The Preparation and Some Properties of Chlorinated Tung Oil

R. S. McKINNEY, FRANK C. MAGNE, DOROTHY C. HEINZELMAN, and L. A. GOLDBLATT,
Southern Regional Research Laboratory,[2] New Orleans, Louisiana

THE MAJOR PORTION of tung oil (about 80%) is used in the preparation of protective coatings and finishes. Although tung oil is an outstanding drying oil and contributes certain desirable properties to dried films, new uses in the formulation of protective coatings and the manufacture of other items are needed to extend its utility and consumption. As part of a program directed toward increased chemical utilization of tung oil, chlorination of the oil was investigated.

Details concerning the chlorination of tung oil do not appear to have been reported in the literature although several patents (1, 2, 3, 4) relating to the production and use of chlorinated tung oil may be found. Although they refer to the chlorination of tung oil and the use of chlorinated tung oil in surface coatings, the patents provide little information concerning the procedures used for chlorination or the nature of the chlorinated products.

Experimental

The tung oil used was domestic tung oil of the species *Aleurites fordii.* The oil was pale yellow in color, had a refractive index $n_D^{25} = 1.5159$, specific gravity at 25°C. of 0.9372, and a hydrogen-iodine value (5) of 225. It contained 76.2% conjugated triene as eleostearic acid, determined spectrophotometrically (6). Typically, chlorinations were carried out on 100-g. batches of tung oil, dissolved in an equal weight of CCl_4, in a 500-ml. flask fitted with an inlet tube, reflux condenser, and a magnetic stirrer and with provision for heating or cooling. Gas from a chlorine cylinder was introduced into the solution by means of a suitable capillary or fritted glass pencil, which effectively dispersed the gas. Unreacted chlorine and by-product hydrogen chloride was freely vented through the condenser. Chlorinations were carried out in the range of 0 to 20°C. and at 75°C., sometimes in diffused daylight but generally in the dark, *i.e.,* the reactor was masked as completely as possible with aluminum foil.

The flask and its contents were weighed from time to time to follow the progress of the chlorination. Also, as the chlorination progressed, suitable aliquots were removed for the determination of chlorine and eleostearate content, for obtaining ultraviolet spectra and occasionally for determination of residual unsaturation. Portions of the aliquots were used without evaporation of solvent for analysis for conjugated triene content and for obtaining ultraviolet spectra. For determination of chlorine content and for residual unsaturation, the aliquots were evaporated to dryness under reduced pressure and at a temperature below 45°C. by using a rotating evaporator. Ultraviolet spectra were taken in cyclohexane solution, using a Cary recording spectrophotometer Model 14. The values for triene content obtained spectrophotometrically on the aliquots were occasionally checked on the solvent-free products by means of a Beckman DU spectrophotometer, using constants previously reported (6). In all cases the triene contents, expressed as eleostearic acid, were in good agreement with those anticipated from the Cary absorption curves. The amount of β-eleostearate present was negligible.

At the conclusion of each chlorination the solvent was evaporated by using a rotary evaporator as in the case of the aliquots. The solvent-free residues were analyzed for chlorine. The refractive index and density were also generally determined. Occasionally the amount of conjugated diene presented was determined using maleic anhydride according to the method of McKinney *et al.* (7), particularly when the triene content was relatively low and the chlorine content was between 15 and 30%.

Solvent-free, chlorinated products were screened, as plasticizers at the 30% level, for polyvinyl chloride resin, using butyl epoxystearate as a stabilizer. The formulation employed in the plasticizer screening tests was as follows:

Vinylite VYDR (vinyl chloride—vinyl acetate copolymer 95-5)	63.5%
Chlorinated tung oil	30.0%
Butyl epoxystearate	5.0%
Stearic acid	0.5%
Basic lead carbonate	1.0%

The control composition contained 35% DOP (di-2-ethylhexyl phthalate) to compensate for the omission of the butyl epoxystearate.

Milling and molding operations were carried out at 310°F., following the procedures previously described (8). Omitting the DOP formulation, these were tested on an Instron Tensile Tester as rigid plastics in conformance to the A.S.T.M. method D 638-52T for Type I except that the test specimens had a width of 0.125 in. and gauge length of 1 in. Because of the brittleness of the molded sheet at room temperature, test specimens had to be die-cut from warmed sheets (158–176°F.).

Heat stability data were obtained by means of the Hunter Multipurpose Reflectometer, using the 45° amber, 0° directional reflectance. Measurements were made every 30 min. during a 2-hr. heating period at 350°F., using specimens 20 mils thick.

Results and Discussion

Chlorination proceeded readily under all conditions used. The reaction was highly exothermal. All the chlorinated products were more or less unstable and decomposed with the evolution of hydrogen chloride when stored at room temperature. Markedly less hydrogen chloride was evolved at refrigerator temperature (+5°C.) and less darkening was observed, but some decomposition occurred even at this tempera-

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[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

ture. Products obtained on chlorination in diffuse daylight appeared to darken more and were more unstable than those obtained by chlorination in the dark. Decomposition was distinctly slower if all dissolved HCl were removed. The chlorinated products darkened appreciably during the early stages of chlorination but generally became lighter in color as the chlorination proceeded further. Some products containing 40% or more of chlorine were almost water-white when freshly prepared and were distinctly paler in color than the original tung oil. However these too darkened somewhat on standing.

The changes that occur in the refractive index and density of the chlorinated products as the chlorination progresses are shown in Figure 1. The refractive index at first decreases (owing to the decrease in triene conjugation) and then increases as the increasing chlorine content becomes more effective. The density increases fairly regularly as the chlorination progresses, and this characteristic may be used as a rough guide to the chlorine content of the solvent-free, chlorinated tung oils.

Attempts to remove unstable chlorine by deliberate heating at relatively high temperature were not successful. For example, a product which had been chlorinated at 10 to 20°C., in the dark, to a chlorine content of 40.8%, when heated for an hour at 100°C., lost only 0.4% of its weight and darkened very markedly. This dark color was only partially reduced by bleaching clay and decolorizing carbon. Additional heating for 4 hr. at 130 to 150°C. resulted in a further loss of 3.4% of its weight and further darkening. When this product was re-chlorinated at 10 to 20°C., additional chlorine was taken up without any significant decrease in color, and the resultant product contained 54.5% chlorine. This product was a very dark-colored, viscous tar (d = 1.362 g./ml. at 30°C.) which evolved hydrogen chloride slowly at room temperature. Since the product obtained by complete saturation with chlorine of all the unsaturation in the tung oil (HIV = 225) could have resulted in a product containing only about 39% of chlorine (63 g. of chlorine per 100 g. of tung oil), it is obvious that considerable substitution as well as addition at the centers of unsaturation must have occurred, both in the original chlorinated product and in the product which had been heated and re-chlorinated.

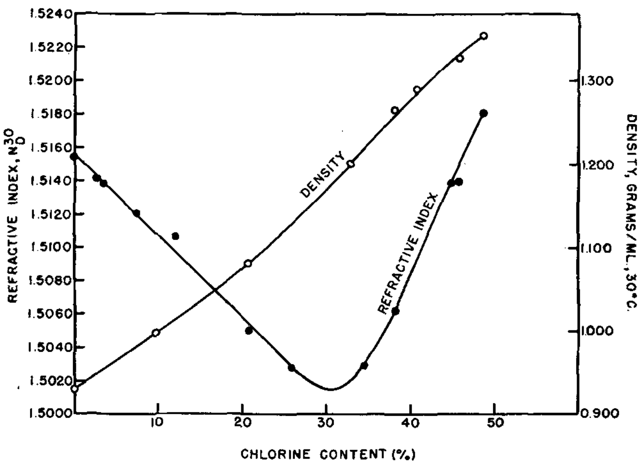

Fig. 1. Effect of chlorine content on refractive index and density of chlorinated tung oil.

The chlorination of conjugated triene to diene appears to be highly selective, at least during the early stages of chlorination. In Table I are shown representative data relating the chlorine uptake and loss of conjugated triene content for two representative chlorinations. Both were carried out in the dark, one at 10 to 20°C., the other at 75°C. It will be noted that in both cases the loss of conjugated triene almost quantitatively parallels the amount of chlorine added, at least as long as a moderate amount of conjugated triene remains. The temperature of chlorination does not seem to have any significant effect on the proportion of triene lost as the chlorination proceeds.

TABLE I

Effect of Time and Temperature on Chlorine and Triene Content of Chlorinated Tung Oil

Time (hours)	Chlorination temp. °C.	Chlorine (% found)	Triene[a] (% found)	G. of chlorine per 100 g. of oil	
				Added	Required[b]
3	10–20	3.96	57.9	4.2	4.1
6	10–20	8.36	40.6	9.2	8.1
9	10–20	21.4	<0.5	26.9	......[c]
1	75	2.70	60.2	3.0	3.6
2	75	11.3	20.6	12.8	13.5
3	75	15.4	7.2	18.2	17.2
4	75	21.1	0	27.0	......[c]

[a] As eleostearic acid.

[b] Calculated as amount required to reduce the triene content from that originally present (76.2%) to that observed.

[c] 19.5% added chlorine would be sufficient to reduce the triene content to zero.

Figures 2 and 3 show typical ultraviolet spectra taken of aliquots of these two chlorinations. It is obvious, from the characteristic absorption observable in the conjugated diene region, that conjugated diene

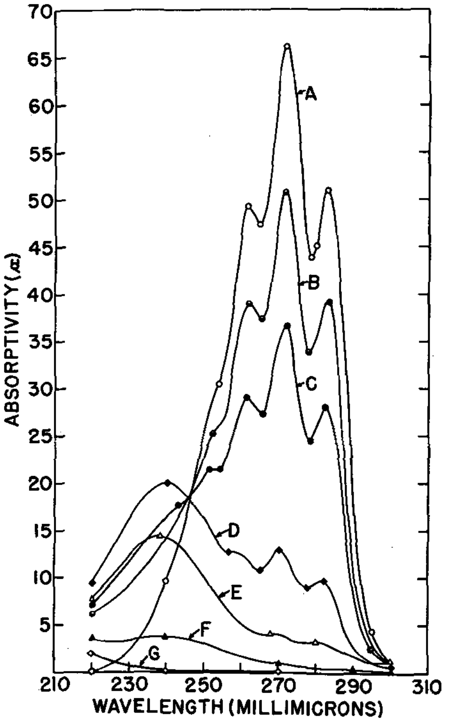

Fig. 2. Ultraviolet spectra of products from chlorination of tung oil at 10 to 20°C. Chlorine content (percentage) of solvent-free products: A, 0; B, 3.96; C, 8.36; D, 15.9; E, 21.4; F, 26.0; G, 31.7.

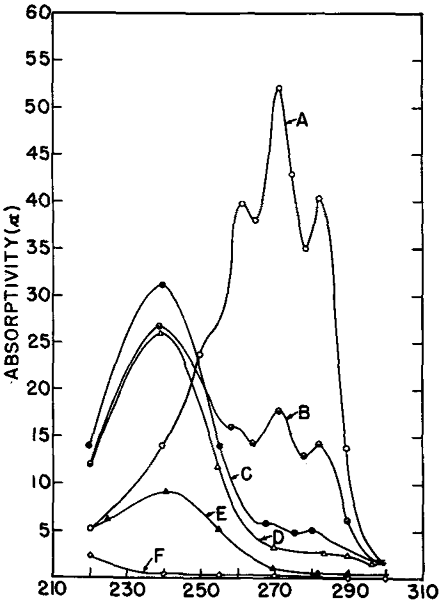

FIG. 3. Ultraviolet spectra of products from chlorination of tung oil at 75°C. Chlorine content (percentage) of solvent-free products: A, 2.70; B, 11.2; C, 15.4; D, 21.2; E, 28.4; F, 34.5.

is being formed during the chlorination. Thus chlorine addition appears to follow a similar course to hydrogen addition in accordance with the observations of Planck *et al.* (9) that considerable conjugated diene is formed during hydrogenation of tung oil. No attempt was made to calculate from these curves the exact amount of conjugated diene because the necessary constants for the chlorinated, conjugated dienes are not known. However it is obvious that considerable diene conjugation is produced, and it would appear, from the relative magnitude of the absorptivity in the diene region, that more conjugated diene is obtained during chlorination at 75°C. than during chlorination at the lower temperature.

In several cases attempts were made to determine the conjugated diene present by reaction with maleic anhydride. The results confirmed the fact that considerable conjugated diene was formed. Diene values of 67.9 and 68.0 were obtained for the tung oil used, in good agreement with those reported (7) for domestic tung oil. One chlorinated product which contained 12.1% chlorine and 31.0% triene, as eleostearic acid, was found to have a diene value of 44.0. After making allowance for the diene value of the remaining triene content, 27, the diene value to be attributed to the presence of conjugated diene would be 17. Another representative chlorinated tung oil which contained 15.8% chlorine and 21.2% triene, as eleostearic acid, was found to have a diene value of 34. After making allowance for the diene value of the remaining triene content, 18, the diene value to be attributed to the conjugated diene would be 16. These values are much too low to account for all the conjugated diene that would have been formed if the triene had been chlorinated quantitatively to conjugated diene and correspond to only about a third to about a half of the calculated amount. However it is known that *cis-cis* and *cis-trans* conjugated dienes do not react readily with dienophiles. Assuming that in these determinations of diene value only the *trans-trans* conjugated dienes are reacting (in addition to the eleostearate triene), it may be inferred that of the order of a third to a half of the chlorine has added to the 9,10-double bond of the eleostearate leaving the *trans, trans* configuration at carbons 11- and 13-. The infrared spectrum of a chlorinated tung oil containing 20.7% chlorine and 5% triene, as eleostearic acid, showed strong characteristic absorption at 10.02 microns (a = 0.15), indicative of considerable *cis-trans* conjugated diene, and also characteristic absorption at 10.32 microns (a = 0.19), indicative of the presence of isolated *trans* unsaturation. It appears therefore that, at least in early stages of chlorination, chlorine adds very selectively to the triene system to produce conjugated diene. Of the order of a third to a half of the chlorine adds at carbons 9 and 10 to produce the *trans, trans*-11,13-conjugated diene which reacts with maleic anhydride; about the same amount adds at carbons 13 to 14 to produce the *cis*-9-*trans*-11-conjugated diene which does not react with maleic anhydride but is revealed by its characteristic absorption in the infrared region at 10.02 microns and finally some chlorine adds 1,4 (*e.g.*, at carbons 9 and 12) to produce nonconjugated diene with isolated *trans* unsaturation at carbons 13-14.

All copolymer compositions obtained with these chlorinated tung oils were essentially rigid plastics. While all had milling temperatures well below unplasticized compositions, none had the flexibility usually associated with plasticized copolymer stock. The behavior of these compositions showed, except for milling temperature, considerable dependence upon the degree of chlorination of the tung oil employed. Those oils containing in excess of 40% chlorine, Table II, yielded copolymer compositions having the highest values of modulus of elasticity, yield-point, tensile strength at break, and elongation. These were, in addition, the most compatible compositions and gave no evidence of degradative darkening during milling and molding. These oils containing 9.8% and 18% chlorine were highly incompatible and gave severely darkened and degraded compositions on milling. Products containing 32.8 to 38% chlorine were intermediate in performance and compatibility and gave millable compositions but exhibited varying degrees of degradation during the molding operations. The values for the physical properties of the 32–38% group were all considerably below those for the more

TABLE II

Physical Characteristics of Chlorinated Tung Oil—Vinyl Chloride Copolymer Stocks

Plasticizer		Chlorine content	Modulus of elasticity	Yield point	Tensile strength at break		Elongation
Sample	Conc.				Original cross section	Reduced cross section	
	%[a]	%	*p.s.i.*	*p.s.i.*	*p.s.i.*	*p.s.i.*	%
1	30	9.8	........[d]	........[d]	........[d]	........[d]	......[d]
2	30	18.0	........[d]	........[d]	........[d]	........[d]	......[d]
3	30[b]	32.8	96,900	1,710	1,570	1,570	40
4	30[b]	36.5	93,300	2,260	1.820	1,820	40
5	30[b]	37.0	86,300	2,940	2,680	4,110	120
6	30	40.8	130,000	3,810	3,690	....	190
7	30	45.7	104,000	3,400	2,980	5,090	110
8	30	48.5	125,000	4,260	3,990	8,930	190
9	30	54.0	123,000	4,620	4,340	10,500	190
DOP (control)	35	None	1,528[c]	....	2,943[c]	....	330[c]

[a] 5% butyl epoxystearate added to all chlorinated plasticizer stocks.
[b] Localized degradation observed after molding.
[c] A.S.T.M. Test D 882–54 T, Method C; for nonrigid compositions; 1,528 lbs./sq. in. represents load for 100% elongation.
[d] Incompatible—degrades on milling.

highly chlorinated oils. It is apparent from Table II that the degree of chlorination is directly related to the thermal stability of the composition. Also the physical properties observed are directly related to the degree of chlorination, and values tend generally to show an increase with increasing amounts of chlorine in the oil.

Heat stability measurements at 350°F. on highly chlorinated compositions indicate greater reflectance loss during the initial 30 min. than that observed for a DOP plasticized composition, 50% as against 25%, respectively. Beyond this point the results favor DOP only slightly. At room temperature no observable color change of these compositions was detected after a period of three months.

The over-all results indicate that highly chlorinated tung oils are effective in lowering the milling temperatures of polyvinyl chloride copolymers, but the products are not very flexible at room temperature.

Summary

The chlorination of tung oil was investigated, and certain chlorinated products were screened as plasticizers for polyvinyl chloride resin. Chlorine readily added at low temperatures (0 to 20°C.) as well as at higher temperature (75°C.). The chlorination was highly selective for triene conjugation as the disappearance of triene closely paralleled the amount of chlorine added during early stages of chlorination. Considerable conjugated diene is formed as indicated by characteristic ultraviolet absorption in the diene region. In later stages of chlorination considerable substitution occurs as evidenced by the fact that products containing more than 40% of chlorine could readily be obtained. All the products were more or less unstable, evolving hydrogen chloride and darkening at room temperature. The chlorinated tung oils were screened as plasticizers, at the 30% level, for polyvinyl chloride by using butyl epoxystearate as a stabilizer. Products containing small proportions of chlorine (less than about 20%) were not compatible with polyvinyl chloride; products containing moderate amounts (about 30%) were compatible and had some plasticizing effect but decomposed excessively on milling. Those products containing the highest proportion of chlorine (more than 40%) were compatible and did not decompose on milling or molding. These highly chlorinated tung oils lowered the milling temperature of polyvinyl chloride copolymer but showed little, if any, ability to product compositions which are flexible at room temperature.

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A New Approach to Continuous Soap Making—Constant Composition Control[1]

FREDRIK T. E. PALMQVIST, Aktiebolaget Separator, Stockholm, Sweden, and
FRANK E. SULLIVAN, The De Laval Separator Company,
Poughkeepsie, New York

The manufacture of soap is one of the oldest industrial processes known in chemical technology. The art of making soap depended upon the skill of the soap boiler and was based upon many years of practical experience. During the past 50 years the rapid development of pure and applied chemistry, especially in the field of colloids, has made it possible to understand many reactions on a scientific basis. Based on this knowledge, soapmaking has now developed from an art into a scientific procedure.

The Centripure Process (1) of continuous soapmaking is an example of the successful application of scientific knowledge to the continuous operation and automatic control of a chemical process basically known since the days of antiquity.

In this process the production of soap from neutral fats is carried out continuously in three stages, each having its importance: saponification of the neutral fatty oils with lye; washing of the soap mass with brine to recover the glycerine released in the process; and fitting of the soap in order to effect further purification.

The Saponification Stage

As is well known, the initial reaction velocity in the saponification of neutral fatty oils with lye is very slow because of the immiscibility of the components. However the reaction may also be regarded as autocatalytic since the soap produced is capable not only of dissolving lye but also of dispersing neutral fatty oils into a colloidal suspension (2, 3). In this way a considerable enlargement of the contact surface re-

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