percentages are small.* As a control for determining percentages of monoglyceride in commercial monoglyceride preparations made from natural fats and oils, the periodate method is undoubtedly suitable because the error involved in the presence of small quantities of periodic acid reactive groups would be insignificant compared to the total calculated per cent of monoglyceride.

Laboratory synthesis of a monoglyceride preparation was performed for the purpose of determining whether the saponification of a fat and subsequent washing of the fatty acid fraction obtained resulted in a product free of glycerol. It might be expected that the presence of glycerol would have a considerable effect on the periodate value of the saponified product (1 mg. glycerol = 0.4 ml. of 0.1 N thiosulfate). The data in Table II indicates however that the washing process was effective in removing the glycerol. This conclusion arises from the fact that the periodate value of the fatty acid obtained by saponification of the monoglyceride preparation was essentially equivalent to that of the fatty acids used in the synthesis. This result reveals clearly that if the periodate value of the original fat is due to monoglyceride only, then the periodate value of the fatty acid fraction should be zero.

Summary

Periodate values were determined on a variety of fats and oils before and after saponification by the periodic acid oxidation method of Handschumaker and Linteris.

The values obtained indicate that the method is not specific for monoglycerides in natural fats and oils. Therefore previous reports of the natural occurrence of monoglycerides in fats and oils, where the periodate method has been used, may be open to question.

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* The method of Pohle, Mehlenbacher, and Cooke was probably not intended to be applied to very small quantities of monoglycerides.

Reactions of Tertiary Butyl Hypochlorite With Vegetable Oils and Their Derivatives. III. Chlorination of Soybean Oil in the Pilot Plant[1]

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A METHOD for the chlorination of soybean oil with *tert*-butyl hypochlorite and subsequent dehydrochlorination of the chlorinated oil has been reported by Teeter *et al.* (2). The preliminary evaluation of the drying properties of the dehydrochlorinated oil was sufficiently encouraging to indicate that an investigation of these reactions on a larger scale would be desirable. This paper describes the results of a study in which these reactions were successfully conducted on a small pilot-plant scale.

The chlorination with *tert*-butyl hypochlorite was conducted in conventional equipment in the pilot plant. However the preparation of the required hypochlorite and the dehydrochlorination of the chlorinated oil were conducted in the laboratory since suitable equipment for handling reactions involving large amounts of moist chlorine and anhydrous hydrogen chloride was not available in the pilot plant. Dehydrochlorination was conducted in an all-glass apparatus designed for continuous operation whereas this step was carried out previously (2) on small batches of oil in a current of steam.

No difficulty was experienced in handling the comparatively large quantities of *tert*-butyl hypochlorite required in the present work. It was of course necessary to avoid undue exposure to light and heat and to prevent contact with extraneous organic compounds which might react exothermically with this reagent. The chemical properties of *tert*-butyl hypochlorite have been described in detail by Teeter *et al.* (2), and by Chattaway and Backeberg (1).

Data obtained for the chlorinated oils are given in Table I which includes, for comparison, corresponding data for a sample prepared in the laboratory. These data show that the oil obtained in the pilot plant contained about 2% less chlorine than the oil prepared in the laboratory and was considerably darker in color. The laboratory and pilot plant oils had approximately the same total conjugation despite the differences in chlorine content. The varying distribution of conjugation among diene, triene, and tetraene forms, observed in the two samples of oil from the pilot plant, was not surprising in view of the results reported previously (2).

The lower chlorine content of the pilot-plant oil was caused primarily by evaporation of hypochlorite through the loading port during the reaction. For reasons described in the Experimental Part it was not convenient to close this port tightly.

The excessive darkening of the oil during chlorination was at first attributed to the rather high temperature (110°C.) reached during removal of byproduct alcohol. In a second run this temperature was not permitted to rise above 80°. Nevertheless the product had a color of 15-16 as compared with a color of 18 in the previous run and a color of 6-7 for a laboratory product which had not been heated above 75°. These observations indicate that the darkening must have been due to local overheating because past experience has shown that darkening is caused only by exposure of the chlorinated oil to excessive heat.

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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

Chlorination of Soybean Oil

Soybean Oil Chlorinated	Max. Temp. Reached Removing By-product Alcohol	Chlorine in Product	Color (Gardner)	Viscosity (Gardner)	Conjugation [1]			
					Diene	Triene	Tetraene	Total
lb.	°*C.*	%			%	%	%	%
35.5	110	8.50	18	I	14.0	5.0	0.3	19.3
54.0	80	8.96	15-16	J	7.3	10.3	2.3	19.9
0.33[2]	75	10.56	6-7	I	18.8	1.3	0.3	20.4

[1] Determined by spectrophotometric analysis.
[2] Sample chlorinated in laboratory.

In these pilot-plant chlorinations it is probable that overheating occurred on the walls of the kettle as a consequence of manual control of the steam used for heating. Removal of by-product alcohol in a falling-film evaporator or a similiar device in which the reaction mixture is brought into contact with a surface maintained at the correct temperature should yield products having a satisfactory color.

PERTINENT data on the operation of the continuous dehydrochlorinator and on the properties of dehydrochlorinated oils are given in Table II. Data for a sample of oil dehydrochlorinated in a flask in a current of steam are included for comparison.

The principal difficulty noted in operation of the continuous dehydrochlorinator was the formation of small particles of gelled oil. During operation of the dehydrochlorinator those parts of the inner tube in contact with the oil gradually became coated with a film of gelled oil. Portions of this film were loosened by the flowing oil and washed from the tube. A settling chamber provided on the fraction cutter of the dehydrochlorinator prevented clogging of the outlet stopcock and obviated filtration of the product.

At low rates of flow of the oil through the tube the gelled particles tended to readhere to the film and obstruct slightly the flow of oil. Oil held up by these particles would then gel, thus increasing the size of the obstruction and leading finally to complete clogging of the tube.

A study of the flow rate of oil through the dehydrochlorinator disclosed that when this apparatus was operated at 300-350°C. and at pressures ranging from about 35 to 50 mm., satisfactory results were obtained at flow rates of 0.073 to 1.5 liters per hour. Under these conditions the dehydrochlorinator could be operated for at least 8 hours without difficulty.

The properties of the dechlorinated oils compared favorably with those of oils obtained by batch dehydrochlorination in a current of steam. The continuous process resulted in removal of more halogen from the chlorinated oil than did the batch process, although somewhat less conjugation was present in the products. The decrease in conjugation appears to be due to increased destruction of triene conjugation at 300-350° as compared to temperatures of 160-180° employed in the batch process.

Low rates of flow in the continuous dehydrochlorinator yielded products containing less halogen than did products obtained at the higher rates of flow. This advantage was partially offset however by increased polymerization at low flow rates which resulted in products having higher viscosities and containing less conjugation, particularly that of the triene type. It is interesting to note that as the flow rate increased, diene conjugation decreased whereas triene conjugation increased. Further fundamental research must be done before this inverse relationship between diene and triene conjugation can be explained.

The drying properties of oils obtained by continuous dehydrochlorination were equivalent to those of the dehydrochlorinated oils previously described (2). Because these dehydrochlorinated oils bleach upon drying, the dark color of the product obtained in the present investigation is not disadvantageous except insofar as white paints appear slightly off-color when viewed in bulk. Films are perfectly white after drying. A comprehensive evaluation of drying properties of these dehydrochlorinated soybean oils as vehicles for paints and varnishes is in progress and will be reported in a subsequent communication.

Experimental

Preparation of tert-Butyl Hypochlorite

The previously described procedure (2) was increased slightly in scale to permit the use of 8 moles of *tert*-butyl alcohol per run. From a total of 20 runs, 32 pounds of *tert*-butyl hypochlorite was obtained in an average yield of 85%. The purity of the hypochlorite was 93 to 96% by iodometric determination. The product was distilled over a water bath in an all-glass apparatus and all material boiling at 79°C. or below was collected. In this way 1 to 3% of a by-product, tentatively identified as a mixture of chlorinated *tert*-butyl alcohols, was removed. The distilled product was stored at 0° in 1-pound, amber-colored bottles stoppered with paraffin-coated cork stoppers.

Chlorination of Soybean Oil

Equipment. A 20-gallon, glass-lined steel reaction kettle fitted with a glass enameled anchor-type agitator was modified to meet conditions necessary for the chlorination. Rubber gaskets and gaskets coated with organic materials were replaced with white asbestos gaskets. The bottom outlet valve was replaced with a cover plate fitted with a glass thermocouple well extending into the kettle.

The glass well was fitted to the cover plate by tapping the latter for three-fourths inch I.P.S. and attaching a ¾- x 3-inch nipple on the outer side. A glass well, 7 mm. in diameter and of sufficient length to reach a point just below the stirrer, was inserted in the nipple and held in place by litharge-glycerine cement. After the cement had completely set, the inside surface was given a heavy coating of dechlorinated soybean oil and allowed to dry. The gasket between the cover plate and the kettle covered the entire surface except for the necessary perforations for the glass well and the mounting bolts. It was made from asbestos sheet which had been soaked in dehydrochlorinated soybean oil and then baked.

The kettle was connected by means of glass-lined pipe to a glass-lined water-cooled condenser and a glass-lined vacuum receiver. Circulation of steam or cold water in the outer jacket of the kettle served to control the temperature. To provide an inert atmosphere during reaction, a carbon dioxide inlet tube was inserted through the loading port in the top of the kettle. For convenience the loading port was covered only by a loose-fitting piece of cardboard.

Procedure. The reaction kettle was charged with 35.5 pounds of alkali-refined soybean oil which was blanketed with carbon dioxide and then heated to 70° C. with stirring. One-half pound of *tert*-butyl hypochlorite was added, and the progress of the reaction was followed by potentiometric measurement of the temperature indicated by a thermocouple inserted in the well. After the induction period (approximately 10 minutes) the mixture was cooled to room temperature, and hypochlorite was added in increasing amounts. It was found that the reaction could be controlled satisfactorily by addition of hypochlorite to the reaction mixture in 1-pound increments. By adding each increment of hypochlorite only after the previous increment had reacted and by circulating cold water in the jacket when necessary, the chlorination was conducted smoothly without exceeding a temperature of 75°C. A total of 15.63 pounds of hypochlorite (equivalent to 14.32 pounds of pure *tert*-butyl hypochlorite) was added over a period of 7 hours. The reaction mixture was allowed to stand overnight to ensure complete reaction.

After the reaction was complete, the by-product *tert*-butyl alcohol was removed by distillation, first at atmospheric pressure and then at reduced pressure (23 inches of vacuum). During the entire distillation the pot temperature was kept below 110°C. A caustic scrubber was placed in the line to the vacuum pump to protect the system from any unreacted hypochlorite. Approximately 63% of the expected amount of *tert*-butyl alcohol was recovered. The chlorinated oil contained less than 1% of *tert*-butyl alcohol after stripping in the kettle. The remaining alcohol was lost by evaporation during the vacuum distillation because no special precautions could conveniently be taken to prevent such a loss.

A second run was made in which 54 pounds of oil were chlorinated. The conditions employed were the same as those just described except that by-product alcohol was removed at 80°C. or below. The constants of the chlorinated oils obtained in the two runs are given in Table I.

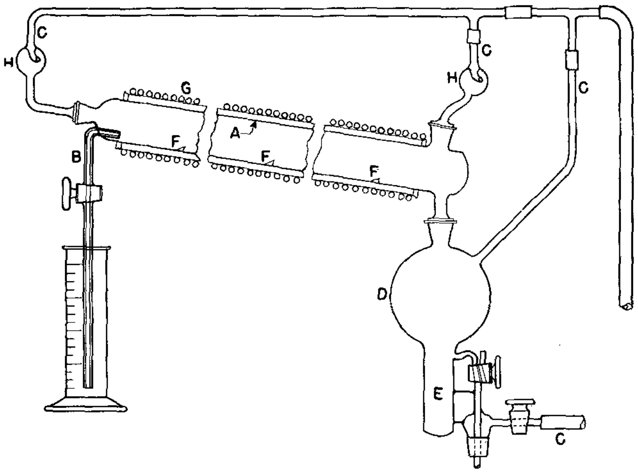

FIG. 1. Dehydrochlorination apparatus.

Thermal Dehydrochlorination

Apparatus. The apparatus for dehydrochlorination, illustrated in Figure 1, consisted of an inclined Pyrex glass tube (A) 48 mm. O.D. and 4 feet long. Three indentations (F) equally spaced along the under side of the tube were utilized as thermocouple wells. The upper end of the tube was provided with an oil inlet tube (B) made from 8 mm. O.D. glass capillary tubing while the lower end was attached to a fraction cutter (D). A stopcock in the oil inlet tube served to control the flow of oil. The fraction cutter included a settling chamber (E) which eliminated clogging of the outlet by particles of gelled oil which occasionally were washed from the tube by the flowing oil. Connections to vacuum (C) were provided at each end of the tube and on the fraction cutter. Distilling traps (H) were placed in the vacuum line running to the dechlorination tube in order to reduce entrainment of oil by the evolved hydrogen chloride. The heating jacket (G) consisted of a Pyrex glass tube, 57 mm. O.D., wound with Nichrome ribbon in three circuits. Each circuit was controlled by a separate variable-voltage transformer.

Vacuum was obtained by means of an aspirator through which a dilute solution of sodium hydroxide containing phenolphthalein was circulated from an 8-gallon reservoir by means of a pump. A stainless steel, positive displacement pump having a capacity of 1.5 gallons per 100 revolutions and driven by a ¾-hp. motor was used. A by-pass controlled the flow of liquid.

TABLE II

Dehydrochlorination of Chlorinated Soybean Oil

Flow Rate	Chlorine Content	Fraction of Original Chlorine Removed	Viscosity[1] (Gardner)	Conjugation[2]			
				Diene	Triene	Tetraene	Total
l./hr.	%	%		%	%	%	%
0.073	2.68	68.2	V	13.6	7.3	0.22	21.0
0.27	2.70	68.2	V	13.2	7.5	0.14	20.8
0.40	3.40	60.0	U	12.4	11.5	0.49	24.4
0.75	3.44	59.5	T-U	12.6	10.2	1.50	24.3
1.50	3.11	63.4	S-T	10.4	14.4	4.30	29.1
....[3]	4.96	52.0	S-T	13.4	20.4	1.15	35.0

[1] Color of all products exceeded 18.
[2] Determined by spectrophotometric analysis.
[3] Sample dehydrochlorinated at 3 mm. in current of steam.

As the alkaline solution was neutralized by hydrogen chloride given off during dehydrochlorination, additional sodium hydroxide was added to maintain alkalinity as shown by the phenolphthalein. Ice was added to the alkaline solution to obtain a better vacuum.

Procedure. The end of the oil-inlet tube was immersed in a quantity of chlorinated soybean oil contained in a large graduated cylinder and oil was drawn into the dehydrochlorination apparatus by vacuum at a rate of flow controlled by means of the stop-cock. The flow rate was determined by timing the withdrawal of oil from the graduated cylinder. It was found that the flow rate could be varied from 0 to a maximum of 1.5 liters per hour. Dehydrochlorinated oil was collected in receivers in the same manner as that employed during the vacuum distillation.

The dehydrochlorinator was operated at 300-350°C. and at pressures ranging from about 25 to 50 mm. Samples of dehydrochlorinated oil were collected for rates of flow varying from 0.073 to 1.5 liters per hour. When necessary, the tube was cleaned by ignition for 1.5 hours in an oven at 538°. Data obtained in these experiments are given in Table II.

Acknowledgment

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Summary

1. Batches of soybean oil weighing up to 54 pounds have been chlorinated with *tert*-butyl hypochlorite in conventional pilot-plant equipment.

2. The chlorinated oil was dehydrochlorinated in an all-glass apparatus designed for continuous operation. Excellent results were obtained when chlorinated oil was passed through this apparatus at a rate of 1.5 liters per hour.

3. The properties of the dehydrochlorinated oil were equivalent to those of oils previously obtained by laboratory procedures.

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Metal Deactivation in Lard[1]

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IN attempting to explain the role of antioxidants, Titoff (1) in 1903 concluded that antioxidants bind up (by complex formation) the positive oxidation catalyst, rendering it inactive and thereby effecting increased resistance to oxidation. He showed that the pro-oxidant effect of copper in the auto-oxidation of dilute solutions of sodium sulfite could be hindered by traces of benzyl alcohol, benzaldehyde, mannite, glycerol, and various phenols. Although these observations did not prove that this hindered oxidation was due exclusively to complexing of metal, his concept was that of metal deactivation rather than a general explanation of the role of antioxidants.

During the past 20 years there has been increasing interest in the effect of metallic contaminants in petroleum products and in fats and oils, and in means of preventing this contamination or in rendering these trace elements ineffective. It is now generally known that copper, cobalt, manganese, and iron in the form of their salts or oxides are powerful promoters of oxidation, and that tin, aluminum, and nickel salts, although far from being inactive, are among the less powerful promoters. Precautions have been taken in plant practice and construction to decrease this contamination by keeping the pumping lines as short as feasible, by eliminating copper-bearing metals in pumps and fittings, and by attempting to keep rust or corrosion of tanks and pipe lines to a minimum. When it is considered however that only one or two parts of copper or 10 to 20 parts of iron per ten million parts of fat or oil may noticeably increase the rate of oxidation or rancidification, it seems probable that such trace contamination could occur despite precautions. Therefore further treatment to inactivate these trace quantities of metals would be of considerable importance. A number of compounds have been patented for use primarily in gasoline, many of which would probably be unsuited for edible fats and oils. Among these are condensation products of ethylene diamine and o-hydroxyacetophenone (2), 2-hydroxyacetophenoxime (3), salicylalaminoguanidine (4), phenyl dihydroxyphosphine (5), lecithin and disalicylal ethylene diamine (6), condensation products of salicylaldehyde and a number of amino acids (7), guanylguanidine (8), stearamidomethylphosphonic acid (9), dihydroxydiazo compounds (10), salicyl glucamine (11), and thiourea (12).

Comparatively little work has been reported on investigations of deactivators for traces of metals in fats and oils. Commercial tannins (13) are effective in the treatment of lard to remove metallic impurities. In this treatment the tannin-metal compounds and excess tannins are removed by filtration. A possible relation of the synergistic effect of certain compounds, when used with antioxidants of the phenolic type, to metal deactivation has been pointed out (14). Citric acid has been shown (15) to extend considerably the oxidative stability of soybean oil containing iron stearate after natural tocopherols (antioxidants) have been removed by adsorption. Evidence was also presented that certain other polyhydric alcohols and

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[1] Presented at the Fall Meeting of the American Oil Chemists' Society, October 31 - November 2, 1949.

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