Reactions of Tertiary Butyl Hypochlorite With Vegetable Oils and Their Derivatives. V. Dechlorination of Chlorinated Soybean Oil With Aqueous Solutions of Salts[1]

H. M. TEETER and R. A. MYREN,[2] Northern Regional Research Laboratory,[3] Peoria, Illinois

PREVIOUS papers (1, 4) in this series have described a method of producing fast drying oils by chlorination of soybean oil with *t*-butyl hypochlorite and subsequent thermal dehydrochlorination. The use of heat to induce elimination of hydrogen chloride has several disadvantages. Halogen removal is not complete, and attempts to increase the amount of halogen removed result in undesirable increases in viscosity. Furthermore large amounts of corrosive gas are evolved during thermal dehydrochlorination. Consideration was therefore given to other methods of eliminating hydrogen chloride from chlorinated soybean oil. This paper describes the results of a study in which dechlorination was effected by the action of aqueous alkaline salt solutions.

It was found that up to 90% of the chlorine originally present in chlorinated soybean oil could be removed by heating the oil in an autoclave with dilute aqueous solutions of sodium salts of weak acids such as sodium bicarbonate, sodium acetate, disodium hydrogen phosphate, and sodium tetraborate. The products were less viscous than products dehydrochlorinated thermally to the same extent and were somewhat lighter in color.

Results and Discussion

Preliminary experiments were conducted on a small scale with chlorinated methyl oleate and solutions of sodium bicarbonate. Data obtained are given in Table I. The chlorine remaining in the products was classified by a previously described method (5) with the results shown in Table II.

These experiments indicated that this procedure gave relatively complete removal of halogen and that substitution of halogen by hydroxyl was not extensive. This tendency for elimination of halogen to occur in preference to substitution had previously been noted (3) in studies of the reaction of brominated soybean methyl esters with cyanides.

When the several types of halides present in chlorinated methyl oleate are heated, the allylic type liberates virtually all of its halogen as hydrogen chloride, the mono chloride type is partially affected, but the dichloride type is comparatively stable (5). The data of Table II showed that all allylic type halogen was removed from chlorinated methyl oleate by autoclaving with sodium bicarbonate solution. When removal of halogen was extensive, halogen of the mono chloride type also was largely eliminated and halogen of the dichloride type was significantly reduced. The halogen remaining after dechlorination with sodium bicarbonate should therefore be more stable to heat than that remaining after thermal dehydrochlorination.

TABLE II

Classification of Halogen in Dechlorinated Methyl Oleate

Run No.	Type of Halogen, %[a]		
	Allylic chloride	Mono-chloride	Dichloride
[b]	5.06	3.26	1.90
10	0.00	0.16	1.19
11	0.00	0.17	1.43
7	0.00	0.20	0.79
8	0.00	2.18	1.99
9	0.00	0.16	1.27

[a] Figures quoted are absolute percentages of halogen in the product corresponding to each type.
[b] Original chlorinated methyl oleate.

Similar small-scale experiments were then conducted with chlorinated soybean oil. Solutions of sodium bicarbonate, sodium acetate, disodium hydrogen phosphate, sodium tetraborate, and the sodium soap of linseed oil fat acids were used as dechlorinating reagents. Inspection of the data in Table III shows that results were comparable to those obtained with chlorinated methyl oleate except for rather low values of conjugation in the runs with disodium hydrogen phosphate and the sodium soap. Color and viscosity of the products were superior to those of products obtained by thermal dehydrochlorination.

In view of these encouraging results, larger scale experiments were made in which 500-g. samples of oil were dechlorinated. Salts used were those mentioned in the preceding paragraph with the exception of the linseed soap. The latter gave exceedingly intractable emulsions, probably due to the continuous mechanical stirring employed during dechlorination.

TABLE I

Dechlorination of Chlorinated Methyl Oleate With Aqueous Sodium Bicarbonate

Run No.	Conc. $NaHCO_3$ %	Time (Min.)	Temp. °C.	Cl[a] %	Cl Removal %	OH %	Conjugation		
							Diene	Triene	Total[b]
6	8	60	195	6.14	40	0.6	26.5	2.2	28.8
12	8	120	195	1.91	81	2.6	30.5	1.6	32.2
10	8	60	225	1.35	87	1.1	28.2	2.3	30.6
11	8	30	250	1.60	84	1.2	30.9	1.9	32.9
7	8	60	250	0.99	90	......	25.4	0.5	25.9
8	15	60	195	4.17	59	1.3	27.3	1.3	28.7
9	15	60	250	1.43	86	......	30.1	1.3	31.5

[a] Original chlorinated methyl oleate contained 10.22% Cl.
[b] All runs except No. 7 contained 0.1% tetraene.

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[1] Presented at the Fall Meeting of the American Oil Chemists' Society in Chicago, Oct. 8-10, 1951.
[2] Present address: Harvard Law School, Cambridge, Mass.
[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE III

Dechlorination of Chlorinated Soybean Oil With Aqueous Salt Solutions. Preliminary Experiments[a]

Salt	Conc. %	Chlorine %	Cl[b] Removal %	OH %	Color	Viscosity	Conjugation, %[c] Diene	Triene	Tetraene	Total
$NaHCO_3$	8	1.79	80	2.3	17-18	F	13.9	14.2	1.9	30.2
$NaC_2H_3O_2$	12	1.11	88	0.0	17-18	D	17.9	7.1	......	25.0
Na_2HPO_4	16	1.32	85	0.9	>18	E	15.8	3.2	......	19.0
$Na_2B_4O_7$	32	1.08	88	1.0	13	E	14.6	10.6	0.1	25.3
Soap[d]	18	0.65	93	0.4	>18	E	12.2	2.1	......	14.3

[a] Experiments conducted for 30 minutes at 240-250°C.
[b] Original oil contained 9.12% Cl except in exp. with $NaHCO_3$ where the value was 8.96%.
[c] Total includes fractional percentage of pentaene conjugation if present.
[d] Sodium soap of linseed oil fat acids.

Experiments were included in which the dechlorinating reagents were water and sodium hydroxide solution. The results of these experiments are given in Table IV, and the properties of the products are given in Table V.

From Tables III and IV it is seen that less halogen was removed in the larger runs than in the preliminary experiments. Removal was however substantially more complete than that usually attained by thermal dechlorination (50-55%). Color and viscosity were superior to those of samples obtained by thermal dehydrochlorination while the amount of conjugation produced was about the same.

TABLE V

Properties of Dechlorinated Soybean Oils

Run No.	Acid value	Color	Viscosity	Conjugation, %[a] Diene	Triene	Tetraene	Total
28	......	17	L	9.0	12.2	1.5	22.7
34	63.4	15	R	8.8	12.9	2.2	24.2
31	37.1	14	M	11.8	14.5	2.4	28.9
32	22.9	14	J	11.7	15.2	2.6	29.8
33	50.2	15	T	8.8	12.5	1.4	22.9
41	171.0[b]	>18	H	10.6	14.8	2.1	27.5
39	28.1	18	M	12.1	15.1	3.4	31.1

[a] Total includes fractional percentage of pentaene conjugation if present.
[b] Free fatty acids obtained.

The oils obtained had acid numbers ranging from about 23 to 63, indicating that appreciable hydrolysis occurred during dechlorination. Since an amount of reagent equivalent to the halogen present was used (except in the case of water, which however gave a product having one of the lower acid values), it is reasonable to assume that little if any complete hydrolysis of the glyceride occurred and that each molecule of free fatty acid present in the product is accompanied by a free hydroxyl group. With this assumption it is possible to calculate both the amount of halogen eliminated with formation of unsaturation and that replaced by hydroxyl groups. The results of such a calculation are shown in Table VI. It is seen that elimination is the dominant reaction in each dechlorination except that with water.

TABLE VI

Elimination and Replacement of Halogen During Dechlorination

Dechlorination reagent	Elimination, %	Replacement, %
Acetate	72.7	27.3
Phosphate	70.3	29.7
Borate	100	0.0
Carbonate	91.4	8.6
Water	10.0	90.0
Hydroxide	92.3	7.7

The drying properties of paints containing oils dechlorinated with alkaline salts and with water were determined in comparison with a similar paint containing non-break soybean oil as the vehicle. As shown by the data of Table VII, paints made with oils dechlorinated with water, sodium acetate, and disodium hydrogen phosphate dried very rapidly whereas those containing oils dechlorinated with carbonate and borate had very poor drying properties.

The poor drying properties of the oils dechlorinated with carbonate and borate appear to be due to the high acid values possessed by these samples. To test this conclusion, a specimen of the borate-dechlorinated oil was reesterified by heating for 5 hours at 125° in the presence of 1% of *p*-toluenesulfonic acid as a catalyst. The acid value of the sample was reduced from 50.2 to 16.6 by this treatment, and the drying time, as shown in Table VII, was reduced from over 60 hours to 20 minutes. The resulting film had only slight tack after 72 hours of drying.

The use of the dechlorinated oils in varnishes was tested with estergum varnishes of 25-gallon oil length. No evolution of hydrogen chloride was detected during preparation of the varnishes. Varnishes containing the dechlorinated oils did not differ significantly from those containing non-break soybean oil as vehicle in respect either to drying time or to properties of the final films. The principal advantage to the use of the dechlorinated oils was found in the reduction of the time required to complete the cook. A cooking time of 45 minutes to one hour was required with the

TABLE IV

Dechlorination of Chlorinated Soybean Oil With Aqueous Salt Solutions

Run No.	Salt	Conc. %	Time (Min.)	Temp. °C.	Pressure lb./sq. in.	Cl, % Before	After	Cl Removed %	OH %
28	$NaHCO_3$	8	119	240	500	9.12	1.15	87	2.3
34	$NaHCO_3$	8	76	238	460	9.25	0.94	90	2.3
31	$NaC_2H_3O_2$	12	85	237	440	9.06	2.34	74	2.0
32	Na_2HPO_4	16	87	240	440	9.06	2.72	70	1.6
33	$Na_2B_4O_7$	17	84	244	460	9.25	2.01	78	1.4
41	NaOH	7.4	76	246	460	9.10	0.95	90	0.3
39	(H_2O)	......	60	229	460	9.25	3.32	63	3.4

TABLE VII

Drying Properties of Paints Containing Dechlorinated Oils

Dechlorination reagent	Set-to-touch time (Min.)	Film properties after 72 hours of drying	
		Tack[a]	Sand removal
Acetate	21	M	Difficult, incomplete
Phosphate	25	M	Difficult, incomplete
Borate	>60 hrs.	C	Impossible
Borate[b]	20	S	Easy
Carbonate	>60 hrs.	C	*Impossible*
Water	30	S	Easy
Control	>60 hrs.	C	Impossible

[a] S, slight; M, moderate; C, considerable.
[b] Re-esterified.

dechlorinated oils whereas an average time of about 3½ hours was required for several controls in which non-break soybean oil was the vehicle.

The data on the performance of these oils in paints and varnishes is preliminary. More intensive evaluation is in progress and will be reported on later.

Experimental

Chlorination With t-Butyl Hypochlorite. Methyl oleate (I. V. 84.0) was chlorinated according to the method described by Teeter and Jackson (5). The product contained 10.22% chlorine. Soybean oil was chlorinated by the procedure of Teeter, Bachmann, Bell, and Cowan (4). Two batches of chlorinated oil were used in the subsequent experiments. One contained 9.12% chlorine and the other 8.96%.

Small-Scale Dechlorinations. A Parr, Series 2100, 22-ml., flame-ignition type bomb was employed as a pressure reaction vessel. As shown in Figure 1, the bomb was placed in a cradle which could be rocked (to secure agitation of the contents) by means of a rod attached to a motor-driven eccentric. The bomb and cradle assembly was inserted in a thermostatically-controlled muffle furnace provided with an opening through which the rod was run to the externally-located eccentric.

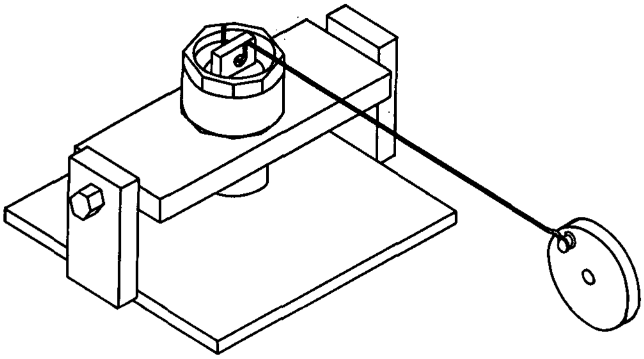

FIG. 1. Device for shaking flame-ignition bomb.

The bomb was charged with 3.0 g. of chlorinated methyl oleate or chlorinated soybean oil, and a volume of aqueous alkaline salt solution containing an amount of salt equivalent to the halogen in the chlorinated material was added. After sealing, the bomb was placed in the furnace at room temperature, agitation was begun, and the furnace was heated to the desired temperature. After the bomb had been held at this temperature for a period of time, it was removed and cooled by immersion in cold water. The product was isolated from the reaction mixture by usual methods.

Salts employed in these experiments were sodium bicarbonate, sodium acetate trihydrate, disodium hydrogen phosphate dodecahydrate, sodium tetraborate decahydrate, and a soap obtained by careful neutralization of linseed fat acids with sodium hydroxide. Details of time, temperature, concentration of salt, and properties of the products are given in Tables I and III.

Large-Scale Dechlorinations. A 1-gallon, electrically heated, stainless-steel autoclave equipped with a mechanical stirrer and an internal stainless-steel cooling coil was employed. Temperature was regulated by means of a thermocouple and a potentiometer controller. The autoclave was charged with 750 g. of chlorinated soybean oil and a volume of alkaline salt solution containing an amount of salt equivalent to the halogen present in the chlorinated oil was added. When aqueous sodium hydroxide was used as dechlorinating agent, a volume containing an amount of base sufficient to saponify the oil as well as react with the halogen was used. When water alone was used as dechlorinating agent, a volume of two liters was employed.

After the contents of the autoclave had been heated at the desired temperature for a period of time, they were cooled as rapidly as possible by passing cold water through the cooling coil. The product was isolated by usual methods. Data describing the conditions of reaction and properties of the products are given in Tables IV and V.

Preparation of Paints. Paints were prepared from the dechlorinated oils and, as a control, from non-break soybean oil in accordance with the following formula:

Basic carbonate white lead	3.0 oz.
Oil (reduced with mineral spirits to a viscosity of B)	1.6 oz.
Oil drier (Federal Specification TT-D-651a, Type I)	2.25 cc.
Mineral spirits	0.4 oz.

Each paint was mixed for 5 minutes in a Waring Blendor, after which the drying time was determined with the Sanderson Drying Machine (2). Results are given in Table VII.

Preparation of Varnishes. Varnishes were prepared according to the following formula:

Estergum	0.25 lb.
Oil	8 fl. oz.
Mineral Spirits	8 fl. oz.
Cobalt Naphthenate (6% Co.)	.5 cc.

Oil and resin were heated at 315°C. until a 5-inch string was obtained. After the mixture had cooled to 200°, mineral spirits were added. When the mixture had cooled to room temperature, drier and sufficient mineral spirits to give the mixture a viscosity of E were added.

The finished varnishes were tested for drying time and resistance to water and solvents. The results are discussed in the introductory part of this report.

Summary

Drying oils have been prepared by dechlorination of chlorinated soybean oil with aqueous solutions of

basic salts such as sodium bicarbonate, sodium acetate, disodium hydrogen phosphate, and sodium tetraborate. These drying oils may prove useful in paints and varnishes.

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Estimation of Skin Content of Peanut Meals and Relative Skin Pigment Content of Isolated Proteins

MACK F. STANSBURY and CARROLL L. HOFFPAUIR, Southern Regional Research Laboratory,[1] New Orleans, Louisiana

ANY residue of red skins in peanut meals imparts color to them and to the protein products derived from them (1, 2). This color is objectionable to the use of these products for industrial purposes and may be an important consideration in the future use of extracted peanut meal in foods. The pigments in the red skins have been shown to consist predominantly of a catechol tannin and to include small amounts of a leuco-anthocyanin, a phlobaphene, and a flavanone (4, 5, 8, 9). A method has been developed for estimating the skin content of peanut meals and relative skin pigment content of isolated proteins based on a characteristic color reaction of the catechol tannin with hydrochloric acid on heating in solution with ethanol (8). It involves Soxhlet extraction of the pigments with ethanol, their precipitation with neutral lead acetate, and treatment with alcoholic hydrochloric acid to give a red product having a characteristic absorption which can be measured colorimetrically. Details of the method are as follows:

Reagents

1. Ethanol, 95% U.S.P.
2. Neutral lead acetate, 10% solution. Dissolve 50 g. of lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, in 450 ml. of water.
3. Sulfuric acid, 5% solution. Add 5.6 ml. of concentrated sulfuric acid to 190 ml. of water.
4. Hydrochloric acid. Concentrated reagent grade.
5. Petroleum ether, commercial pentane.

Analytical Procedure

Weigh 20 g. of meal or protein, ground to pass a 1-mm. sieve, into a paper extraction thimble (preferably 33×118-mm. size for meals and 33×80-mm. size for proteins). Place a cotton plug in the top of the thimble. Extract the sample in a Soxhlet extractor with 125-150 ml. of 95% ethanol for 3 hours at a rate to provide syphoning approximately every 6 minutes. Concentrate the extract to approximately 30-35 ml., taking care not to concentrate to less than this volume. Transfer the concentrate to a 50-ml. conical-tipped centrifuge tube, rinsing the extraction flask with several small portions of ethanol to give approximately a 40-ml. volume in the centrifuge tube. Centrifuge for 10 minutes at 2,000 r.p.m. and decant the supernatant into a clean 50-ml. centrifuge tube. This centrifugation step may be omitted in the case of proteins.

Add by pipette 5 ml. of 10% neutral lead acetate solution to the ethanol extract. Mix by swirling. Heat the tube in a water bath at 75°C. for 10 minutes with occasional swirling. Remove from the bath and allow to cool for approximately 30 minutes. Separate the coagulated lead salts by centrifuging for 10 minutes at 2,000 r.p.m., decanting and discarding the supernatant liquid. Add by pipette 1.5 ml. of 5% sulfuric acid, stir for several minutes with a slender glass rod to allow decomposition of the lead salts, and then add sufficient ethanol to make a total volume of 15 ml. Wash the walls of the tube with ethanol, rubbing with the rod. Replace the tube in the water bath and heat for 10 minutes, stirring occasionally with the rod. Remove from the bath, rinse off the rod with ethanol, then centrifuge for 10 minutes to remove the lead sulfate. Decant the supernatant through a small filter of medium retentivity paper into a 50-ml. volumetric flask. Wash the filter with several portions of ethanol so that the volume of liquid in the flask is about 25 ml. Pipette 5 ml. of concentrated hydrochloric acid into the flask, mix by swirling, stopper, immerse in the water bath, and heat for 1 hour at 75°C. with occasional swirling. Remove, cool to room temperature, make to volume with ethanol, and mix. At the same time run a reagent blank consisting of ethanol and hydrochloric acid.

Determine the transmittance at approximately 540 mμ. An Evelyn photoelectric colorimeter equipped with a No. 540 filter was used in this investigation.[2] If the final solution is slightly turbid due to the presence of lipids, shake gently in the colorimeter tube with about ⅓ volume of petroleum ether, allow to layer, and determine the color intensity of the lower layer.

Compare the intensity of the color obtained with that of suitable standards in order to estimate the amounts of skins or the relative amount of pigments. In the case of meals these standards can be prepared

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

[2] Mention of trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over similar products not mentioned.