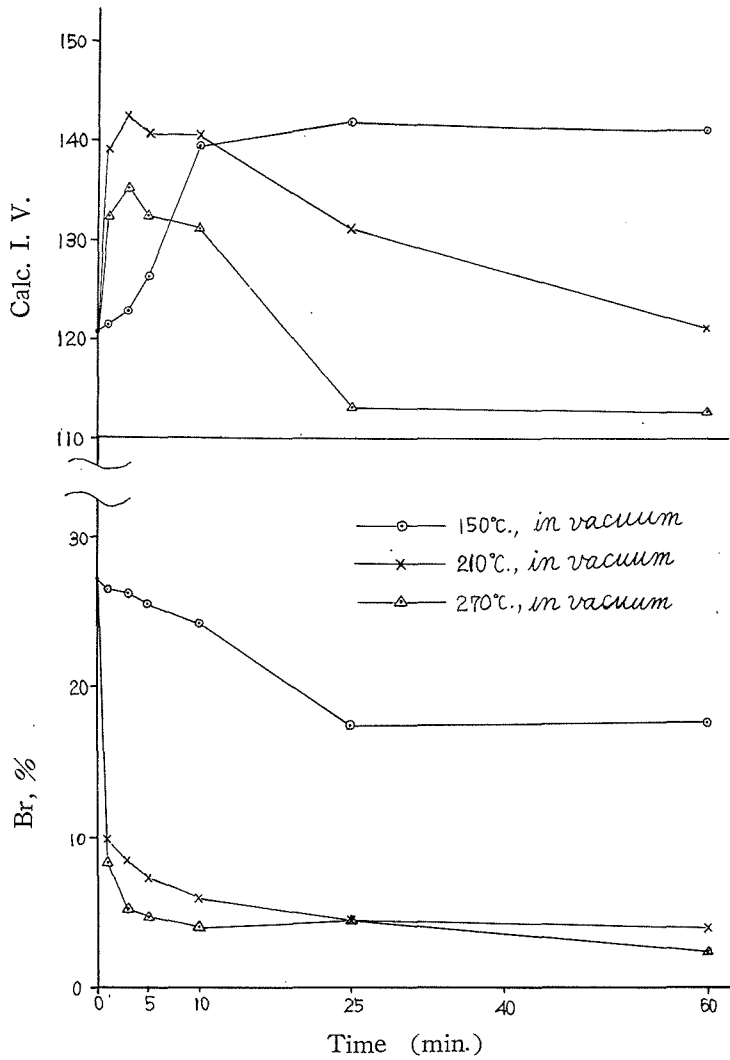


Fig. 1. Dehydrobromination of the highly brominated oil (Br, 27.2%) in vacuum.

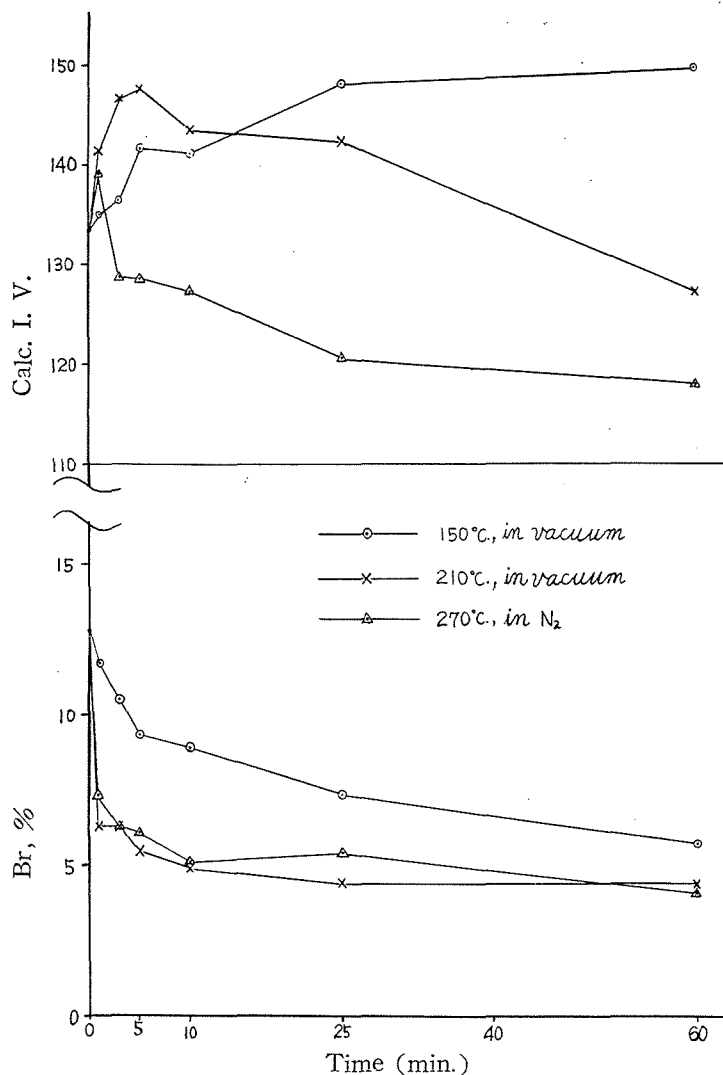


Fig. 2. Dehydrobromination of the partly brominated oil (Br, 12.8%) in vacuum or in nitrogen.

*Bromine Content.* - It will be noted from these Figures that in general the dehydrobromination reaction at a higher temperature proceeds to a higher extent and more rapidly than at a lower temperature, and that the dehydrobromination rate for the highly brominated oil increases greatly as the temperature increases, whereas that for the partly brominated oil is not affected so greatly by the temperature change. Unfortunately, in the limited experiments carried out in this Laboratory, no bromine-free product could be obtained.

*Iodine Value.* - Although iodine value should increase proportionally to the amount of bromine removed, its increase was found considerably less than that calculated on the basis of the decrease in bromine content. It may be assumed that this drop in iodine value, which is more remarkable at a higher temperature, is probably due to the polymerization of the resulting polyenes during the reaction. Furthermore, it will be noted from the above Figures that, at 150°C., the iodine value reaches a maximum in 25 to 60 minutes, while at 210°C. or 270°C., it reaches a maximum in 3 minutes and then decreases as the polymerization proceeds, and that the drop in iodine value for the partly brominated oil (Br, 12.8%) is less under the comparable conditions than that for the highly brominated oil (Br, 27.2%).

*Drying Time.* - Although no obvious relationship of the debromination conditions or the product characterizations to the drying properties of the products was observed, it may be said that the temperature at which the debromination reaction is conducted is an important factor in determining the drying speed for the products: most of the products obtained by heating at 150°C. for 25 to 60 minutes dried rapidly (set-to-touch time, 2 hours) even when the substantial increase in iodine value reached only 10%, whereas all the products obtained by heating at 270°C. did not dry easily even when its increase exceeded 10%. Since the drop in iodine value resulting on the dehydrobromination, as stated before, becomes more remarkable as the temperature increases, it may be responsible for the lack of drying properties of the products obtained by heating at a higher temperature (270°C.). However, the experimental data indicate that this may not be the case. The drop in iodine value for some of the products obtained from the partly brominated oil (Br, 12.8%) by heating at 270°C. was less than that for some of those obtained from the highly brominated oil (Br, 27.2%) by heating at 150°C. Nevertheless, the former products did not dry easily, while the latter dried easily.

The fact that the dehydrobromination at a higher temperature (270°C.) does not give any drying oil may be explained by the assumption that newly formed polyunsaturated acids are isomerized into isomers, which do not dry easily, by heating at such an elevated temperature.

Apart from the properties of the dried films, the drying speed seemed to be independent of the residual bromine content in the products. Examination of the influence of atmosphere showed that the reaction in nitrogen or in vacuum was somewhat more favorable than that in air.

*Conjugation.* - In order to obtain further information regarding the amount and type of conjugation which might be expected to result, other brominated oils (Br, 9.8% and 16.9%) were spectrophotometrically examined for diene, triene and tetraene, before and after dehydrobromination under various conditions;



absorption measurements were made with a Shimadzu photoelectric spectrophotometer (QB-50) and amounts of conjugation were calculated in the usual way, on the assumption that spectra of naturally conjugated and artificially conjugated fatty acids are essentially same. Table IV gives the details.

Table IV  
Properties of Brominated Soybean Oil, before and after  
Dehydrobromination<sup>a)</sup>

No.	Treatment	Br, %	Br removed, %	Conjugation			
				Diene	Triene	Tetraene	Total
1	Soybean oil			0.5	0.0	0.0	0.5
2	Bromo-oil	9.8		4.3	0.7	0.5	5.5
3	No.2 heated 1 hr. at 150°C.	4.9	50	10.2	3.8	2.2	16.2
4	No.2 heated 2 hrs. at 150°C	4.3	56	10.4	2.5	1.8	14.7
5	No.2 heated 3 hrs. at 150°C	3.3	66	10.7	2.5	1.8	15.0
6	Bromo-oil	16.9		6.6	0.4	0.9	7.9
7	No.6 heated 1 hr. at 150°C.	2.4	85.7	15.1	3.6	4.7	23.4
8	No.6 heated 1 hr. at 200°C.	1.9	89.0	14.6	1.1	0.0	15.7
9	No.6 heated 1 hr. at 250°C.	1.4	91.1	9.7	0.2	0.0	9.9

No.	$n_D^{25}$	$d_4^{25}$	Viscosity, poise, at 25°C	Drying properties (set-to-touch time)
1	1.4764	0.9208	0.4846	
2	1.4873	0.9899	1.311	
3	1.4895	0.9617	1.698	about 20 hours.
4	1.4889	0.9585	1.741	"
5	1.4873	0.9553	1.768	"
6	1.5003	1.0722	3.321	
7	1.5063	0.9892	3.332	40-50 minutes.
8	1.4990	0.9899	4.854	about 48 hours
9	1.5002	0.9892	5.137	—

<sup>a)</sup> In dehydrobromination, 30-45 g. of brominated oil was heated in vacuum.

It will be observed from Table IV that diene conjugation occurs to an

appreciable degree during the allylic bromination and it tends to increase with the increase of the bromine content. This observation is in accordance with that made by Teeter et al.<sup>10</sup> in the chlorination of soybean oil by means of tert.-butyl hypochlorite. They suggested that such substitution of an unsaturated acid was generally accompanied by shift of a double bond to produce conjugation.

Furthermore, it is evident from the same Table that the dehydrobromination produces a considerable amount of diene conjugation, together with small amounts of triene and tetraene conjugation, and the resulting conjugation is relatively stable at 150°C., but at a higher temperature (200°C. or 250°C.) it undergoes destruction more rapidly than it is formed, as indicated by a decrease in its amount. The amounts of produced conjugation and of removed bromine eventually changed with the dehydrobromination temperature or with the bromine content in the original oil. The dehydrobromination of the brominated oil (Br, 16.9%) at 150°C. for one hour permitted removal of about 86% of the halogen originally present and gave a product which contained 15.1% diene, 3.6% triene and 4.7% tetraene conjugation and dried very rapidly (set-to-touch time. 40-50 minutes). On the other hand, the dehydrobromination at a higher temperature (250°C.) removed as much as 91.1% of combined halogen, but the product contained a decreased amount of conjugation (diene, 9.7%; triene, 0.2%; tetraene, 0.0%), and consequently did not dry easily. An additional spectrophotometric study is now in progress.

#### Summary

Soybean oil was brominated by using NBS as a brominating agent. The transfer of bromine from this agent to the oil was essentially quantitative under controlled conditions.

The drying properties and characteristics of the debrominated products were greatly affected by conditions under which the dehydrobromination was carried out. Particularly, the dehydrobromination temperature was an important factor in determining the drying properties of the products, and a relatively lower temperature (150°C.) was suitable for the purpose of this research. The thermal dehydrobromination of the brominated oil (Br, 16.9%) at 150°C. for one hour produced a quantity of conjugation (23.4%) sufficient to impart an improved drying property to the resulting oil.

The removal of bromine from brominated oil was not complete under the conditions employed in this Laboratory. The dehydrobromination at 250°C. for one hour removed bromine up to 91.1% of combined halogen, but the drying property of the resultant oil was poor. Further work on this problem is necessary to develop this process.

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## 大豆油のアリリック臭素化及び脱臭化水素

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本研究は半乾性油の乾燥性を改善する目的で行ったものである。

*N*-ブロモ琥珀酸イミドによって大豆油を臭素化した。適当な条件に於ては、殆んど定量的に、アリルの位置に臭素が導入されることがわかった。

かくして得られた臭素化大豆油を各種条件の下で加熱脱臭化水素を行った。脱臭化水素油の特数及び乾燥性は反応条件により著しく影響されるが、特に脱臭化水素温度が生成油の乾燥性を決定する重要な因子であつて、比較的低温(150°C.)が最も適当であることを明かにした。例えば、臭素化油(*Br*, 16.9%)を真空, 150°C, 1時間で脱臭化水素すると、15.1%の共役ジエン, 3.6%の共役トリエン及び4.7%の共役テトラエンを含む油が得られた。この油は極めて速かに乾燥し、その指触乾燥時間は、乾燥剤なしで、40~50分であつた。なお脱臭素率は約86%であつた。もっと高い温度(250°C.)では、脱臭素率は91%まで向上したが、生成油の共役成分含量は却つて減少し、乾燥性は良くなかつた。