the recirculation tank is drawn off from a point below the surface and recycled through the degassing tank.

The self-opening type of centrifuge, with its complete bowl opening feature, is not influenced by the fibrous material in the feed and can be operated for long periods of time without stopping for cleaning.

Conclusions

This modern continuous acidulation process discharges only two streams, crude oil and the spent acid mixture, which is returned to the mill. For this reason, it is quite simple to calculate the yields of the plant.

The spent acid mixture produced from the average plant amounts to about 1.8 times the tall oil output, by volume. The average spent acid specific gravity is 1.10 to 1.18.

The oil content of the spent acid stream is below 2%, usually between 1 and 2%. This oil is not lost since it is returned to the chemical recovery system and recycled in the process until it again returns to the splitting process.

The yield of crude tall oil is from 98 to 99% of the oil available in the feed.

The quality of the crude tall oil produced by this continuous acidulation system is excellent.

There are, of course, some variations in the tall oil, depending upon the type of wood used, the section of the country from which it comes, climatic conditions, etc.

An average plant utilizing this method of recovery can be expected to produce a crude tall oil with a typical analysis as indicated in Table II and having the following amounts of major impurities: ash content, 0.02 to 0.03%; residual lignin content, 0.2 to 0.06%; free mineral acid, 0.009%.

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Plasticizing Properties of Esters of Monohydric Alcohols and Tall Oil Fatty Acids

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Abstract

Tall oil fatty acid esters prepared as intermediates in an epoxy ester plasticizer program were similarly evaluated as low-temp plasticizers in polyvinyl chloride resins. Performance characteristics as primary and secondary plasticizers in polyvinyl sheeting and extruded tapes were determined on esters from methyl to heptadecyl tallate.

Results indicate that these materials impart low-temp properties which would make them of value as low-cost plasticizers in extruded and molded products where light and heat stability are not primary factors.

Introduction

SIMPLE ALKYL ESTERS of saturated fatty acids exhibit a relatively low degree of compatibility and solvency with most polymeric materials. This is said to be due to the low ratio of oxygen to hydrocarbon units of the aliphatic chain. In polyvinyl chloride where these esters are partially compatible, they find specialty uses as secondary plasticizers. Mixed octyl esters of fatty acids have also proved useful in providing low-temp flexibility as primary plasticizers for chloroprene and other synthetic rubbers. The above is also true of the unsaturated fatty alkyl esters where their low volatility, light color, mild odor and low toxicity permits their usage as low-temp plasticizers in many polymeric materials (1).

TABLE I

Evaluation of Tall Oil Esters as Low-Temp Plasticizers in Polyvinyl Chloride Tapes

	Ester					
% DOP Replaced	DOP Control	2-Ethyl hexyl	Iso octyl	Tetra hydro furfuryl		
Property	0	25	25	5	20	40
Ultimate tensile strength psi	3140	3000	3060	3090	3000	3250
Ultimate elongation	350	330	370	370	350	355
100% Secant mod.	1560	1550	1570	1320	1315	1440
Volatility (24 hr at 90C) loss %	3.7	1.9	2.0	2.3	3.0	2.2
Extraction soap soln. loss %	0.2	0.2	0.2	0.4	0.4	0.5
Gasoline 10 hr @25C loss %	5.5	8.3	6.6	5.1	7.6	7.0
Low-temp properties Clash-Berg T_F 135,000 —°C.	—21	—32	—31	—22	—26	—32

While as stated above that long chain aliphatic compounds generally exhert a flexibilizing effect upon materials with which they are compatible, introduction of a polar functional group was found to be necessary to insure this compatibility.

The monumental work of Swern and co-workers (2–5) at the Eastern Regional Research Laboratory has been greatly responsible for the tremendous usage of fatty epoxy derivatives as plasticizer-stabilizer components of polyvinyl chloride film.

Initial investigations into the introduction of oxirane groups at the unsaturated bonds of the fatty acid chains of soybean oil resulted in materials which imparted excellent low-temp plasticizing properties to polyvinyl resins. The interest and research of commerical producers of hydrogen peroxide resulted in commercially feasible processes for the manufacture of economically priced epoxy derivatives (6–8).

After the initial impact of these investigations, attention was directed to the possible functional performance of fatty acid epoxy esters of monohydric alcohols. One of the most prevelent sources of high purity fatty acids of the semi-drying type is by fractional distillation of tall oil. Tall oil fatty acid esters of essentially all the commercially available monohydric alcohols have been prepared and in most instances converted to the epoxy derivative for testing in these programs.

During our investigation of the plasticizer-stabilizer properties of a variety of tall oil monoalcohol epoxy esters, it was decided to subject a number of the ester

TABLE II

Evaluation of Tallate Tetrahydrofurfuryl Esters as Secondary Plasticizers in Polyvinyl Film

% DOP Replaced	5	20	50
Property			
Original			
Ultimate tensile strength psi	3122	3184	3297
100% Modulus	1673	1580	1600
Ultimate elongation	383	387	413
7 Days aging @ 100C			
Ultimate tensile strength psi	3260	3032	3736
100% Modulus	3240	2940	1960
Ultimate elongation	130	160	120
Volatility			
Loss carbon black			
24 Hr @ 70C	.....	.....	2.2
Air 7 days @ 100C	10.5	7.8	9.7
Extraction			
24 Hr @ 70C			
Water	+0.7	+0.7	+0.4
Soapy water	1.5	1.5	7.4
Mineral oil	6.1	8.2	11.8
Hexane 1 hr @ 73F	4.0	14.0	12.7
Low-temp properties			
Clash-Berg			
T_F °C	−20	−26	−37
T_4 °C	+11	+7.0	+4.0

TABLE III

Plasticizing Characteristics of Methyl Tallate Esters with DOP in Polyvinyl Films

% As secondary	0	5	20	50
Property				
Original				
Ultimate tensile strength psi	3174	3202	3139	3226
100% Modulus	1855	1840	1547	1640
Ultimate elongation	345	333	380	405
7 Days aging @ 100C				
Ultimate tensile strength psi	3184	3036	4144	6000
100% Modulus	2730	3010	.....	.....
Ultimate elongation	265	185	0	0
Volatility				
Loss carbon black				
24 Hr @ 70C	0.7	1.7	3.1	7.1
Air 7 days @ 100C	6.8	9.5	13.9	16.9
Extraction				
24 Hr @ 70C				
Water	0.6	0.6	0.7	0.5
Soapy water	1.1	2.0	2.8	7.2
Mineral oil	7.8	9.6	9.2	9.8
Hexane 1 hr @ 73F	3.6	10.5	7.7	17.3
Low-temp properties				
Clash-Berg				
T_F °C	−19	−19	−30	−38
T_4 °C	+10	+10.5	+7.0	+2.5

intermediate products to a similar testing program. Calculations also indicated that elimination of the epoxidation step would result in an appreciable reduction in product cost and place most of the tall oil fatty acid esters in a competitive price range with phthalate esters, presently used in typical formulations.

In attempting this supplemental investigation, it was realized that the straight ester could not be expected to perform as well as it epoxy counterpart. Our main concern was with low-temp plasticizing and compatibility properties which might be attributed to a secondary plasticizer. Light and heat color stability were not considered of importance where the polyvinyl film was used in low-temp insulation such as refrigerator gaskets, etc.

This investigation encompassed testing of a variety of tall oil esters as low-temp plasticizers in both milled sheets and polyvinyl chloride extruded tapes.

Experimental

Tall oil fatty acid esters of commercially available monohydric alcohols were prepared as previously described (9). Tall oil fatty acids used where highly purified fractions containing 0.5% or less rosin acids.

Esterifications using acid catalysts were run until acid values were five or lower. The ester was water washed and finally refined with 8% alkali solution to remove unreacted rosin and fatty acids. The resultant ester was heated under vacuum to a temp approximating the atmospheric boiling range of the alcohol in order to insure complete removal of this diluent.

Sheets or films used in the various testing procedures were fabricated as follows:

Geon 101 *	100 Parts
Plasticizer **	50 Parts
Mark M ***	1.0 Parts
Stearic acid	0.25 Parts

* B. F. Goodrich Chemical Co.

** Ester substituted in formula for 5, 10, 25 parts DOP or DIOP.

*** Argus Chemical Co.

Materials were mixed together and then compounded for seven min at 300F on a two-roll Thropp Mill (3 in. x 8 in. rolls). Observations were made as to flux time of the components, clearity and color of sheet. The formed sheet was placed in a stainless steel mold, conditioned for 10 min at 320F and then compressed under a pressure of 1000 lb/sq in. for an additional 10 min. Specimens were cut from these sheets for the various tensile strength measurements. Films used in volatility and extraction tests were also made by hydraulic pressing to the desired thickness of 0.025 in.

Testing of all specimens was done in accordance with ASTM Standards on Plastics as described in the following methods:

TEST METHODS—POLYVINYL CHLORIDE RESINS

Tensile strength 100% Modulus Ultimate elongation	Scott Tester, Model L-5, 75 lb capacity, 20 in./min speed, ASTM D-412, Die D specimen.
Torsional stiffness	Tinius Olsen Torsion Stiffness Tester (ASTM 1043). T_f is centigrade temp at which modulus of elasticity is 135,000 psi. T_4 is centigrade temp at which modulus of elasticity is 10,000 psi.
Volatile loss (air)	Cell type oven—100C for 7 days. Percentage loss based on original wt.
Volatile loss (carbon black)	Loss when specimen 2 in. diam x .025 in. is heated in activated carbon at 70C for 24 hr (ASTM 1203). Percentage loss based on original wt.
Water extraction Soapy water extraction (1%) Mineral oil extraction	Specimen 2 in. diam x .025 in. immersed in liquid at 70C for 24 hr. Percentage gain or loss in wt based on original wt.
Hexane extraction	Specimen 2 in. diam x .025 in. immersed at 73F for 1 hr. Percentage loss based on original wt.
Oven heat stability	Specimens 1.5 in. x 0.5 in. stapled to cardboard faced with aluminum foil and placed in oven at 350F. Specimens observed at 15-min intervals for color degradation.
Migration	Specimens of 1.5 x 0.5 x .060 in. bent double and clamped between steel bars to form fold of three-eights in. diam extending one-half in. out from bars. Assembly held at 70C for 24 hr and inside of fold observed for any greasiness.
Light stability	Specimens of 2.0 x 0.5 x .060 in. exposed to a carbon arc UV light source in an Atlas Electric Devices' Fadeometer, Model FDA-R. Specimens examined at 24 hr intervals for color degradation and plasticizer migration.

Discussion

Data of Table I are those obtained in a testing program by a Consultant Laboratory (10).

Test tapes were prepared by extruding the polyvinyl-plasticizer mixture through a strip die with a slit opening of 1 in. x 0.025 in. Excellent extrusion was obtained on all samples. All formulations yielded crystal clear extrudates thus demonstrating adequate compatibility between the components. This also was confirmed by lack of plasticizer exudation from the tape.

Table II contains data showing the effects of various

TABLE IV

Evaluation of Tallate Esters as Low-Temp Secondary Plasticizers in Polyvinyl Film

% As secondary	Ester								
	Hexyl			2-Ethyl hexyl			Iso octyl		
	5	20	30	5	20	30	5	20	30
Properties									
Ultimate tensile strength psi	3226	3324	2936	3074	3168	3140	3231	3190	3104
100% Modulus	1640	1735	1767	1753	1885	1807	1735	1820	1930
Ultimate elongation	405	395	330	373	318	370	385	333	325
After 7 days aging at 100C									
Ultimate tensile strength psi	3136	3104	2440	2436	3044	2756	3164	2872	2664
100% Modulus	2590	2720	2460	2800	2920	2670	2690	2780	2600
Ultimate elongation	270	260	170	200	170	150	285	210	130
Retained tensile strength %	103	93.4	83.1	95.5	96.1	87.8	97.9	90.0	85.8
Retained elongation %	79.9	65.8	51.5	53.6	53.5	40.5	74.0	63.0	40.0
Volatility									
Loss carbon black									
24 Hr @ 70C	0.8	0.8	.....	0.6	0.6	.....	0.6	0.7	.....
Air 7 days @ 100C	8.0	9.8	9.7	9.0	9.3	8.0	7.8	10.1	8.2
Extraction									
24 Hr @ 70C									
H_2O	+.8	+.8	+0.9	+.8	+.8	+1.6	+.8	+.8	+.8
Soap solution	1.2	1.3	1.7	1.2	1.5	1.3	1.1	1.0	1.6
Mineral oil	6.6	9.6	11.2	6.9	6.7	11.8	6.3	7.6	11.2
Hexane 1 hr @ 73C	4.0	13.4	20.1	6.0	6.8	19.4	5.2	12.1	20.9
Low-temp properties									
Clash-Berg									
T_F °C	−22	−23	−36	−19.5	−24	−34.5	−22.5	−30	−34
T_4 °C	+10	+10	+10	+10	+11	+12.5	+10	+11	+14

TABLE V

Plasticizer Evaluation: Comparison of Effect of Chain Length of Tallate Esters

Property	DOP	Methyl	Hexyl	2-Ethyl hexyl	Decyl	Tri decyl
Original						
Ultimate tensile strength psi	3174	3139	3324	3068	3093	3083
100% Modulus	1855	1547	1735	1810	1687	1720
Ultimate elongation	345	380	395	353	383	383
After 7 days aging at 100C						
Ultimate tensile strength psi	3184	4144	3104	2976	3050	2752
100% Modulus	2730	.....	2720	3000	2630	2480
Ultimate elongation	265	0	260	100	260	200
Volatility						
Loss carbon black						
24 Hr @ 70C	0.7	3.1	0.8	0.8	.....	.....
Air 7 days @ 100C	6.8	13.9	9.8	9.8	8.9	7.8
Extraction						
24 Hr @ 70C						
H_2O	0.6	+0.7	+0.8	+1.0	+0.6	+0.7
Soap solution	1.1	2.8	1.3	1.5	1.9	1.5
Mineral oil	7.8	9.2	9.6	8.5	7.6	8.2
Hexane 1 hr @ 73C	3.6	7.7	13.4	14.0	8.9	14.0
Low-temp properties						
Clash-Berg						
T_F °C	−19	−30.0	−23	−29.5	−30	−29
T_4 °C	+10	+7.0	+10	+11.5	+11.5	+13.5

percentages of tetrahydrofurfuryl tallate when used as a secondary plasticizer to replace DOP. Measurements were made on milled and pressed sheets and films.

These data indicate relatively little change in tensile strength with increase in secondary plasticizer. A pronounced change in low-temp flexibility is noted with increase in percentage of tallate ester. Adverse effects in volatility and mineral oil solubility implies limited uses for this ester in formulations requiring more than 10% replacement of DOP.

Tables III and IV present similar sets of data showing results obtained from substitution of various percentages of a number of tallate esters as replacement for DOP in standard P.V.C. sheets and films.

Here again it will be noted that tensile properties of films plasticized with higher esters were uniformly good both on initial testing and after aging. While similar properties of intial strength were obtained with methyl tallates, aging had adverse effects. All of the

TABLE VI

Tallate Ester Plasticized Films: Oven Heat Stability @ 350C

Ester	% As secondary	Min to reach color code[a]				
		1	2	3	4	5
Methyl	5	....	15	30	45	60
Methyl	20	....	15	30	45	60
Methyl	50	15	....	30	60	75
Hexyl	5	0	15	30	45	75
Hexyl	10	0	15	30	45	75
Ethyl hexyl	5	0	15	30	45	60
Ethyl hexyl	10	0	15	....	30	60
Ethyl hexyl	20	0	15	30	45	60
Iso octyl	5	0	30	....	45	60
Iso octyl	20	0	15	30	45	60
Decyl	5	....	15	30	45	60
Decyl	20	....	15	30	45	60
Tri decyl	5	....	15	30	45	60
Tri decyl	20	15	....	30	45	60
Tetra hydro furfuryl	5	15	30	45	60	75
Tetra hydro furfuryl	50	15	....	30	45	75
Control	0	0	75	....	95	110

[a] Color code: 1—pale yellow; 2—yellow; 3—orange; 4—dark orange; 5—black.

TABLE VII

Light Stability—Tallate Ester Plasticizers Polyvinyl Resins

Ester type	% Of total plasticizers	Hours to code[a]			Remarks[b]
		1	2	3	
Methyl	5	24	×		
Methyl	20	648	×		
Methyl	30		96	×	G-672
Hexyl	5	24	×		S-600
Hexyl	20	24	×		G-480
Hexyl	30		×		G-240
Ethyl hexyl	5	24	600	×	S-336
Ethyl hexyl	10	24	×		G-480
Ethyl hexyl	30		×		G-120
Iso octyl	5	24	×		G-480
Iso octyl	20	24	72	×	G-288
Iso octyl	30		×		G- 96
Decyl	5	24	672	×	S-480
Decyl	20	384	×		G-384
Decyl	30		×		G- 72
Tri decyl	5	24	480	×	S-408
Tri decyl	20	408	×		G-288
Hexa decyl	30	120	×		G- 72
Tetra hydro furfuryl	5	24	×		G-384
Tetra hydro furfuryl	20	672	×		G-264
Control DIOP	100	480	×		S-192

×—Greater than 696 hr.
[a] Color code: 1—pale yellow; 2—yellow; 3—orange.
[b] G—Greasiness (exudation); S—spotting.

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

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Abstract

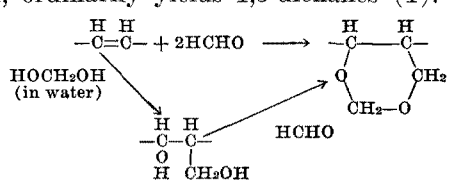
Acid-catalyzed condensations of tall oil fatty acid and related materials with formaldehyde, in the absence of a carboxylic acid solvent, led to acidic products, lower in unsaturation, but partially polymeric due to formation of interester linkages. Hydrolysis of these linkages furnished products lower 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.

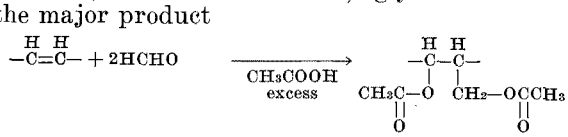
A preliminary study on the acid-catalyzed reaction of ethyl tallate with anhydrous formaldehyde gave promise that an improved alternate route to fatty acid-formaldehyde esters could be developed.

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



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