Viscosity Characteristics of Esters of Hydroxystearic Acids

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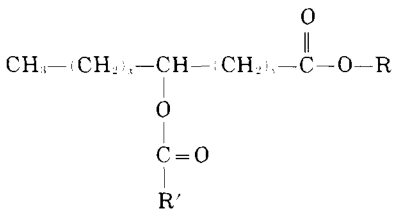
THE MOST widely used plasticizer for poly(vinyl chloride) compositions to be employed at low temperatures (below −30° C.) are certain diesters of adipic, azelaic, and sebacic acids. In general, these esters have low pour points and ASTM slopes, and high viscosity indices (*5*). The relationship between 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.

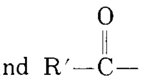
In this laboratory numerous long chain esters have been prepared containing the oxirane (*9*), organophosphorus (*7*), or acyloxy (*6*) groups, and many of them are efficient low temperature plasticizers for poly(vinyl chloride). The pour point, viscosity index, ASTM slope and viscosity from +98.6° to −50° 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-monoacetoxystearic acid ($R' = CH_3$):



$$CH_3-(CH_2)_x-\underset{\underset{\underset{\underset{R'}{|}}{C=O}}{\underset{|}{\underset{O}{|}}}}{CH}-(CH_2)_y-\overset{\overset{O}{\|}}{C}-O-R$$

(when $x = 5$, $y = 10$; when $x = 8$ or 7, $y = 7$ or 8)

In several instances R is alkoxyalkyl, aryloxyalkyl, or phenyl, and  $R'-\overset{\overset{O}{\|}}{C}-O-$ is butyroxy or benzoxy. Four glycol esters of 12-monoacetoxystearic acid are also included to determine the effect of two acylated fatty acid chains in one molecule. Several esters of di-, tri-, and polyacetoxystearic 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° C. (209° F.) −50° C. (−58° 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° 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° 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° C. is obtained only if the viscosity of the plasticizer does not exceed 250 centistokes at −10° C., and 1350 centistokes at −30° C. It was possible to determine the viscosity of all the compounds at −10° 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° C., and stiffness temperature. Thus, *n*-octyl 9(10)-acetoxystearate, the compound with the lowest viscosity (102 centistokes) at −10° C. of all the compounds studied, has a stiffness temperature of only −53° C., whereas isooctyl 9(10)-acetoxy stearate with a viscosity of 249 centistokes at −10° C. has a stiffness temperature of −62° C. The compound with the lowest stiffness temperature, butyl 9(10)-monoacetoxy stearate (−67° C.), has a viscosity of 146 centistokes at −10° 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 stearates 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-butyroxy 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

	Kinematic Viscosity in Centistokes, at ° C.						ASTM		Pour Point,	Stiffness, Temp.,[a]
Esters	98.6°	38.0°	10°	−10°	−30°	−50°	Slope	V. I.	° C.	° C.
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
n-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 butyroxy	2.78	10.8	34.7	105.4	553.1	...	0.77	119	−35[b]	−54
Butyl butyroxy	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 (commerical distilled)	3.47	14.2	44.0	...	...	...	0.71	143	−20[b]	−46
Butyl (commerical)	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	1550-1731	18,700-23,000	...	0.74	102	−50	−33
Methoxyethoxyethyl	4.43	20.5	67.2	283.8	...	...	0.71	149	−40	−46
Alkylene glycol di(12-monoacetoxy syearates)										
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	1880-2400	19,000-21,000	...	...	0.58	121	−42	6
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	640-725	...	0.70	158	−28[b]	−44
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

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Stability of Liquid Ozone in Glass and in Contact with Various Substances

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ALTHOUGH ozone is thermodynamically unstable, pure liquid ozone can be stored for long periods of time at the temperature of liquid oxygen (−183° C.) with no apparent decomposition (*6*). Kinetic data for the decomposition of solutions of ozone in carbon tetrachloride at room temperature (*1*) may be extrapolated to lower temperatures in the range −183° to −112° C., the boiling point of liquid ozone. Such extrapolations suggest, in agreement with past observations (*6*), that the rate of decomposition of pure liquid ozone in this temperature range should be immeasurably small.

However, extrapolation of kinetic data over a range which encompasses a two- to threefold variation in temperature is undesirable. Some studies have been made of liquid ozone (2-10). As an additional observation at the Lewis Research Center on the storage stability of liquid ozone in the range between −183° C. and its boiling point, samples were held in glass vials for one to a few days and the extent of any decomposition was noted.

In addition, liquid ozone was contacted with different materials and chemical compounds, and any decomposition was noted. Although some of these results have verified previous work (*7*), the stability of ozone with a number of materials and laboratory reagents was reported for the first time.

APPARATUS AND PROCEDURE

Ozone was prepared from 99.6% pure extra-dry oxygen (Matheson Co.) in an all-glass silent discharge-type ozonizer (*5*). The oxygen was passed through copper oxide at 950° C. to remove hydrocarbons and then through Drierite, Ascarite, and a trap immersed in dry ice and acetone before it entered the ozonizer. After passing through a second dry ice-acetone trap, the ozone-oxygen mixture was condensed in a glass receiver cooled by liquid oxygen. A schematic diagram of the ozone concentration and purification apparatus is shown in Figure 1. The oxygen was pumped off through a trap filled with crystalline, metal aluminosilicates (Molecular Sieves, Type 5A, 1/16-inch pellets, Linde Air Products Co.), which destroyed any ozone vapors passing through with the oxygen. The last traces of oxygen were eliminated by vaporization and recondensation of the ozone followed by pumping until the pressure was 0.1 mm. of mercury, the vapor pressure of ozone at −183° C. (*7*). Ozone in 2- to 3-ml. quantities not needed for immediate use was stored indefinitely in a liquid nitrogen bath.

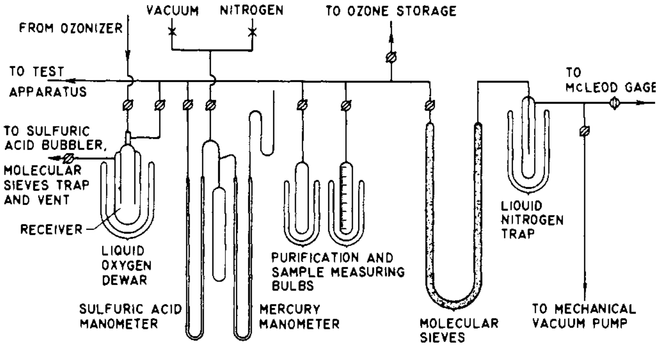

Figure 1. Ozone concentration and purification apparatus

Figure 2 shows the test apparatus and associated equipment, which was designed to operate over the temperature range of −183° to −110° C. The test bulb was immersed in a 2-liter Dewar vessel, which was cooled by a refrigerated stream of air dried by passage through an alumina column and a liquid nitrogen–cooled trap. Precooling of the airstream took place in a coil immersed in a dry ice–acetone bath, and final cooling in a U-tube immersed in liquid nitrogen in a 4-liter Dewar vessel. The temperature could be regulated by varying the airflow rate and by immersing