esters contributed low-temp flexibility to the films with increases in secondary plasticizer resulting in a greater low-temp tolerance. In all cases, however, resistance to detergent, mineral oil and hexane extraction indicated superiority of phthalate esters.

Properties contributed by esters of various chain length monohydric alcohols and tall oil fatty acids are listed in Table V. Tests were made on films compounded with tallate esters as 20% replacements for DOP. Of those tested, all were compatible with the exception of the hexadecyl ester. This latter ester did flux and form film from which the plasticizer exuded very rapidly on aging at room temperature.

These data indicate very little change in tensile properties or low-temp flexibility with increase in chain length of alcohol group. Hexane extractibility of the DOP (control) was superior to the fatty esters.

Table VI and VII present data concerned with heat and light stability of the various plasticized sheets. The specimens (1.5 in. x 0.5 in.) were checked for heat oven stability with observations made at 15-min intervals to note color changes.

Data concerned with oven heat stability of the various tallate esters as secondary plasticizers indicate that no benefits are obtained from either increase in chain length of alcohol portion of the molecule or from amt. used as the replacement for primary phthalate plasticizers.

Data of a similar sort was obtained from plasticized sheets exposed to ultra violet light for periods up to 696 hours.

Most of the esters showed more resistance to spotting than the phthalate control, although in most cases exudation would be a problem if the tallate plasticized resins were exposed to sunlight for long periods of time. This effect was most noticeable above the 20% level.

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Tall Oil Fatty Acid-Formaldehyde Derivatives and Their Application as Vinyl Plasticizers

E. P. DiBELLA, RICHARD GREEN, W. M. KRAFT and R. T. GOTTESMAN,
Heyden Newport Chemical Corporation, Garfield, New Jersey

Abstract

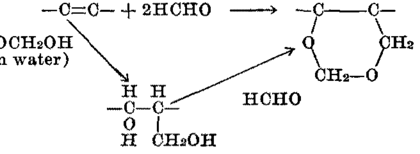
Acid-catalyzed condensations of tall oil fatty acid and related materials with formaldehyde, in the absence of a carboxylic acid solvent, led to acidic products, lower in unsaturation, but partially polymeric due to formation of interester linkages. Hydrolysis of these linkages furnished products lower in mol wt but higher in free hydroxyl content. Some modified esters of these materials were evaluated as primary plasticizers for polyvinyl chloride by comparison with dioctyl phthalate and, when applicable, to Monsanto S409.

In general, those plasticizer candidates in which free hydroxyl contents were lowered by acetylation exhibited a good overall balance of physical and permanence properties but possessed poor heat stability and borderline compatibility.

A preliminary study on the acid-catalyzed reaction of ethyl tallate with anhydrous formaldehyde gave promise that an improved alternate route to fatty acid-formaldehyde esters could be developed.

Introduction

The acid-catalyzed addition of anhydrous or aqueous formaldehyde to simple olefins, i.e., the Prins reaction, ordinarily yields 1,3-dioxanes (1).



In the presence of a carboxylic acid solvent, e.g., acetic acid, the diester of the 1,3-glycol intermediate is the major product

$$-\overset{H}{C}=\overset{H}{C}- + 2HCHO \xrightarrow[\text{excess}]{CH_3COOH} -\overset{H}{C}(-O-\overset{O}{\overset{\|}{C}}CH_3)-\overset{H}{C}(-CH_2-O\overset{O}{\overset{\|}{C}}CH_3)-$$

Our interest in the utilization of tall oil fatty acid (TOFA) recently prompted us to study TOFA-formaldehyde reaction products and the possible application of esters of these materials as plasticizers for polyvinyl chloride. Surprisingly, few studies on the reaction of long chain unsaturated fatty acids with formaldehyde have been reported (2,4–6,8,9) and only one (6) suggested plasticizer utility.

Experimental

Condensation of Formaldehyde with Unsaturated Fatty Acids. On the basis of preliminary information obtained elsewhere (7), we have found that 75% H_2SO_4 is an effective medium for attaining near complete interaction of TOFA and paraformaldehyde. The following procedure was used:

In a three-liter, three-necked flask, equipped with stirrer, thermometer, dropping funnel and reflux condenser, was placed a mixture of 774 g of 75% H_2SO_4 and 405 g (ca. 12.9 moles HCHO) technical paraformaldehyde, 95–96% assay. Over two hr at 50–60C, there was added 858 g (3.0 moles —COOH, 4.3 moles —C=C—) TOFA [acid value (A.V.), 194.4; sap. value (S.V.), 197.8; iodine value (I.V.), 127.1; hydroxyl value (OH.V.), 0.08]. External

TABLE I

Fatty Acid-Formaldehyde Condensates (in 75% H_2SO_4)

Condensate	A.V.	S.V.	I.V.	OH.V.	Mol wt
A. Calculated values[a]					
TOFA	149.8[b]	149.8	0.0	0.0	374
	157.1[c]	157.1	0.0	13.7	357
Aromatized TOFA-formaldehyde	156.1[b]	156.1	0.0	0.0	359
	160.1[c]	160.1	0.0	7.3	350
Oleic-formaldehyde	164.0[b]	164.0	0.0	0.0	342
	170.1[c]	170.1	0.0	10.3	330
Linoleic-formaldehyde	140.2[b]	140.2	0.0	0.0	400
	149.1[c]	149.1	0.0	18.1	376
B. Found[b]					
TOFA-formaldehyde monomeric	138.7	149.8	4.6	2.5	400
TOFA-formaldehyde polymeric	101.9	159.2	4.0	0.6	880
Aromatized TOFA-formaldehyde monomeric	142.9	159.3	3.7	4.3	437
Aromatized TOFA-formaldehyde polymeric	105.8	167.3	4.0	1.3	562
Oleic-formaldehyde polymeric	128.9	170.0	2.7	1.5	410
Linoleic-formaldehyde polymeric	107.2	165.9	4.1	0.7	552

[a] Calc'd for saturated monomeric derivatives from acid and I.V. of TOFA.
[b] Calc'd for 1,3-dioxane derivative.
[c] Calc'd for methylene glycol adduct.
[d] Approx mol wt by osmometry.

cooling was required throughout the addition. The mixture was then stirred at 50–60C for four hr cooled to room temp and extracted with 1500 g benzene.

The organic layer was filtered, washed free of strong acidity with water and stripped of solvent to obtain 1070 g of a dark viscous oil.

The analytical values (Table I) indicated ca. 96% saturation of double bonds as well as participation of at least 36% of the carboxyl groups in the formation of polymeric interester linkages (difference in acid and saponification numbers and higher approx mol wt value). Thus, even in the absence of a high M excess of carboxylic acid solvent, significant though incomplete carboxyl interaction with formaldehyde or the intermediate glycol did occur to yield polymeric interester linkages and free hydroxyl groups. This "polymeric" TOFA-formaldehyde condensate was saponified as follows:

One part of the "polymeric" condensate was stirred at 90–100C with 1.7 parts of 20% aqueous sodium hydroxide solution for two hr. The resulting mixture was cooled to room temp, acidified with dilute H_2SO_4, extracted with benzene and worked up as in the previous example to obtain 0.96 parts of a dark but less viscous material.

The analytical data (Table I) for this "monomeric" product indicate the following approx disposition of the original double bonds of TOFA: 1) 70% saturation with 1,3-dioxane rings; 2) 19% saturation with the elements of methylene glycol; 3) 7% saturation with hydroxyl groups and residual interester linkages; and 4) 4% unreacted.

Reaction with paraformaldehyde in 75% H_2SO_4 was also applied to oleic acid, linoleic acid and "aromatized" TOFA. The last raw material (A.V., 178.4; I.V., 60.6) was obtained via an aromatization-hydrogen transfer reaction by treating TOFA at 270C with palladium-on-carbon according to the description of Floyd and co-workers (3). "Polymeric" condensates, similar to that formed with TOFA were obtained, and with the aromatized TOFA a monomeric product was also prepared. The analytical data for these related fatty acid derivatives are also summarized in Table I.

It was also possible to use boron fluoride at a level of 0.21 moles/mole $-C{=}C-$ as a catalyst for the condensation of unsaturated fatty acids with formaldehyde. At 50–60C similar polymeric products were obtained but the degrees of double bond saturation were *only 65–70%.*

Formation of Esters and Plasticizer Evaluations. In the early stages of our work when we were interested in delineating the gross structural requirements of a vinyl plasticizer based on esters of TOFA-formaldehyde condensates, the boron fluoride-catalyzed reaction was employed as a route to methyl esters of polymeric type products from oleic, linoleic and TOFA. The esters were prepared by adding excess methanol to the final reaction mixture (the boron fluoride served also as the esterification catalyst) and refluxing for eight hr, at 67–70C. After distillation of excess methanol, the product was dissolved in heptane and washed free of acidity with water and sodium carbonate solution. The heptane was distilled.

Each of the resulting three crude methyl esters (yellow, somewhat viscous oils) was then submitted to the following classical procedures to obtain the corresponding modified esters: 1) hydrogenation at 40–50 psi (Parr-shaker) at 25–30C over platinum oxide to lower residual unsaturation; 2) acetylation with excess acetic anhydride at 140–145C to remove free hydroxyl; and 3) hydrogenation of the acetylated derivative. The results are summarized in Table II.

These twelve compositions as well as those described below were evaluated as plasticizers in polyvinyl chloride test sheets formulated as follows:

	parts
Geon 101EP (vinyl chloride polymer)	100
Plasticizer candidate	45
Paraplex G-62 (an epoxidized soybean oil)	5

TABLE II

Methyl Esters of "Polymeric" Fatty Acid-Formaldehyde Condensates (BF_3 Catalyzed) with Variation in Unsaturation and Hydroxyl Contents

Methyl ester	Reaction	S.V.	A.V.	I.V.	OH.V.
Oleic-formaldehyde	none	164.8	1.2	17.8	1.5
Oleic-formaldehyde	hydrogenation	164.1	1.4	3.4	1.4
Oleic-formaldehyde	acetylation	204.1	3.6	17.3	<0.1
Oleic-formaldehyde	acetylation + hydrogenation	202.9	2.7	4.0	<0.1
Linoleic-formaldehyde	none	159.3	6.3	35.6	1.4
Linoleic-formaldehyde	hydrogenation	160.8	7.3	10.5	1.3
Linoleic-formaldehyde	acetylation	205.7	2.2	33.4	<0.1
Linoleic-formaldehyde	acetylation + hydrogenation	204.9	3.9	9.5	<0.1
TOFA-formaldehyde	none	145.4	3.1	37.7	1.2
TOFA-formaldehyde	hydrogenation	146.7	3.6	11.3	1.5
TOFA-formaldehyde	acetylation	195.4	4.2	38.1	<0.1
TOFA-formaldehyde	acetylation + hydrogenation	194.9	3.9	9.5	<0.1

TABLE III

Comparison of Plasticizing Efficiency of Modified Methyl Esters of FA-Formaldehyde Condensates

	Oleic-formaldehyde	Linoleic-formaldehyde		TOFA-formaldehyde		DOP
	Acetylation	Acetylation	Acetylation + H_2	Acetylation	Acetylation + H_2	
Tensile psi	2990	2885	2770	2843	3070	2680
100% Modulus	1490	1470	1430	1530	1950	1400
% Elongation	375	385	365	350	350	345
Hardness (15 sec)	74	70	75	73	88	77
Brittle pt., °C	−32	−28	−19	−22	−33	−31
Volatility (11 days)	5.7	4.7	5.1	4.4	5.2	3.30
Hexane ext. (3 days)	15.1	11.3	11.9	12.6	11.4	13.0
Mineral oil ext. (10 days)	6.97	4.94	5.41	1.94	2.30	2.48
Soapy water ext. (7 days)	2.5	3.82	4.17	6.6	7.4	0.68
Heat stability, min	60	60	60	60	60	120
Light stability, hr	426	138	420	138	138	>500

Nuostabe VI34 barium-cadmium stabilizer)	2
Stearic acid	0.5

The sheet processing and tests for evaluating the pasticizing efficiency of each candidate were based upon the general procedures described in the 1955 Book of ASTM Standards, Part 6. Comparison was made to dioctyl phthalate (DOP), a commercial standard, and, when applicable, to Monsanto S409, a typical polymeric plasticizer.

Seven of these materials, viz., the three untreated esters, their hydrogenated derivatives as well as the hydrogenated-acetylated oleic ester were not sufficiently compatible to warrant further evaluation. Data on the other materials are presented in Table III.

These results indicated a) acetylation of free hydroxyl improved compatibility, b) compatibility is not improved by reduction of residual unsaturation by hydrogenation, and c) the corresponding formaldehyde derivatives of the major components (oleic and linoleic acids) of TOFA do not reveal differences of a magnitude which would suggest a need for the prior separation of one of these.

Besides other shortcomings, the methyl esters appeared too volatile for practical utility. Therefore, a number of less volatile esters in which residual hydroxyl contents were lowered by acetylation were prepared. These included derivatives of both polymeric and monomeric condensates, and three of the latter type were distilled materials. The use of boron fluoride as an esterification catalyst was carried out in a manner similar to that described above for the methyl esters. Where H_2SO_4 was employed as the catalyst, lower yields of crude products resulted because of the formation of some heptane-insoluble gums which were discarded.

Tetrahydrofurfuryl (THF) esters were prepared in the absence of catalyst by heating the formaldehyde condensates with excess tetrahydrofurfuryl alcohol to a point (ca. 180C) where the distillate from the mixture contained no water.

The crude esters were dark, somewhat viscous oils while the distilled materials were yellow and less viscous. These products are listed in Table IV.

Plasticizer evaluation of these esters indicated promise of utility as primary plasticizers for vinyl chloride polymers. As shown in Table V, they exhibit good overall balance of physical and permanence properties, but possesses poor heat stability and borderline compatibility (as evidenced by partial exudation during light stability evaluation).

The distilled acetylated propyl ester of the monomeric TOFA-formaldehyde condensate appeared to be the best fatty ester. By comparison with DOP, this had only a poor soapy water extraction, heat stability and lasted only 396 hr in the light stability test before tack development. The poor heat stability is, of course, the most serious deficiency, but the borderline compatibility as indicated by tack development could be troublesome in long term usage. However, this material probably represents the best compromise between lowered volatility and compatibility.

The tetrahydrofurfuryl esters were intended as potentially better solvating materials and were compared to Monsanto S409, a polymeric plasticizer, as well as DOP. But this ester proved to be relatively too volatile and impermanent for further consideration.

Attempts to Condense Ethyl Tallate with Formaldehyde. The above evaluation data, while not entirely satisfactory, led us to initiate studies on a possible alternate synthetic route to esters of TOFA-formaldehyde, viz. the direct addition of anhydrous formaldehyde (trioxane) to tallate esters. It was expected that this approach would preclude participation of carboxyl groups in the condensation, thereby circumventing the formation of polymeric interester linkages and free

TABLE IV

Acetylated Esters of FA-Formaldehyde Condensates

Ester	Condensate used as RM	Catalysts used		BP °C (mmHg)	Approx % yield	S.V.	A.V.	OH.V.	I.V.	Approx %saturation —C=C—
		For prep. of condensate	For esterification							
From polymeric condensates										
Methyl	TOFA-form.	75% H_2SO_4	H_2SO_4	....	50	225.6	1.1	neg.	4.3	95
Ethyl	TOFA-form.	BF_3	BF_3	....	93	189.7	2.5	neg.	26.7	73
Ethyl	TOFA-form.	75% H_2SO_4	H_2SO_4	....	56	196.1	2.1	neg.	5.9	94
Isopropyl	TOFA-form.	BF_3	BF_3	....	90	181.6	2.8	neg.	30.0	68
n-Propyl	TOFA-form.	BF_3	BF_3	....	94	181.0	1.6	neg.	37.5	59
n-Propyl	TOFA-form.	75% H_2SO_4	H_2SO_4	....	52	206.5	2.7	neg.	4.7	95
THF	TOFA-form.	75% H_2SO_4	None	....	46	149.2	2.0	0.23	8.1	91
From monomeric condensates										
Ethyl	Aromatized TOFA-form.	75% H_2SO_4	H_2SO_4	192–260 (1.2 mm)	52	232.6	2.8	0.31	0.3	99
n-Propyl	TOFA-form.	75% H_2SO_4	H_2SO_4	Crude product	92	213.0	2.0	neg.	7.4	93
n-Propyl	TOFA-form.	75% H_2SO_4	H_2SO_4	Flash dist. 285–300 (1.0 mm)	65	214.9	2.0	neg.	7.8	92
THF	TOFA-form.	75% H_2SO_4	None	230–280 (1.1 mm)	26	166.3	6.8	0.22	13.7	85

TABLE V

Comparison of Plasticizing Efficiency of Selected Acetylated TOFA-Formaldehyde Esters

	Tensile, psi	100% Modulus	% Elongation	Hardness (15 sec)	Brittle pt., °C	Volatility (11 days)	Hexane ext. (3 days)	Mineral oil ext. (10 days)	Soapy water ext. (7 days)	Heat stability, min	Light stability, hr
Esters of polymeric condensates (degree of —C=C—saturation)											
Methyl TOFA-formaldehyde (95%)	3190	1930	340	76	−10	2.3	4.65	0.61	2.0	60	456
Ethyl TOFA-formaldehyde (89%)	2610	1200	360	84	−28	3.3	11.2	2.2	2.6	60	144
Ethyl TOFA-formaldehyde (95%)	3150	1930	360	81	−10	1.7	5.75	0.85	1.4	60	340
Isopropyl TOFA-formaldehyde (69%)	2730	1750	340	91	−31	3.0	17.2	4.1	4.1	60	......
n-Propyl TOFA-formaldehyde (69%)	2085	842	370	84	−32	2.8	14.0	3.3	1.9	90	144
n-Propyl TOFA-formaldehyde (95%)	3010	1970	275	80	−9	1.1	5.60	0.52	1.4	90	483
THF TOFA-formaldehyde (90%)	3070	2050	280	81	−4	1.1	1.17	0.39	2.3	90	166
Esters of monomeric condensates (degree of —C=C—saturation)											
Ethyl aromatized TOFA-formaldehyde (99%)	3040	1415	360	66	−30	5.1	13.1	4.4	2.4	90	......
n-Propyl TOFA-formaldehyde (93%)[a]	3400	1970	345	78	−12	1.8	4.15	2.3	0.6	60	......
n-Propyl TOFA-formaldehyde (92%)	2905	1475	340	74	−24	2.3	6.60	1.1	2.3	90	396
THF TOFA-formaldehyde (85%)	3220	1580	350	78	−42	3.3	12.75	7.1	3.0	90	117
DOP	2680	1400	345	77	−31	3.30	13.0	2.48	0.68	120	>500
S409	3020	1901	340	86	−13	0.64	4.9	2.90	0.90		>600

[a] Crude prod.

hydroxyl groups and leading exclusively to 1,3-dioxane ring formation.

In the best experiment, the ethyl ester of TOFA (bp$_{0.4}$ 152–157C; S.V., 178.2; A.V., 1.8; I.V., 112.2) was stirred for eight hr at 70C with 0.33 part trioxane and 0.15 part anhydrous ferric chloride. The reaction mixture was dissolved in heptane, filtered and washed with water to remove ferric ion and excess formaldehyde. The heptane was distilled to obtain 1.10 parts of a yellow oil.

Anal. Calc'd for addn. of 2 HCHO to —C=C—: S.V., 153.8; A.V., 0.0; I.V., 0.0; OH.V., 0.0. Found: S.V., 173.8; A.V., 10.3; I.V., 38.9; OH.V., 0.19.

The data on this crude product indicate ca. 61% saturation of double bonds with only ca. 3% conversion to hydroxyl-containing derivatives and 5% cleavage of ester groups. The active hydrogens required for these side reactions were derived, presumably, from the water wash.

The similar use of 100% H_2SO_4 and boron fluoride as condensation catalysts instead of ferric chloride were less satisfactory. The degrees of double bond saturation were lower and the side reactions were not avoided. Ferric chloride, or possibly other weak Lewis acids, would thus appear to be the catalysts of choice for future development work along this line.

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A Study of the Influence of Storing Wood on the Yield and Quality of Tall Oil

WALTER COWART and D. C. TATE, Champion Papers, Inc., Canton, North Carolina, and JOHN CHURCHILL, Champion Papers, Inc., Hamilton Ohio

Abstract

In 12 weeks of storage time pine roundwood lost approximately 11% in tall oil yield, while for the same length of time purchased slabwood chips (pine) lost 64%. Most of the loss in yield occurred within six weeks. The purchased chips lost more tall oil yield in one week than the roundwood in 12 weeks.

The loss in yield from the roundwood was due entirely to the loss in yield of fatty acids. The loss in yield in the purchased slabwood chips was due predominantly to the loss in yield in fatty acids; however, there was, in addition, a small loss in resin acids, and a very small loss in unsaponifiables.

As for tall oil quality, by the end of 12 weeks of storage the acid number of tall oil from both roundwood and purchased chips had dropped below 160.

In correlating the yield of tall oil from the wood extractions with the yield of tall oil from the black liquor from digester cooks, it appears that on the average about 80% to 88% of the extracted tall oil can be found in the black liquor.

Introduction

IN AN EFFORT to insure maximum possible tall oil production, a laboratory fact-finding program was initiated to secure more information and data concerning the fluctuations in tall oil production and the reasons behind these fluctuations. The study of age vs. tall oil yield for roundwood and purchased slabwood chips was a part of this overall program. Other aspects of this program, to be covered in additional reports, are the solvent extractions of weekly composites of wood to the digesters, the weekly determinations of tall oil potential to the smelters and the waste treatment plant, and the study of the effect of mixing hardwood and pine liquors on tall oil recoveries.

It is important to have the above data in order to determine how much tall oil is available, how