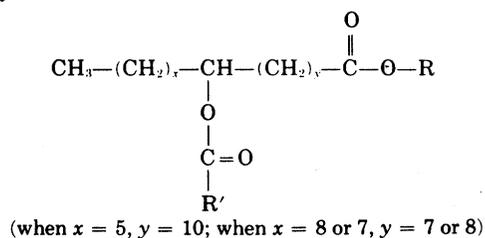


Viscosity Characteristics of Esters of Hydroxystearic Acids

THE MOST widely used plasticizer for poly(vinyl chloride) compositions to be employed at low temperatures (below $-30^{\circ}\text{C}.$) are certain diesters of adipic, azelaic, and sebacic acids. In general, these esters have low pour points and ASTM slopes, and high viscosity indices (5). The relationship between these physical properties and plasticizer efficiency at low temperatures has not been systematically studied, although it is frequently assumed that a low pour point and low viscosity at reduced temperatures and a high viscosity index are essential attributes of an efficient low temperature plasticizer.

In this laboratory numerous long chain esters have been prepared containing the oxirane (9), organophosphorus (7), or acyloxy (6) groups, and many of them are efficient low temperature plasticizers for poly(vinyl chloride). The pour point, viscosity index, ASTM slope and viscosity from $+98.6^{\circ}$ to $-50^{\circ}\text{C}.$ (whenever possible) have been determined on the acyloxy compounds to ascertain whether any relationship exists between these physical characteristics and plasticizer efficiency at low temperatures. A report on the viscosity characteristics of the long-chain phosphorus compounds is planned.

Most of the compounds whose viscosity characteristics are reported here are alkyl esters of 9(10)- or 12-monoacetoxysebacic acid ($\text{R}' = \text{CH}_3$):



In several instances R is alkoxyalkyl, aryloxyalkyl, or phenyl, and $\text{R}'-\text{C}(=\text{O})-\text{O}-$ is butyryloxy or benzyloxy. Four glycol esters of 12-monoacetoxysebacic acid are also included to determine the effect of two acylated fatty acid chains in one molecule. Several esters of di-, tri-, and polyacetoxysebacic acid have also been studied to determine the effect of number and position of acyloxy substituents on viscosity characteristics.

Published work on the viscosity characteristics of certain esters of hydroxystearic acids (8) showed that some of the compounds have characteristics which suggest their possible utility as synthetic lubricants. Therefore, it was desirable to study additional members of this general class.

EXPERIMENTAL

Compounds Studied. The preparation and characteristics of the esters of hydroxystearic acids have been published (6, 7, 9). Di(2-ethylhexyl) sebacate, azelate, adipate, and phthalate were the purest commercial materials and were used as received.

Physical Test Methods. Kinematic viscosity were obtained with calibrated Cannon-Manning semimicroviscometers

(a modified Ostwald type) according to ASTM D 445-53T (2). Viscosities were run over the temperature range $+98.6^{\circ}\text{C}.$ ($209^{\circ}\text{F}.$) $-50^{\circ}\text{C}.$ ($-58^{\circ}\text{F}.$) whenever possible.

Pour points were obtained according to ASTM D 97-47 (3) except for the size of the sample and tube. Ten milliliters of sample was placed in a test tube, 16×150 mm., which was then placed in a larger tube, with an air space between them. The apparatus was then placed in an alcohol-dry ice bath held at about $-70^{\circ}\text{C}.$

The freezing point reported was the temperature at which a sample crystallized during the test. Viscosities could not be determined closer than 10° to the pour or freezing point.

Viscosity index was calculated as described in ASTM D 507-53 (4). ASTM slopes were calculated from plots on charts, as shown in ASTM D 341-43 (1). All slopes were calculated from the highest to the lowest test temperatures at which viscosities could be measured.

Stiffening or Clash-Berg temperatures have been taken from a previous publication (6). These values were obtained on compositions containing 35% by weight of plasticizer and 65% by weight of a vinyl chloride-vinyl acetate copolymer (95:5 by weight).

RESULTS AND DISCUSSION

Table I summarizes the viscosity and pour point data obtained on esters of hydroxystearic acids and the stiffening temperatures of a poly(vinyl chloride-acetate) copolymer containing these compounds. Included for comparison are some corresponding data on the four control diesters. The data lead to the following conclusions:

1. Little or no correlation exists between viscosity index (V.I.), pour point, ASTM slope, and stiffness temperature.

2. A definite correlation exists between low stiffness temperature ($-50^{\circ}\text{C}.$ or below with 35% by weight of plasticizer) and low plasticizer viscosity at low temperatures. In the series of compounds described here, a stiffness temperature below $-50^{\circ}\text{C}.$ is obtained only if the viscosity of the plasticizer does not exceed 250 centistokes at $-10^{\circ}\text{C}.$, and 1350 centistokes at $-30^{\circ}\text{C}.$ It was possible to determine the viscosity of all the compounds at $-10^{\circ}\text{C}.$, so the former value is considered to be more reliable.

3. There is no apparent correlation between the absolute value of the viscosity, below a viscosity of 250 centistokes at $-10^{\circ}\text{C}.$, and stiffness temperature. Thus, *n*-octyl 9(10)-acetoxysebacate, the compound with the lowest viscosity (102 centistokes) at $-10^{\circ}\text{C}.$ of all the compounds studied, has a stiffness temperature of only $-53^{\circ}\text{C}.$, whereas iso-octyl 9(10)-acetoxy sebacate with a viscosity of 249 centistokes at $-10^{\circ}\text{C}.$ has a stiffness temperature of $-62^{\circ}\text{C}.$ The compound with the lowest stiffness temperature, butyl 9(10)-monoacetoxy sebacate ($-67^{\circ}\text{C}.$), has a viscosity of 146 centistokes at $-10^{\circ}\text{C}.$ A low viscosity is only one factor which contributes to high plasticizer efficiency at low temperature; other factors also play an important role.

4. The ASTM slope of the alkyl monoacetoxy sebacates is essentially the same as that of di(2-ethylhexyl) sebacate and azelate. The glycol esters, however, have a considerably lower ASTM slope. Their low-temperature performance is only fair.

Many of the compounds in Table I, in the temperature range of -10° to -30° C., have viscosities which are close to those of adipates, azelates, and sebacates (5) with the same or similar alkyl groups. Also, esters with straight-chain alkyl groups—*butyl* and *octyl*, for example—have relatively low viscosities at -10° which are even lower than the values for homologous esters with branched-chain alkyl groups (2-ethylbutyl and 2-ethylhexyl). The esters with straight-chain alkyl groups had higher pour points, as expected.

Several of the compounds in Table [butyl 9(10)-butyryoxy stearate, butyl 12-monoacetoxy stearate, methoxyethoxyethyl 12-monoacetoxy stearate, and butyl 12-(monomethyladipoxy) stearate] have essentially the same viscosity index as di(2-ethylhexyl) sebacate or azelate. None of these compounds, however, has the desirably low pour point of the sebacate or azelate. The compounds with the lowest pour points (-50° C. or below) are 2-ethylbutyl, 2-ethylhexyl, and iso-octyl 9(10)-acetoxy stearate (-54° ,

-60° , and -62° C., respectively, butyl 9(10)-benzoxy stearate (-63° C.), and 2-ethylbutyl- and phenoxyethyl-12-acetoxy stearates (-53° and -50° C., respectively). None of these has an unusually high viscosity index.

The viscosity index range in Table I is 38 to 158 (controls excepted), with an average of about 130. The lowest value was obtained with butyl triacetoxy stearate and the highest with butyl 12-(monomethyladipoxy) stearate. More than one substituent on the alkyl-chain, or an aromatic carboxylic ester group, produces a lowering in viscosity index. Butyl 2-acetoxy stearate, an exception, has a low viscosity index, even though it contains only one substituent and is an aliphatic ester. The long, unsubstituted chain of 16 carbon atoms probably contributes to this effect.

The viscosity is increased markedly both by introducing a benzoxy group or three acetoxy groups in the chain. A benzoxy group in the chain of a phenyl ester (phenyl 12-benzoxy stearate) gave the highest viscosity obtained—

Table I. Viscosity Characteristics of Esters of Hydroxystearic Acids and Controls

Esters	Kinematic Viscosity in Centistokes, at $^{\circ}$ C.						ASTM Slope	V. I.	Pour Point, $^{\circ}$ C.	Stiffness, Temp., $^{\circ}$ C.
	98.6 $^{\circ}$	38.0 $^{\circ}$	10 $^{\circ}$	-10 $^{\circ}$	-30 $^{\circ}$	-50 $^{\circ}$				
Alkyl 9(10)-monoacetoxy stearates										
Methyl	2.85	11.6	37.8	138.2	0.78	102	-37	-50
Butyl	3.38	13.7	40.8	145.9	644.5	...	0.73	138	-49	-67
2-Ethyl-1-butyl	3.72	16.7	57.3	214.3	1081	...	0.73	127	-54	-53
<i>n</i> -Octyl	3.86	16.9	57.2	102.3	0.71	142	-34 ^b	-53
2-Ethyl-1-hexyl	3.88	18.0	64.2	246.9	1340	20,350	0.73	126	-60	-57
Iso-octyl	4.05	18.6	66.3	249.4	1353	19,630	0.72	121	-62	-60
Alkyl 9(10)-monoacyloxy stearates										
Methyl butyryoxy	2.78	10.8	34.7	105.4	553.1	...	0.77	119	-35 ^b	-54
Butyl butyryoxy	3.30	12.8	37.1	117.8	461.5	...	0.71	148	-41	-62
Butyl benzoxy	5.20	28.4	116.0	499.9	3239	...	0.73	127	-63	-43
Alkyl 12-monoacetoxy stearates										
Butyl	3.51	13.9	45.3	154.4	0.71	154	-35 ^b	-54
Butyl (commercial distilled)	3.47	14.2	44.0	0.71	143	-20 ^b	-46
Butyl (commercial)	3.98	17.7	59.9	0.72	144	-20 ^b	...
2-Ethyl-1-butyl	3.83	17.3	59.8	225.1	1188	...	0.72	129	-53	-54
Methoxyethyl	3.65	15.6	50.3	189.4	0.72	138	-35	-51
Phenoxyethyl	5.77	38.0	205.4	1550-	18,700-	...	0.74	102	-50	-33
				1731	23,000					
Methoxyethoxyethyl	4.43	20.5	67.2	283.8	0.71	149	-40	-46
Alkylene glycol di(12-monoacetoxy stearates)										
Ethylene glycol	12.07	85.2	506.5	0.62	130	-21 ^b	-35
Diethylene glycol	12.76	92.4	484.3	3327	0.60	129	-23	-35
1, 2-Propylene glycol	11.85	85.4	462.1	2803	0.65	128	-29	-35
1, 3-Propylene glycol	12.45	89.5	458.5	0.63	129	-16	-35
Miscellaneous										
Phenyl 12-acetoxy stearate	4.58	26.2	110.3	0.79	97	-16 ^b	-28
Phenyl 12-benzoxy stearate	29.4	304.6	1880-	19,000-	0.58	121	-42	6
			2400	21,000						
Butyl 2-acetoxy stearate	3.08	13.5	45.8	0.78	94	-6 ^b	-37
Butyl 9,10-diacetoxy stearate (comm.)	5.10	31.5	146.1	0.76	97	-33 ^b	-32
Butyl 9,10,12-triacetoxy stearate (comm.)	7.44	80.9	624.1	6389	0.82	38	-39	-15
Butyl polyacetoxy stearate (comm.)	6.27	42.4	199.1	1079	0.73	105	-18	-22
Butyl 12-(monomethyladipoxy) stearate	4.74	21.8	72.8	290.3	640-	...	0.70	158	-28 ^b	-44
					725					
Controls										
Di (2-ethylhexyl) sebacate							0.71	154	-55 ^b	-61
Di (2-ethylhexyl) azelate							0.72	146	< -75 ^b	-59
Di (2-ethylhexyl) adipate							0.77	121	-68	-58
Di (2-ethylhexyl) phthalate							0.94	20	< -55 ^b	-29

^a Determined on compositions containing 35% by weight of plasticizer and 65% by weight of vinyl chloride-vinyl acetate copolymer (95:5 by weight) (6).

^b Freezing point.

namely, 29 centistokes, at 98.6° C. and 305 centistokes at 38° C.,—compared to the usual range of 3 to 12, and 11 to 92 centistokes, respectively.

SUMMARY

Viscosity characteristics were determined on 27 long-chain plasticizers. Most of these compounds are alkyl, aryl, or glycol esters of 9(10)- or 12-monoacetoxystearic acid. It is concluded that a low viscosity at low temperatures (below 250 centistokes at -10° C.) is an essential requirement for obtaining a low stiffness temperature in a plasticized poly(vinyl chloride-acetate) copolymer (95:5). No correlation could be found between high viscosity index or low pour point and low stiffness temperature.

ACKNOWLEDGMENT

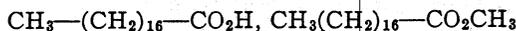
The authors thank R. E. Koos for assistance in the preparation of the compounds.

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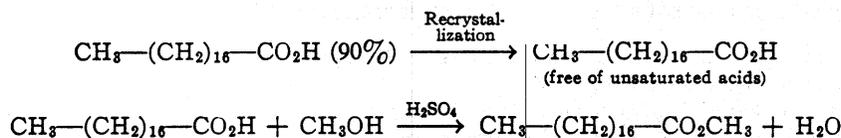
STEARIC ACID, METHYL STEARATE,
AND HOMOLOGOUS COMPOUNDS



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I. Principle



II. Procedure

A. Stearic acid. Fifteen hundred grams of commercial stearic acid, m. p. 63–64°,¹ are dissolved in 10.5 l. of acetone in a 3.5-gallon Pyrex bottle, and the solution is cooled to 0°. The stearic acid which precipitates is filtered by suction and air-dried. The yield is 1200–1250 gm. Its melting point is about 66–67°.^{2,3}

B. Methyl stearate. The stearic acid is refluxed for 5–6 hours with 670–705 gm. of anhydrous methanol containing 24–25 gm. of concentrated sulfuric acid ($d = 1.84$).⁴ The reaction mixture is diluted with a large quantity of hot water (50–70°) in a separatory funnel, and well shaken. The lower aqueous layer is discarded, and the hot

¹ This material is sold by Armour and Company, Chicago, Illinois, under the trade name Neo-Fat 1-65 (90% stearic acid). The usual commercial stearic acids contain approximately equal amounts of palmitic and stearic acids, and they are not convenient starting materials.

² Upon recrystallization of this product, 1100–1150 gm. of fairly pure stearic acid, m.p. about 69°, are obtained (82–85% yield).

³ If small quantities of unsaturated compounds can be tolerated in the final product, the recrystallization may be omitted. In some cases, treatment with activated carbon is required in order to obtain an odorless product.

⁴ The reaction mixture is not homogenous, but this does not interfere with the esterification.

water wash is repeated until the aqueous layer is free of sulfuric acid. The crude methyl stearate is dried by heating to 100–105° under moderate vacuum in a stream of inert gas. The yield is 1200–1250 gm.⁵ This is fractionally distilled under vacuum.⁶ The constant refractive index fraction, $n_D^{40} = 1.4364$, boiling at 180–182°/4 mm., consists of pure methyl stearate. The yield is 1120–1170 gm. (85–90%, based on the stearic acid content of the starting material). Its melting point is 38–39°.⁷

III. Methods of Preparation

Pure fatty acids have been prepared by fractional distillation and crystallization of mixtures of acids obtained from fats.^{8,9} The esters have been prepared by esterification of the corresponding acids with methanol in the presence of concentrated sulfuric acid as catalyst.^{10,11}

⁵ This product, which is suitable for some purposes without further purification, has an acid number of about 5 and a melting point of about 36–37°.

⁶ A well-insulated, electrically heated Vigreux column, 30 inches long and 1 inch in diameter or a column packed with ¼-inch Berl saddles (8–10 theoretical plates) is satisfactory. A total reflux, partial take-off still head should be employed.

⁷ Palmitic acid, m. p. 61°, and pure methyl palmitate, m. p. 28–29°, b. p. 161–162°/4 mm., $n_D^{40} = 1.4331$, can be prepared from commercial palmitic acid (Armour and Company Neo-Fat 1-56, 90% palmitic acid) by the procedures described. Myristic acid, m. p. 52–53°, and pure methyl myristate, b. p. 156–157°/8 mm., $n_D^{30} = 1.4328$, can be similarly prepared from commercial myristic acid (Armour and Company Neo-Fat 13), but the crystallizations of the acid must be conducted at –20° in order to obtain good yields. Lauric acid, m. p. 41–42°, and pure methyl laurate, b. p. 132–133°/8 mm., $n_D^{30} = 1.4275$, can be similarly prepared from commercial lauric acid (Armour and Company Neo-Fat 11), but the crystallizations of the acid must be conducted at –40°. To obtain pure lauric acid, m. p. 44°, and pure myristic acid, m. p. 54°, fractional distillation of the recrystallized acids is required. The former has a boiling point of 167–168°/8 mm., $n_D^{45} = 1.4316$, the latter, 190–191°/8 mm. Capric acid, b. p. 145–146°/8 mm. and m. p. 30–31°, and caprylic acid, b. p. 124–125°/8 mm. and $n_D^{30} = 1.4241$, can be prepared by fractional distillation of commercial capric and caprylic acids, respectively (Armour Neo Fats 7 and 15). Methyl caprylate, b. p. 127–128°/100 mm., $n_D^{30} = 1.4130$, and methyl caprate, b. p. 106–107°/10 mm., $n_D^{30} = 1.4215$, can be prepared by esterification of the pure acids or by esterification of the commercial acids, followed by fractional distillation. The yields are about 60–85% [cf. *Org. Syntheses*, 20, 67 (1940)].

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