Retardation of Polymerization in Substituted Styrenes by Chelated Nitrophenols

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The polymerization of vinyl monomers has been inhibited or retarded by many substances including quinoid, hydroquinoid, and nitrophenolic compounds; the terms "inhibition" and "retardation" are differentiated in this article according to the definitions given by Foord (*21*). A comparison is made of the behavior of these compounds, particularly the nitrophenolic compounds, as polymerization retarders, studying the effect of temperatures and chelation upon their relative efficiency. The temperature effect is important in the selection of an inhibitor (or retarder) because a compound suitable to prevent polymerization of a monomer at room temperature and at low concentration during storage does not necessarily prevent polymerization during distillation. This fact is especially true when hydroquinoid compounds are compared with nitrophenolic compounds, and/or sulfur is compared with phenolic compounds. Apparently, an inhibitor (or retarder) has a certain operable temperature range, and a higher temperature destroys the inhibitor by its reaction with a growing polymer chain, or by thermal decomposition. Therefore, the stabilizing effect produced by chelation would be important in the inhibition of monomer at higher temperatures.

EXPERIMENTAL

Apparatus. The polymerization bath and the constant temperature water bath were identical, consisting of a borosilicate glass battery jar 12 inches high and 12 inches in diameter, set in a plywood box with an open front and an asbestos board top which had openings for heating and cooling coils, stirrer, supports for the sample tubes, and temperature-regulating devices. The temperature was controlled by a No. 7530 thermoregulator (A & B Instrument Co.) in connection with an electronic switch relay, Model 8284 (The United Cinephone Corp.). This control operated a Low-Lag (American Instrument Co.) immersion heater; its capacity was determined by the operating temperature of the bath. The heat transfer medium in the polymerization bath was paraffin oil. The water bath operated at 25.0° ± 0.2° C.; the temperature of the polymerization bath could be regulated within 1° C.

The viscometer used (Figure 1) is a modification of the type described by Foord (*21*). The end of the capillary is well above the volume mark *D*. A clamp is used to secure the cap. The ball joint used was § 35/25. The indentations in the funnel permit the liquid to run easily into the upper part of the viscometer when the assembly is inverted.

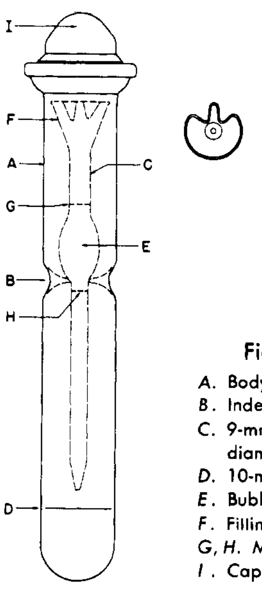


Figure 1. Diagram of viscometer

A. Body, 20 cm. long, 2.5 cm. in diameter
B. Indentations to support internal viscometer tube, *C*
C. 9-mm. O.D. tubing with capillary 1.5 mm. in diameter. bubble, *E*, and filling funnel, *F*
D. 10-ml. volume mark
E. Bubble blown in tubing to rest on indentations
F. Filling tunnel, top view at right
G, *H*. Marks for determining time of flow
I. Cap

Procedure. Fifteen grams of monomer and inhibitor mixture (see figures) were prepared, and 10 ml. was placed in the tube. The sample was then placed in the 25.0° C. constant temperature water bath for 30 minutes and the flow time determined (average of five readings). The samples were polymerized for the required period, removed from the polymerization bath, cooled quickly, and replaced in the constant temperature water bath. The same procedure was used for obtaining average flow times. This sequence was repeated until the inhibition or retardation period was adequately determined. The relative viscosity at time *t* is calculated by dividing the flow time at time *t* by the initial flow time.

Materials. The *o,p*-chlorostyrene monomer was prepared by dehydrating the corresponding chlorophenylethanol and consisted of approximately 5% ortho isomer and the rest para, and titrated 99+% by the bromide-bromate method. The "*m*"-chlorostyrene, prepared by dehydrogenation of the ethylated chlorobenzene, consisted of 20% ortho, 60% meta, 20% para isomers, with an unsaturation of 98.6% by the mercuric acetate method described by Marquardt and Luce (*31*). *ar,ar*-Dimethylstyrene (*ar*-vinylxylene) was prepared by dehydration of α,α'-bis(xylyl) diethyl ether and titrated 98.6% pure by the mercuric acetate method. The divinylbenzene, commercial Dow material, consisted of a solution of 40% divinylbenzene in ethylvinylbenzene. The vinyltoluene was prepared by dehydration of tolylethanol and was 99.2% pure according to the mercuric acetate determination. The 2,5-dichlorostyrene was obtained from Monsanto Chemical Co.

The compounds used as inhibitors with their sources, are as follows:

	M.P., ° C.
Paragon	
2-Nitrophenol	44.9-5.9
Eastman	
4-Nitrophenol	113.2-14.0
2,6-Dinitrophenol	62.0-3.1
4-Chloro-2,6-dinitrophenol	75.2-6.7
Dow	
4-*tert*-Butylpyrocatechol	56-7
2,4-Dichloro-6-nitrophenol	121.4-2.4
2-Cyclohexyl-4,6-dinitrophenol	101.4-3.2
2,4,6-Trinitrophenol	120.2-1.6
4-*tert*-butyl-2,6-dinitrophenol	91.5-2.5
4-Methyl-2,6-dinitrophenol	78.0-8.5
4-*sec*-butyl-2,6-dinitrophenol	43.0-5.0
4-Ethyl-2,6-dinitrophenol	36.5-7.5
4-Isopropyl-2,6-dinitrophenol	69.5

DISCUSSION

Hydroquinones (*3, 9, 13, 14, 17-21, 23, 26, 28, 29, 32, 34-40, 43, 49-53*), quinones (*8, 10, 13, 20-29, 32, 33, 36, 37, 40-42, 45, 49-51*), and sulfur (*2, 4, 11, 14, 30, 40, 48*) are suitable stabilizers for various polymerizable substances at room temperature and at the temperatures used in distillation of monomers which have relatively low boiling points and/or comparatively low polymerization rates. However, when they are used during the distillation of a higher boiling, readily polymerizable monomer such as monochlorostyrene, their performance is definitely unsatisfactory.

For comparison purposes, sulfur, 4-*tert*-butylpyrocatechol, and 2,4-dichloro-6-nitrophenol were selected as compounds representative of the classes of known retarders for chlorostyrene. The initial experiments with these compounds, and first tests (Figure 2) with the other compounds were carried out at 100° C. to determine the relative polymerization rates. Therefore, the polymerization interval at 130° C. could be adjusted to observe the induction and retardation periods of the polymerization.

Polymerizations were studied at 100° C. using chlorostyrene solutions containing 1% of various nitrophenolic compounds; some were studied previously (*1, 5, 15, 16, 21, 22, 25, 26, 46*). The compounds included were: 2-nitrophenol, 4-nitrophenol, 2,4 - dichloro - 6 - nitrophenol, 4 - methyl - 2 - nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, and 2-chloro-4,6-dinitrophenol. Foord (*21*) postulated that the period of retardation effectiveness of a nitrophenolic compound was related to the number of nitro groups contained by the compound. The results (Figure 3) showed that dinitro compounds were better retarders than mononitro compounds, and the position of the nitro group is an important factor in the duration of the induction period. Comparing the data for 2-nitrophenol and 4-nitrophenol, and for 2,4-dinitrophenol and 2,6-dinitrophenol, shows that the nitrophenol with the greater number of the nitro groups ortho to the phenolic group is more effective. This ortho nitro group may chelate (*47*), and the resulting stability appears to prevent premature breakdown of the molecule by heat. Therefore, the actual number of molecules of the retarder which was present in the monomer to react with free radicals was greater for these chelated compounds than the number present when an isomer was used which was not chelated to the same extent.

To establish the role of chelation, 4-*tert*-butylpyrocatechol and 2,4-dichloro-6-nitrophenol at 50°, 80°, and 100° C. were compared from the data of Rubens (*44*). There is a reversal in the order of effectiveness of these compounds over this temperature range (Table I), as expected if it were assumed that 4-*tert*-butylpyrocatechol reacts at high temperature in some other manner than with the growing polymer chain. The 2,4-dichloro-6-nitrophenol, on the other hand, being stabilized to a greater degree by chelation, while not as susceptible to attack by the free radical of the growing polymer chain at low temperatures, is less susceptible to thermal decomposition at the higher temperatures. Therefore, it is able to act more effectively as a terminator of polymerizing chains at these higher temperatures.

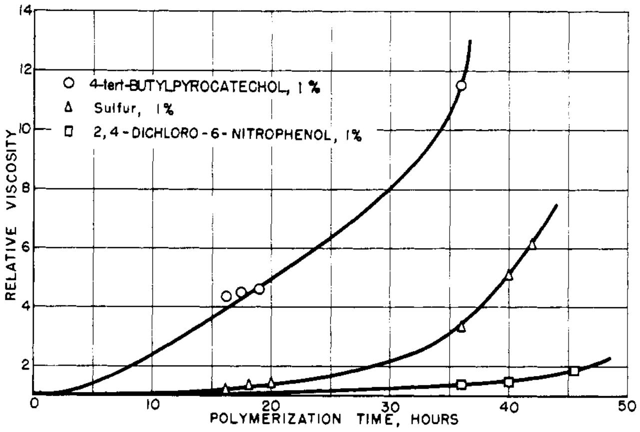


Figure 2. Inhibition of *m*-chlorostyrene at 100° C.

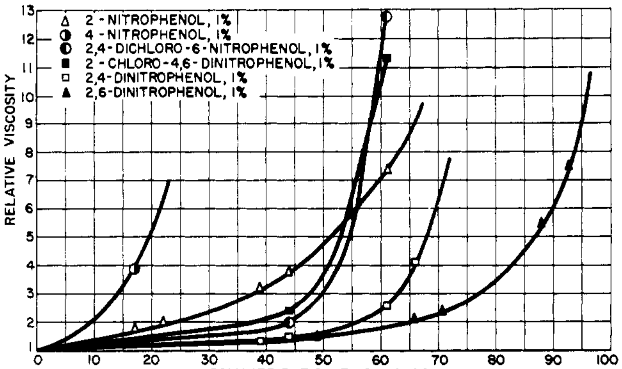


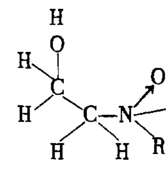
Figure 3. Inhibition of o,*p*-chlorostyrene at 100° C.

Table I. Effect of Temperature and Chelation on Effectiveness of Inhibitors

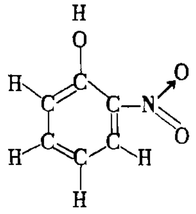
	Relative Inhibition Period[a]		
Inhibitor	T = 50° C. 5 p.p.m. concn.	T = 80° C. 500 p.p.m. concn.	T = 100° C. 1000 p.p.m. concn.
4-*tert*-butylpyrocatechol (*a*)	525	142	4
2,4-dichloro-6-nitrophenol (*b*)	185	162	26
Ratio, $\frac{\text{Inh. period } (a)}{\text{Inh. period } (b)}$	2.84	0.879	0.154

[a] Time at which relative viscosity = 2.0.

The concentrations at a particular polymerization temperature were selected for a reasonable inhibition period and with due regard to reversal at higher concentrations observed by Boyer and Rubens (*6*). The data concerning the inhibition of a styrene monomer by hydroquinone, phenol, and catechol given by Boyer and Rubens (*7*) also shows that the chelated inhibitor stabilized most effectively at temperatures used for distillation of the monomer. This concept is also supported by the work reported by Moureau (*35–40*), and the observations of Claver (*12*) regarding *N*,*N*-dialkylethanolamine-*N*-oxide, if the structures are compared, thus:



***N*,*N*-Dialkylethanolamine-*N*-oxide**



***O*-Nitrophenol**

The behavior of several members of the homologous series of 2,6-dinitrophenols and a chlorine derivative was investigated. These compounds, being chelated, had shown a greater effect on the polymerization than any other type. The compounds used were 4-methyl-, 4-ethyl-, 4-isopropyl-, 4-*sec*-butyl-, 4-*tert*-butyl-, 4-cyclohexyl-, 4-chloro-2,6-dinitrophenols and 2,6-dinitrophenol. The order of effectiveness of the alkyl homologs at a given weight concentration was in the inverse order of molecular weight, as expected (Figure 4).

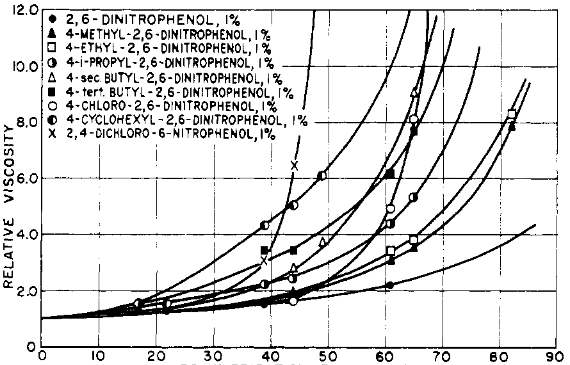


Figure 4. Inhibition of chlorostyrene at 100° C.

The chlorine derivatives investigated by Boyer and Rubens (*5*) apparently conform more nearly to the characteristics of a "true inhibitor" as defined by Foord (*21*) than do the alkyl homologs of 2,6-dinitrophenol. The alkyl homologs and the parent nitrophenol are retarders by his definition. When the chlorostyrene solutions of these compounds were heated for prolonged periods, the ones containing 2,6-dinitrophenol and its alkyl homologs became very dark red, but remained clear, whereas the chlorine compounds, under the same conditions, produced a flocculent precipitate and were lighter in color. The separation of the adduct produced by the reaction of the retarder and a free radical, or more probably, a growing polymer chain, as an insoluble material would not increase viscosity as would a soluble adduct of the same general size, even though the same amount of monomer was being polymerized. Kharasch, Kawahara, and Nudenberg (*29*) state that there is a difference in the behavior of quinone and chloranil, which may well be related to the difference observed here.

Another series of solutions of these compounds in chlorostyrene monomer was prepared using 1% by weight of the nitrophenols. The solutions were polymerized at 130° C. to determine the retardation at this temperature. The data are presented in Figure 5. Comparison of Figures 4 and 5 shows that the positions of the curves for the chlorine-substituted nitrophenols changed in relationship to the curves for the alkyl homologs.

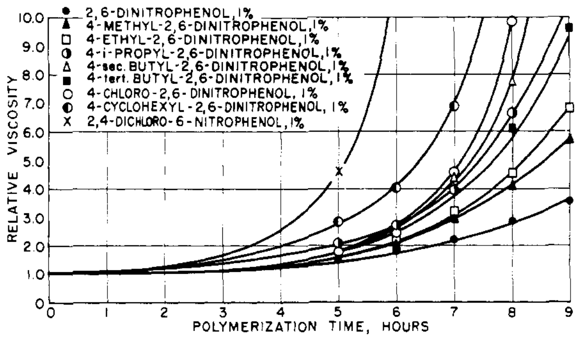


Figure 5. Inhibition of chlorostyrene at 130° C.

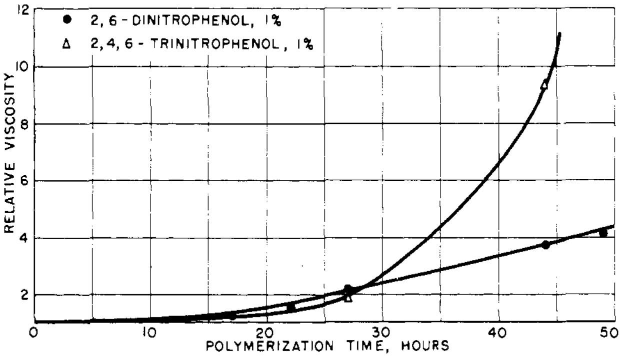


Figure 6. Inhibition of o,p-chlorostyrene at 100° C.

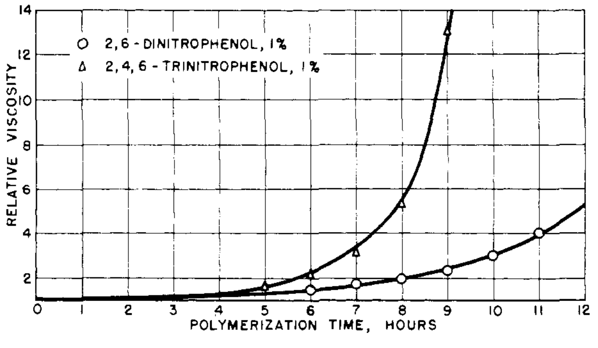


Figure 7. Inhibition of o,p-chlorostyrene at 130° C.

As a further test of the relationship between the position of the nitro groups and the retarding action, a series of samples was prepared to compare the effect of 2,6-dinitrophenol with that of 2,4,6-trinitrophenol upon the polymerization rate of *o,p*-chlorostyrene at 100° and 130° C., using 1% by weight of these compounds. Figures 6 and 7 show that 2,4,6-trinitrophenol is inferior to 2,6-dinitrophenol as a polymerization retarder for chlorostyrene under these conditions.

Several substituted styrenes were inhibited with 1% 2,6-dinitrophenol and polymerized at 100° C. to determine the inhibition period for these monomers by this chelated inhibitor. The data are given in Table II; the inhibition period varies inversely with the polymerization rate. The inhibition period produced by 2,6-dinitrophenol at this concentration is long enough to permit its use as an inhibitor in the distillation of these monomers.

Table II. Inhibition of Substituted Styrenes at 100° C. by 1% 2,6-Dinitrophenol.

Monomer	Inhibition Period[a]
Vinyltoluene	206
Vinylxylene	137
Divinylbenzene	45
Chlorostyrene	61
2,5-Dichlorostyrene	9

[a] Time in hours at which relative viscosity = 2.0.

SUMMARY

Comparing the behavior of various chelated and nonchelated polymerization inhibitors and/or retarders leads to the following conclusion:

1. The position, as well as the number of nitro groups, is a factor in the effectiveness of polymerization retardation by nitrophenols.
2. The duration of effectiveness of a polymerization retarder at temperatures in the range 50° to 130° C. depends on the stability of the group causing the retarding effect.
3. Chelation is a means of stabilizing such a group.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Amos, J. L., Soderquist, F. J. (to Dow Chemical Co.), U. S. Patent **2,443,217** (June 15, 1948).
(2) Bartlett, P. D., Trifan, D. S., *J. Polymer Sci.* **20,** 457–76 (1956).
(3) Bickford, W. G., Pack, F. C., Castillon, L. E., Mack, C. H., *J. Am. Oil Chemists' Soc.* **31,** 91–3 (1954).
(4) Blaikie, K. B. (to Canadian Electro Products Co.), Can. Patent **282,860** (Aug. 28, 1928).
(5) Boyer, R. F., Rubens, L. C. (to Dow Chemical Co.), U. S. Patent **2,304,728** (Dec. 8, 1942).
(6) Boyer, R. F., Rubens, L. C., ACS Monograph No. **115,** p. 262, Reinhold, New York, 1952.
(7) *Ibid.*, p. 265.
(8) Breitenbach, J. W., Horeischy, K., *Ber.* **74B,** 1836–9 (1941).
(9) Breitenbach, J. W., Springer, A., Horeischy, K., *Ibid.*, **71B,** 1438–41 (1938).
(10) Breitenbach, J. W., Taglicher, V. *Ibid.*, **76B,** 272–80 (1943).
(11) Britton, J. W., Prescott, R. F., Dosser, R. C. (to Dow Chemical Co.), U. S. Patent **2,166,125** (July 18, 1939).
(12) Claver, G. C. Jr. (to Monsanto Chemical Co.), *Ibid.*, **2,687,442** (Aug. 24, 1954).
(13) Cohen, S. G., *J. Polymer Sci.* **2,** 511–21 (1947).
(14) D'Alelio, G. F. (to General Electric Corp.), U. S. Patent **2,363,836** (Nov. 28, 1944).
(15) Drake, S. S., Lang, J. L. (to Dow Chemical Co.), *Ibid.*, **2,526,567** (Oct. 17, 1950).
(16) Dreisbach, R. R. (to Dow Chemical Co.), *Ibid.*, **2,445,941** (July 27, 1948).

(17) Erikson, E. R., (to Mathieson Alkali Works) Brit. Patent **578,965** (July 18, 1946).
(18) *Ibid.*, **586,537** (March 21, 1947); Can. Patent **452,350** (Nov. 2, 1948).
(19) *Ibid.*, **618,478** (Feb. 22, 1949).
(20) Eustis, W. (to Kendall Co.), U. S. Patent **2,675,914** (April 20, 1954).
(21) Foord, S. G., *J. Chem. Soc.*, **1940,** 48-56.
(22) Foord, S. G. (to Standard Telephones and Cables, Ltd.), Brit. Patent **504,765** (May 1, 1939).
(23) Foord, S. G. (to International Standard Electric Corp.), U. S. Patent **2,225,471** (Dec. 17, 1940).
(24) *Ibid.*, **2,226,714** (Dec. 31, 1940).
(25) *Ibid.*, **2,320,859** (June 1, 1943).
(26) Frank, R. L., Adams, C. E., *J. Am. Chem. Soc.* **68,** 908 (1948).
(27) Goldfinger, G., Skeist, F., Mark, H., *J. Phys. Chem.* **47,** 578-87 (1943).
(28) Kern, W., Feuerstein, K., *J. prakt. Chem.* **158,** 186-97 (1941).
(29) Kharasch, M. S., Kawahara, F., Nudenberg, W., *J. Org. Chem.* **19,** 1977-90 (1954).
(30) Krakau, A., *Ber.* **11,** 1261 (1878).
(31) Marquardt, R. P., Luce, E. N., *Anal. Chem.* **21,** 1194 (1949).
(32) Mathieson Alkali Works and Erikson, E. R., Brit. Patent **628,485** (Aug. 30, 1949).
(33) Melville, H. W., Watson, W. F., *Trans. Faraday Soc.* **44,** 886-905 (1948).
(34) Mesrobian, R. S., *Conf. on Biol. Antioxidants, Trans. 2nd Conf.*, **1947,** 20-6.
(35) Moureau, C., *Ann. chim.* **15,** No. 9, 158-211 (1921).
(36) Moureau, C., *Compt. rend.* **169,** 1068-72 (1919).
(37) *Ibid.*, **170,** 26-31 (1920).
(38) *Ibid.*, **174,** 258-64 (1922).
(39) Moureau, C., Dufraisse, C., Brit. Patent **181,365** (June 7, 1922).
(40) Moureau, C., Dufraisse, C., *J. Soc. Chem. Ind. (London)* **47,** 819-28 (1928).
(41) Ostromislensky, I., Brit. Patent **236,891** (July 12, 1924).
(42) Ostromislensky, I., Shephard, M. G. (to Naugatuck Chemical Co.), U. S. Patent **1,550,324** (Aug. 18, 1925).
(43) Perkins, R. P., Bryner, F. (to Dow Chemical Co.), *Ibid.*, **2,247,403** (July 1, 1941).
(44) Rubens, L. C., Dow Chemical Co. Private communication.
(45) Schulz, G. V., *Kunststoffe* **33,** 223-7 (1943).
(46) Schulz, G. V., Strassberger, M., Glinderman, E., *Makromol. Chem.* **1,** 94-105 (1947).
(47) Sidgwick, N. V., "Electronic Theory of Valency," Oxford University Press, Oxford, 1929.
(48) Smith, O. H. (to Dominion Rubber Co.), Can. Patent **308,122** (Jan. 27, 1931); (to Naugatuck Chemical Co.), U. S. Patent **1,870,876** (Aug. 9, 1932).
(49) Springer, A., *Kautschuk* **14,** 159-63; 197-201; 212-8 (1938).
(50) Suess, J., Pilch, K., Rudorfer, H., *Z. physik. Chem.* **A179,** 361-70 (1937).
(51) Szwarc, M., *J. Polymer Sci.* **16,** 367-82 (1955).
(52) Taylor, H. S., Vernon, A. A., Jorden, C. W., *J. Am. Chem. Soc.* **53,** 2527-36 (1931).
(53) Ward, A. L., Fulweiler, W. H., *Ind. Eng. Chem.* **24,** 1238-47 (1932).

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Plasticizers from Tetrahydrofurfuryl Alcohol

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The solvency toward vinyl polymers contributed by the tetrahydrofuran ring is known, since tetrahydrofurfuryl oleate has been used as a secondary plasticizer for poly(vinyl chloride). Tall oil esters of tetrahydrofurfuryl alcohol are potentially of interest in the same field, and their use has been patented by Valko (*11*). Tuttle and Kester (*10*) indicate that various fatty acid esters of tetrahydrofurfuryl alcohol are efficient plasticizers for poly(vinyl chloride) and poly(vinyl butyral). Thinius (*9*) describes the relationship between fatty acid chain length and compatibility. With the advent of commercial, light colored, low-rosin tall oils, an evaluation of their tetrahydrofurfuryl esters is justified.

Interest in commercial utilization of tetrahydrofurfuryl alcohol derivatives has been stimulated by development of a process for production of the alcohol by continuous, vapor-phase hydrogenation of furfural (*13*). Several dibasic acid esters of tetrahydrofurfuryl alcohol (THFA, Quaker Oats brand) have been studied. Imoto (*5*) indicates that the diphthalate is less efficient than dioctyl phthalate. Yamanouchi (*12*) has evaluated several esters, and reports that butyl tetrahydrofurfuryl phthalate is superior to dioctyl phthalate in poly(vinyl chloride).

This paper deals with preparation and evaluation of esters of tetrahydrofurfuryl alcohol and adipic, azelaic, diglycolic, phthalic, succinic, sebacic, and tall oil fatty acids. Also, the esters of tetrahydrofurfuryl alcohol and iso-octyl and decyl alcohols with most of the above acids are described. For some of these esters, efficiencies as poly(vinyl chloride) plasticizers and as swelling agents for cellulose triacetate are described in addition to physical properties of the esters.

EXPERIMENTAL

Preparation of Dibasic Acid Esters. A typical preparation of a mixed ester involved reacting equimolar quantities of THFA and the dibasic acid or anhydride at temperatures of 100° to 130° C. If the acid was used, benzene was added, and water was removed azeotropically. After completion of this initial reaction, as evidenced by the acid number or the volume of water collected, 15 to 25 mole % excess of the second alcohol was added. Concentrated sulfuric acid (1% based on theoretical yield of ester) was added at this point.

Benzene was added to control the boiling point of the mixture between 100° and 130° C. The rate at this temperature generally was such that the second step could be completed in about four hours.

When most of the theoretical amount of water was removed, acid numbers were run periodically to determine when the reaction was essentially complete. The product was washed with an equal volume of 5% sodium hydroxide and then with successive equal-volume washes of distilled water until a neutral pH was obtained. In the case of the di(tetrahydrofurfuryl) esters, this step washed away most of the excess THFA.

The crude batch was distilled at reduced pressure through a 15-inch Vigreux column, and the constant boiling fraction was collected. Distillation was repeated when the initial fractionation failed to remove essentially all of the color. In some cases, it was necessary to use activated carbon to bring the color below American Public Health Association color standard, APHA 100. All reactions and distillations were carried out under nitrogen. 0.1% of bisphenol A (4,4′-isopropylidenediphenol) was added as an antioxidant to all of the esters after distillation.

Discoloration was kept to a minimum as follows: first, by flash distillation of THFA prior to esterification; second, by use of reaction temperatures below 130° C.; and third, by reaction by THFA first in a mixed ester.

Preparation of Tall Oil Fatty Acid Ester. The tall oil fatty acid ester of THFA was prepared at a higher temperature (180° to 205° C.) without benzene and with a milder catalyst, phosphoric acid. At the completion of the reaction, sodium carbonate was added to neutralize residual acid. The crude batch was fractionated through a 15-inch Vigreux column.

Vinyl specimens plasticized with di(2-ethylhexyl) phthalate and the resulting tall oil ester fractions were exposed to ultra-