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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 ultraviolet light to determine which fractions were color-stable. The yield of color-stable material was 85.8% of the theoretical yield based on the tall oil acids reacted. The particular grade of tall oil acids used contained 95% oleic-linoleic acid.

Evaluation of Esters as Vinyl Plasticizers. The esters were evaluated in comparison with di(2-ethylhexyl) phthalate (Flexol DOP, Union Carbide Chemicals Co., Division of Union Carbide) as plasticizers for a vinyl copolymer. The tall oil fatty acid ester was compared with tetrahydrofurfuryl oleate (Plastolein 9250 THFO, Emery Industries, Inc.) as a secondary plasticizer. The formulation was as follows:

Material	Parts by Weight	Supplier
Vinylite VYNW-5	100	Bakelite Div. of Union Carbide Corp.
Plumb-O-Sil B	3	National Lead Co.
DS-207	1	National Lead Co.
Plasticizer		As specified in Table I

The tests were conducted in accordance with the following ASTM specifications:

Test	ASTM Specifications
Tensile strength	D 412-51T
Elongation at break	D 412-51T
Shore A Durometer	D 676-49T
Modulus	D 412-51T
Oil extraction	D 543-52T (7-day immersion at 23° C.)
Water extraction	D 543-52T
Ultraviolet light exposure	D 1300-53T (48 hours)
Brittle point	D 746-52T

The temperature at Young's modulus of 10,000 p.s.i. was determined using a modification of the Jolly balance stiffness test (*1*). The test was modified as follows: Samples 2 × 0.5 × 0.07 inch were mounted with staples on a wooden board, but were stapled to the board 1.75 inches from the hook end. Each sample was conditioned at the test temperature for at least 20 minutes prior to testing. The sample was raised in increments of 0.2 to 0.5 cm. and the force was measured. The force required to raise a sample 1 cm. was determined by interpolation from a plot of stress *vs.* strain. Tests were run at 70°, 45°, 25°, and 15° F. The temperature at which the modulus was 10,000 p.s.i. was obtained by interpolation from a plot of modulus *vs.* temperature.

The volatile loss was determined according to (*3*). The lacquer marring test (*7*) was modified as follows: Duplicate specimens of each sample 1 inch square by 0.07 inch thick were placed against a glass plate coated with a solution of 25 parts of butyl acetate, 25 parts of toluene, and 50 parts of nitrocellulose lacquer 1334 (Raffi and Swanson Co.). The plate and samples were covered with polyethylene, and a force of 1.5 p.s.i. provided by a sand bag was exerted on the samples for two weeks, after which time the lacquer and specimens were inspected.

Preliminary Evaluation of Esters as Plasticizers for Cellulose Triacetate. To perform this test, a 2-gram sample of cellulose triacetate was placed in a test tube and an 8-gram sample of the ester was added. The test tube was immersed in an oil bath at 180° ± 10° C. When the contents of the test tube reached bath temperature, the sample was stirred briefly to release entrapped air. After 1 hour, heat was removed; the sample was permitted to cool, and inspected.

Determination of Ester Properties. Water solubility was determined by adding small drops of plasticizer from a weighing bottle to 100 ml. of distilled water at 25° C. When turbidity developed or when small droplets were still visible after 2 to 3 minutes of stirring the bottle was reweighed. The accuracy of this method is estimated at ±10%.

About half of the saponification equivalents were determined by the alcoholic sodium hydroxide method. With the higher molecular weight esters it was necessary to use the method of Shaefer and Balling (*8*).

The boiling points were determined in an apparatus which gave a boiling point for dibutyl phthalate of 163° C. at 2 mm. compared to a literature value of 160° C. at 2 mm. (*6*).

Tetrahydrofurfuryl Esters as Vinyl Plasticizers. One of the most common methods of comparing plasticizers is to adjust the concentration of the plasticizer in the vinyl so that on application of a given load, the specimens will all be elongated to the same degree. This concentration is sometimes called the "efficiency percentage." All other physical tests are performed on the material plasticized at this efficiency percentage. For the tests in Table I a plasticizer level was chosen which gave 1000 p.s.i. at 100% elongation.

It is apparent from Table I that di(tetrahydrofurfuryl) sebacate is considerably more efficient than di(2-ethylhexyl) phthalate and the other plasticizers evaluated. If one tetrahydrofuran ring is replaced by an alkyl radical, such as decyl, efficiency drops off but the brittle point is lowered. Di(tetrahydrofurfuryl) phthalate, a three-ring structure, is less efficient than di(2-ethylhexyl) phthalate. In this case, replacement of a tetrahydrofuran ring with the decyl radical has little effect on efficiency but lowers the brittle point. The temperature at Young's modulus of 10,000 p.s.i. follows the same pattern as the brittle point with like variation in structure.

All of the dibasic acid esters containing the tetrahydrofuran ring have a lower volatile loss than the control, di(2-ethylhexyl) phthalate. Water extractions are comparable to the control. The oil extractions are comparable to the control (0.3% loss) with the exception of tetrahydrofurfuryl decyl sebacate and di(tetrahydrofurfuryl) phthalate, which give 1.0 and 0.7% loss, respectively.

Table I also shows it is possible to replace up to half of the di(2-ethylhexyl) phthalate in a vinyl with tetrahydrofurfuryl oleate or the tetrahydrofurfuryl tall oil fatty acid ester with no loss of efficiency. This substitution improves the brittle point and temperature at Young's modulus of 10,000 p.s.i. Oil extraction increases with this substitution from 0.3 to 3%.

The ultraviolet stability of specimens plasticized with equal parts of di(2-ethylhexyl) phthalate and tall oil ester is poor, as

Table I. Summary of Plasticization Tests of Poly(vinyl Chloride)[a]

Plasticizer	PHR[b]	Tensile Strength, P.S.I.	Elongation, %	Hardness[c]	Stiffening Temp.[d]	Brittle Point, °F.	Volatile Loss, %
Di(2-ethylhexyl) phthalate	62.5	2620	360	85	33	−58	4.5
Di(tetrahydrofurfuryl) sebacate	47.0	2700	300	85	33	−32	1.3
Tetrahydrofurfuryldecyl sebacate	62.0	2090	370	80	5	−77	3.7
Di(tetrahydrofurfuryl) phthalate	74.5	2730	340	83	35	13	3.2
Tetrahydrofurfuryldecyl phthalate	73.4	2270	380	75	20	−33	2.3
Tetrahydrofurfuryl oleate[e]	30.0	2413	350	83	22	−75	6.4
Tetrahydrofurfuryl tallate[e]	30.0	2313	340	83	22	−65	6.0

[a] Tests performed by Frederick S. Bacon Laboratories, 172 Pleasant St., Watertown, Mass. [b] Parts of plasticizer per 100 parts of resin. [c] Shore A Durometer. [d] Temperature at Young's modulus of 10,000 p.s.i. (±5° F.). [e] Evaluated as a secondary plasticizer, with 30 PHR of di(2-ethylhexyl) phthalate added also.

Table II. Properties of THFA Esters

Ester	Refractive Index n_D^{20}	Viscosity Cps. at 20° C.	Boiling Range °C. at 2 Mm.	Water Solubility at 25° C. G./100 Ml.	Saponification Equivalent		Sp. Gr. 20/20
					Theoret.	Obsd.	
Di(tetrahydrofurfuryl) adipate	1.4712	42.6	207–208	0.83	157	156	1.1236
Di(tetrahydrofurfuryl) azelate	1.4697	48.3	220–222	< 0.01	178	174	1.0823
Di(tetrahydrofurfuryl) diglycolate	1.4737	162.5	205–207	100.0	151	154	1.2049
Tetrahydrofurfuryl decyl diglycolate	1.4553	63.1	208–211	< 0.01	179	. . .	0.9947
Tetrahydrofurfuryl iso-octyl diglycolate	1.4533	45.4	195–196	< 0.01	165	173	1.0166
Di(tetrahydrofurfuryl) phthalate	1.5240	1028	226–227	0.13	167	170	1.2020
Tetrahydrofurfuryl decyl phthalate	1.4949	180.0	229–231	< 0.01	195	199	1.0275
Tetrahydrofurfuryl iso-octyl phthalate	1.4967	132.4	217–218	< 0.01	182	180	1.0433
Di(tetrahydrofurfuryl) sebacate	1.4696	52.2	233–235	0.03	185	184	1.0661
Tetrahydrofurfuryl decyl sebacate	1.4588	40.2	244–245	< 0.01	213	221	0.9551
Di(tetrahydrofurfuryl) succinate	1.4715	59.7	189–190	9.1	143	145	1.1632
Tetrahydrofurfuryl iso-octyl succinate	1.4507	19.2	184–185	< 0.01	157	164	0.9812
Tetrahydrofurfuryl tall oil fatty acid ester	1.4718	17.7	208–216	< 0.01	375	385	0.9363

plasticizer bleed-out is observed. This phenomenon has been considerably reduced by replacing less di(2-ethylhexyl) phthalate with tall oil ester, but it has not been eliminated. As much as 50% of the di(2-ethylhexyl) phthalate in a compound can be replaced with a mixture of equal parts of tetrahydrofurfuryl tall oil fatty acid ester and tetrahydrofurfuryl rosin ester without sacrifice in stability to ultraviolet light, and 20% can be replaced with tetrahydrofurfuryl oleate.

All the esters tested gave slight lacquer marring except tetrahydrofurfuryl decyl phthalate and tetrahydrofurfuryl decyl sebacate. Of these, the former gave moderate marring and the latter made the lacquer tacky.

Plasticizers for Cellulose Triacetate. This simple screening test was run to determine if any of the esters prepared might be of interest as plasticizers for cellulose triacetate. The particular grade of cellulose triacetate (acetyl value 43.5%) used has been regarded as difficult to plasticize.

The tetrahydrofuran ring strongly influenced swelling. All di(tetrahydrofurfuryl) esters swelled cellulose triacetate more than dibutyl phthalate. Replacement of one of the tetrahydrofuran rings with a higher molecular weight alcohol resulted in decreased swelling. As alcohol molecular weight increased, the swelling of the cellulose ester decreased. Thus, di(tetrahydrofurfuryl) phthalate swelled cellulose triacetate to a greater degree than tetrahydrofurfuryl iso-octyl phthalate which in turn swelled the material to a greater degree than tetrahydrofurfuryl decyl phthalate. This observation held true in the diglycolate series.

Another efficient swelling agent was 1,2,5-triacetoxypentane, which was synthesized from THFA and acetic anhydride via a ring opening reaction (*4*). Substitution of an oleate radical for one acetate radical resulted in decreased swelling of the cellulose triacetate.

Properties of the Esters. Acid numbers for all the esters except the diglycolate derivatives and the tallate were one or lower. The value for the tallate was 2.3. The diglycolic acid esters were found to be very easily saponified at room temperature in a slightly alkaline system—i.e., during titration to a phenolphthalein end point for acid number determinations. Until the ester was completely saponified, no stable phenolphthalein end point could be obtained. In Table II the boiling point and refractive index given for di(tetrahydrofurfuryl) diglycolate do not agree with those reported by Bruner (*2*).

The di(tetrahydrofurfuryl) diglycolate was found to be miscible with water in all proportions, but water solubility drops almost to zero by replacing one tetrahydrofurfuryl group with a long-chain alkyl radical. Water solubility of the succinates followed essentially the same pattern, but the di(tetrahydrofurfuryl)-substituted ester was not miscible in all ratios. The succinates were the lowest-boiling esters prepared.

As would be expected, the phthalates, azelates, and sebacates are all higher boiling and less water-soluble than the lower molecular weight esters. Di(tetrahydrofurfuryl) azelate, a 9 carbon acid, is less soluble than di(tetrahydrofurfuryl) sebacate, a 10 carbon acid. This unexpected difference may be a result of the odd carbon structure of the acid. The high viscosity of the di(tetrahydrofurfuryl) phthalate is a characteristic not shared by the other di(tetrahydrofurfuryl) esters.

SUMMARY

Di(tetrahydrofurfuryl) sebacate and tetrahydrofurfuryl decyl sebacate are more efficient plasticizers for poly(vinyl chloride) than di(2-ethylhexyl) phthalate. As much as 20% of di(2-ethylhexyl) phthalate can be replaced with tetrahydrofurfuryl oleate in a vinyl formulation without loss of efficiency or ultraviolet stability. Although the specimens lack complete ultraviolet stability, a tetrahydrofurfuryl–tall oil fatty acid ester replaces up to half of the di(2-ethylhexyl) phthalate in a vinyl formulation with no loss of efficiency. Di(tetrahydrofurfuryl) phthalate, di(tetrahydrofurfuryl) azelate, di(tetrahydrofurfuryl) adipate, di(tetrahydrofurfuryl) diglycolate, di(tetrahydrofurfuryl) succinate, and 1,2,5-triacetoxypentane appear to be better solvents than dibutyl phthalate in preliminary screening tests on cellulose triacetate.

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