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The Acetoglycerides as Plasticizers for Vinyl Resin

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THE increased use of sheet plastics for a wide variety of purposes has led to the search for plasticizers that contribute properties essential for different end uses. Among these properties is a low brittle point. The acetoglycerides, in which acetic acid is substituted for one or two of the long chain fatty acids, may prove useful for this purpose and can be produced rather inexpensively by ester interchange. The present report deals with screening tests on a number of acetoglycerides as plasticizers for Vinylite (VYDR),[2] a polyvinyl chloride — polyvinyl acetate copolymer.

Data have been obtained on eight acetoglycerides or mixtures of acetoglycerides representing differences in degrees of acetylation, unsaturation, and polyunsaturation (Table I). Six of these samples were products of commercial pilot-plant research conducted as a consequence of cooperative work with the Southern Regional Research Laboratory. The other two were prepared in this laboratory by direct acetylation of the monoglyceride (1, 2, 3). One of the latter two (aceto-olein A) was a mixture synthesized from commercial oleic acid and consisted mainly of diacetomonoolein with considerable amounts of monoacetodiolein and some triolein. The other (aceto-olein E) was predominantly (95%) 1,2-diaceto-3-olein. Since the theoretical acetyl content is 6.5% for monoacetylated diolein or distearin, and 19.5% for diacetylated olein or stearin, it is apparent that acetoglycerides listed in Table I represent gradations from well above the mono- up to the diacetylation stage. Attention is called to the fact that the term "aceto-olein" or "acetostearin," as applied to the pilot-plant samples, does not necessarily imply that the materials are derivatives of oleic or stearic acid, respectively, but identifies them as predominantly unsaturated in the case of "oleins" or saturated in the case of "stearins."

The acetoglycerides were evaluated as primary plasticizers and in some cases as co-plasticizers, *i.e.*, in admixture with either di-2-ethylhexyl phthalate (DOP), tricresyl phosphate (TCP), Santicizer 141 (S-141), or dioctyl sebacate (DOS). These will hereafter be referred to as the primary plasticizers in blends with the acetoglycerides.

Evaluation Procedure

The test formulation was as follows:

Vinylite VYDR (95% polyvinyl chloride—5% polyvinyl acetate)	63.5%
Plasticizer	35.0%
Stearic acid	0.5%
Basic lead carbonate	1.0%

When more or less than 35% overall plasticizer was used, the resin content was varied in accordance with the formula

% resin = (98.5 — x), where x is the % plasticizer.

The plasticizer or plasticizer blend was added to the dry mixture of the other three components just before milling. This operation was performed on a 6 x 12-inch rubber mill at a temperature of 310°F. The sheeted resin was then molded in a standard 6 x 6 x 0.075-inch four-cavity mold. Since the sheeted resin was too thin to fill the mold completely several layers, usually four, were placed in each mold with the milling axes parallel. The molds were gradually pressured, over a 10-minute period, to a maximum pressure of 500 p.s.i. and then held for an additional 10 minutes at the molding temperature, 310°F. The pressure was not released until the molds were cold.

Dumbbell specimens for the determinations of tensile strength, 100% modulus, and ultimate elongation were die-cut (ASTM D412-41) from the molded sheets parallel to the milling axis. The measurements were

TABLE I

Description and Properties of the Acetoglycerides

Plasticizer	Description of sample	Iodine value	Acetyl	Linoleic acid
		Wijs	%	%
Aceto-olein A	Mixture of diaceto-monoolein, monoaceto-diolein and triolein prepared from commercial oleic acid	64.4	13.9	<0.3
Aceto-olein B	Highly acetylated aceto-olein from lard	42.0	19.8	6.0
Aceto-olein C	Highly acetylated aceto-olein from cottonseed oil	73.2	17.9	32.9
Aceto-olein D	Highly acetylated aceto-olein from cottonseed oil, distilled and deodorized	74.9	18.9	33.8
Aceto-olein E	1,2-diaceto-3-olein (95%), synthesized from oleic acid	59.5	18.8	1.4
Aceto-stearin A	Partially acetylated aceto-stearin from hydrogenated lard	1.1	11.5	0.15
Aceto-stearin B	Highly acetylated aceto-stearin from hydrogenated lard	0.9	18.4	0.01
Aceto-stearin C	Highly acetylated aceto-stearin from hydrogenated lard	0.7	16.2	0.04

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[2] Mention of firms or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

TABLE II

Properties of Vinyl Copolymer (VYDR) Plasticized[a] With Acetoglycerides or Their Blends With DOP, TCP, S-141, or DOS

Plasticizer	Acetoglyceride in plasticizer	Tensile strength	100% modulus	Elongation	Brittle temperature	Volatility (loss)	Compatibility, days to bleeding
	%	*p.s.i.*	*p.s.i.*	%	°C.	%	
Aceto-olein A	100	......*	......*	......*	......*	......	......
Aceto-olein B	100	2790	1630	280	−43	......	70
Aceto-olein C	100	2830	1550	300	−47	......	30
Aceto-olein D	100	2910	1570	310	−44	......	14
Aceto-olein E	100	2920	1530	330	−47	......	25
Aceto-stearin A	100	......†	......†	......†	......†	......	......
Aceto-stearin B	100	2710	1860	240	−16[g]	......	1
Aceto-stearin C	100	2760	1740	260	−23[h]	......	1
DOP	0	2950	1490	330	−35	2.0	139+
Aceto-olein A—DOP	33	2960	1580	330	−41	......	365+
Aceto-olein A—DOP	50	2880	1580	340	−44	......	365+
Aceto-olein A—DOP	67	2820	1610	320	−43	......	365+
Aceto-olein B—DOP	50	2900	1470	320	−39	1.9	139+
Aceto-olein C—DOP	50	2970	1480	310	−41	2.9	40
Aceto-olein C—DOP	50[c]	3560	2210	260	−31	......	30-40
Aceto-olein C—DOP	50[d]	2440	1110	410	−45	......	30-40
Aceto-olein D—DOP	50	3120	1600	300	−36	......	30
Aceto-olein D—DOP	25	3110	1560	340	−32	......	96+
Aceto-olein E—DOP	50	3050	1520	320	−37	......	62+
Aceto-stearin A—DOP	50	3020	1950	280	−24	......	5
Aceto-stearin B—DOP	50	2870	1610	290	−24	1.3	139+
Aceto-stearin C—DOP	50	3060	1600	330	−33	1.3	139+
Aceto-olein B - aceto-stearin C—DOP	50[e]	3090	1540	330	−33	......	55+
Aceto-olein C - aceto-stearin C—DOP	50[f]	2960	1510	330	−33	......	55+
Tricresyl phosphate	0	3600	2430	280	0	......	106+
Aceto-olein C—TCP	20	3530	2040	260	−10	......	106+
Aceto-olein C—TCP	40	3380	1810	280	−20	......	106+
Aceto-olein C—TCP	50	3340	1820	290	−26	......	40
Aceto-olein C—TCP	60	3160	1650	300	−32	......	40
Aceto-olein C—TCP	80	3090	1620	320	−38	......	30
Aceto-stearin C—TCP	50	3190	1650	290	−16	......	67+
Santicizer 141[b]	0	3020	1410	290	−34	......	99+
Aceto-olein C—S-141	25	3010	1430	310	−36	......	99+
Aceto-olein C—S-141	50	2990	1420	310	−40	......	30
Aceto-olein C—S-141	75	2950	1510	320	−44	......	17
DOS	0	2700	1430	310	−60[i]	......	118+
Aceto-olein C—DOS	50	2820	1470	310	−53	......	40

[a] 35% plasticizer concentration, exceptions noted.
[b] Alkyl aryl phosphate.
[c] 30% plasticizer concentration.
[d] 40% plasticizer concentration.
[e] One part aceto-olein B—1 part aceto-stearin C.
[f] One part aceto-olein C—1 part aceto-stearin C.
[g] Six days after molding; −10°C. after an additional 24 hours.
[h] After molding, −16°C. six days later.
[i] Literature value.
[j] + indicates no bleeding during time specified.
* Could not mill.
† Millable but spews on cooling.

made on an IP-4 Scott tester at a loading rate of 200 lbs. per minute at 70°F. and 65 ± 2% R.H., the specimen having first been equilibrated to these conditions for 24 hours.

The brittle points were determined on specimens die-cut from the molded sheets following the procedure given in ASTM test D746-44T. Volatilities were determined by an oven method (4) and represent the weight-percentage loss recorded for the plasticized specimens during a 96-hour period at 100 ± 2° C. The relative compatibilities were judged by observing the lapse of time before the onset of bleeding in the molded sheets during storage at room temperature.

Results and Discussion

The results summarized in Table II indicate that as primary plasticizers the aceto-oleins impart a better modulus, elongation, brittle point, and slightly better tensile strength than the aceto-stearins. In addition, the aceto-oleins impart better low temperature characteristics than DOP and are comparable in respect to tensile strength, modulus, and elongation. While none of the acetoglycerides tested were completely compatible with VYDR resin, some of the aceto-oleins showed a decided superiority in this respect, being compatible for periods of 14 to 70 days as compared to less than one day for the aceto-stearins.

There was a vast improvement in compatibility and milling when the acetoglycerides were blended with either DOP, TCP, S-141, or DOS. Several acetoglycerides in such blends have shown no signs of incompatibility over a 4½-month period and one, aceto-olein A, over a one-year period. Milling was best for those blends employing TCP as the primary plasticizer, but all four primary plasticizers were effective, to approximately the same degree, in compatibilizing any one of the acetoglycerides.

Since blending seems to average out the characteristics imparted to the vinyl resin by the individual plasticizers, addition of the acetoglyceride produces improvement only in those plasticizing properties in which they excel those of the primary placticizer used in the blend. Thus the greatest improvement in modulus and brittle point is obtained in the TCP-acetoglyceride blends since here we have the greatest disparity in these properties. Similarly, the tensile strength of plasticized vinyl resin is higher for the acetoglyceride-TCP blends than for any other investigated. Elongation, modulus, and brittle point are best in the blends employing an aceto-olein while tensile strength is favored in those of the aceto-stearins.

Further adjustment of the plasticizing effects can be attained by varying the overall concentration of the plasticizer blend in the resin mixture as shown by the 50-50 aceto-olein C-DOP blend, which was employed in overall concentrations of 30, 35, and 40% (see footnotes c and d of Table II).

The volatilities observed and reported in Table II for 50-50 blends of DOP with either an aceto-olein or an aceto-stearin did not exceed that for DOP alone in the molded sheet, with the exception of the 50-50 blend with aceto-olein C. There was some yellowing in all the specimens during this test, the aceto-oleins being less resistant in this respect than the acetostearins. These molded specimens were originally an opaque white or light cream color, as were all the molded sheets plasticized with acetoglycerides. It may be postulated that any development of odors by oxidative rancidity may be arrested by the use of antioxidants.

The overall results of the screening tests suggest the following generalities:

1. Unsaturation seems to effect improvement in efficiency and brittle point.
2. Mono-unsaturation tends to increase the compatibility but, as shown by aceto-oleins C and D, the presence of di-unsaturation (linoleic acid radical) tends to nullify this effect. This is partially confirmed by the better compatibility exhibited by the 50-50 blends of DOP with aceto-stearins than by a similar blend with aceto-olein C.
3. A higher degree of acetylation, as exemplified by the aceto-stearins, also tends to improve compatibility.

Summary

The screening evaluation experiments on a number of acetoglycerides have indicated that they can be used as secondary plasticizers to improve some of the plasticizing qualities of plasticizers, such as tricresyl phosphate and Santicizer 141, and as extenders for plasticizers, such as dioctyl sebacate. Additional information will be necessary in order to confirm the tentative conclusions drawn as to the effect of unsaturation, polyunsaturation, and degree of acetylation upon the plasticizing characteristics of the acetoglycerides to determine more precisely their potentialities for vinyl chloride resins and to extend the possible use of the acetoglycerides as plasticizers to other resins.

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Tall Oil Studies. I. Effect of Chain Length and Composition on Detergency of Built Polyethenoxy Tallates

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A COMPREHENSIVE study of the condensation of ethylene oxide with a variety of fatty acids, alcohols, and amines to form the respective non-ionic, detergent polyethenoxy derivatives (polyoxyethyleneglycol esters) was carried out by Schoeller and Wittwer (1) in 1934. More recently Harris and Kosmin (2, 3) described non-ionic detergent compositions containing ethylene oxide condensation products of tall oil, a by-product of the pine-wood paper industry. The major constituents of this oil consist of approximately seven rosin acids related to abietic acid and three fatty acids related to oleic acid (4). The proportions of rosin acids to fatty acids may vary with the source and grade as well as the processing of the tall oil. Representing the tall oil acids by the conventional formula R-COOH, the corresponding non-ionic detergent esters with ethylene oxide, polyethenoxy tallates, may be written as follows:

$$\mathrm{R{-}C{-}O{-}O(CH_2{-}CH_2{-}O)_x{-}CH_2{-}CH_2{-}OH}$$

It seemed desirable to study the effect of composition of tall oil as well as the polyethenoxy chain length upon detergency. With that in mind various grades and compositions of tall oil were condensed with ethylene oxide, and soil removal and whiteness retention assays were determined on the resultant polyethenoxy tallates in alkaline-built detergent compositions. In like manner two tall oil samples, one rich in rosin acid and the other rich in fatty acid, were condensed with ethylene oxide progressively, and detergency values were obtained on built compositions of the polyethenoxy tallates of varying ethenoxy chain length. As a check on the number of ethenoxy groups in the various esters a saponification method was applied to these substances, and details are described herein.

Detergency Tests

The procedure used for evaluating detergency, *i.e.*, soil removal and whiteness retention in hard and soft water, of the various polyethenoxy tallates was essentially the method described by Vaughn and Suter (5) except that the swatches in the whiteness retention tests were dried in an oven at 110°C. for 30 minutes, with subsequent hand-ironing. Test mixtures were prepared, using 20% by weight of the polyethenoxy tallate, 20% tetrasodium pyrophosphate, 20% sodium tripolyphosphate, 39% soda ash, and 1% carboxymethyl cellulose. All results are comparative, *i.e.*, based on an arbitrary standard. For this purpose a commercially available similar, non-ionic built detergent mixture was chosen, and detergency of the test solutions containing 0.25% (0.25 g. test mixture/100 ml. water) of the standard was taken as 100% (see Table I). Detergency of the test solutions of the unknown were also determined at 0.25% concentration.

Effect of Tall Oil Composition on Detergency

Six polyethenoxy tallates were prepared by condensing tall oils, varying in composition from pure abietic acid to pure oleic acid, with ethylene oxide gas in an inert atmosphere at 170-190°C., using potassium carbonate as a catalyst. In each case approximately 14 ethenoxy units were added to the carboxyl group. Detergency values of the products are compared in Table I.