pared with the spectrum of a pure sample of erucyl alcohol (13-docosene-1-OL). The two spectra are essentially identical, further confirming that the products from the sodium reduction are highly purified long-chain unsaturated alcohols.

Summary

Jojoba oil is a liquid wax composed essentially of C_{20} and C_{22} straight-chain monoethylenic acids and alcohols in the form of esters. Sodium reduction of the wax fatty esters in jojoba oil yielded quantitatively a mixture of unsaturated, long-chain alcohols from the acid moiety of the jojoba oil. Yields of about 91% were obtained in the laboratory-scale experiments and 82 to 86 for the pilot-plant experiments. Analytical data, including detailed infrared spectra information, are given for the resulting product alcohols.

Acknowledgments

The authors extend their thanks to A. F. Cucullu for determinations of the % hydroxyl, to V. A. Cirino for determinations of free fatty acid, unsaponifiable matter, and iodine value, to E. F. DuPré for the infrared curves, and to J. M. Funderburk for preparing the drawing of the equipment used.

REFERENCES

1. American Oil Chemists' Society "Official and Tentative Methods," edited by V. C. Mehlenbacher and T. H. Hopper, 2nd ed., rev. to 1957, Chicago (1946–57).
2. Blinka, J., and Peddicord, H. J. (to Procter and Gamble Co.), U. S. Patent 2,647,932 (August 4, 1953).
3. Daugherty, P. M., Seneath, H. H., and Wastler, T. A., Georgia Inst. Technol. Eng. Expt. Sta. Bull. No. *17*, 2, 6 (1953).
4. Hansley, V. L., Ind. Eng. Chem., *39*, 55–62 (1947).
5. Hansley, V. L. (to E. I. duPont de Nemours & Co.)., U. S. Patent 2,096,036 (October 19, 1937).
6. Jones, M. A., and Knoepfler, N. B., Chemurgic Digest, *16* (1), 5, 6, 11 (1957).
7. Kastens, M. L., and Peddicord, H. J., Ind. Eng. Chem., *41*, 438–446 (1949).
8. Knoepfler, N. B., and Vix, H. L. E., J. Agr. Food Chem., *6*, 118–121 (1958).
9. McKinney, R. S., and Jamieson, G. S., Oil & Soap, *13*, 289–292 (1936).
10. O'Connor, R. T., Field, E. T., and Singleton, W. S., J. Am. Oil Chemists' Soc., *28*, 154–160 (1951).
11. O'Connor, R. T., DuPré, E. F., and Feuge, R. O., J. Am. Oil Chemists' Soc., *32*, 88–93 (1955).
12. Smith, F. A., and Creitz, E. C., J. Research, Natl. Bur. Standards, *46*, 154–164 (1951).
13. Warth, A. H., "The Chemistry and Technology of Waxes," 2nd ed., pp. 302–307 incl., Reinhold Publishing Corporation, New York (1956).

[Received July 11, 1958]

Esters of Hydroxystearic Acids as Primary Low-Temperature Plasticizers for a Vinyl Chloride—Vinyl Acetate Copolymer

H. B. KNIGHT, LEE P. WITNAUER, W. E. PALM, R. E. KOOS, and DANIEL SWERN,
Eastern Regional Research Laboratory,[1] Philadelphia, Pennsylvania

THE USE OF FATTY DERIVATIVES in formulations with vinyl chloride resins has usually been limited to applications utilizing their properties as stabilizers, mold lubricants, or as secondary plasticizers or extenders. The principal exception is the use of alkyl epoxystearates, which may be considered to be primary plasticizers as well as stabilizers (19, 10) since they are highly compatible and efficient, as indicated by their effect on modulus, elongation, and tensile strength.

The literature contains some mention of esters of acyloxystearates as plasticizers and as lubricants. Aliphatic esters of diacetoxystearates (11) and diacetomonoglycerides (16) have been proposed as plasticizers for polyvinyl chloride. The methyl, ethyl, *n*-butyl, and 2-ethylhexyl 12-acetoxystearates have been mentioned as plasticizers for ethyl cellulose (12). A series of alkyl acyloxystearates, in which the alkyl is a branched chain (2-ethylhexyl, isopropyl, or 2-methylpentyl) and the acyloxy group (acetoxy, diethylacetoxy, propionoxy, or butyroxy) is situated at either the 9,10, or 12 position in the chain, has been evaluated as lubricants (18).

Adequate compatibility of a plasticizer with vinyl chloride resins depends on the proper kind, number, and arrangement of polar groups (13). Ester groups are the most effective (15). With dibasic acid esters of mono- or polyhydric alcohols, the compatibility limit is about a total of 26 carbon atoms (8). With phthalates, adipates, and thiodibutyrates, compatibility decreases as the alcohols increase to a chain length of C_9-C_{11}.

In this report it will be shown that many acyloxy and aryloxy compounds prepared from hydroxystearic acids are not only primary plasticizers but impart outstanding low-temperature flexibility when formulated with a vinyl chloride-vinyl acetate copolymer. This has been accomplished without any undesirable changes in modulus and tensile strength, when compared to similar compositions containing di-2-ethylhexyl phthalate.

Experimental

Butyl 12-Acetoxystearate. This was isolated from the commercial product by distillation; b.p. 155°C./0.05 mm.; saponification no. 256; acid no. 3.9; $n^{30/D}$ 1.4436.

Butyl 9,10-Diacetoxystearate. A commercial material prepared from fairly pure 9,10-dihydroxystearic acid was employed as received; saponification no. 329; acid no. 3.5; $n^{30/D}$ 1.4462.

Butyl 9,10,12-Triacetoxystearate. This was isolated from the commercial material by distillation; b.p. 194°C./0.10 mm.; saponification no. 392; acid no. 3.5; $n^{30/D}$ 1.4473.

Methyl 12-Acetoxystearate. Methyl 12-hydroxystearate was heated and stirred for 3 hrs. at 110° with a 100% molar excess of acetic anhydride. Hot water was slowly added to the stirred reaction mixture to hydrolyze the excess acetic anhydride. The aqueous

---

[1] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

layer was discarded, and the oil was washed with water until acid-free and then dried under vacuum. Distillation gave methyl 12-acetoxystearate, b.p. 184–186°C./0.2 mm.; saponification no. 312; acid no. 4.5; $n^{30/D}$ 1.4429.

Methyl 9,10-Diacetoxystearate. Methyl 9,10-dihydroxystearate was acetylated as described above. Distillation gave methyl 9,10-diacetoxystearate, b.p. 203–206°C./0.5 mm.; saponification no. 401; acid no. 1.8; $n^{30/D}$ 1.4444.

Methyl 9(10)-Acetoxystearate. This compound was prepared by the acetylation of methyl 9(10)-hydroxystearate (14), b.p. 150°C./0.02 mm.; saponification no. 314; acid no. 2.2; $n^{30/D}$ 1.4427.

Butyl 9(10)-Acetoxystearate. This compound was prepared by the acetylation of butyl 9(10)-hydroxystearate; b.p. 164°C./0.01 mm.; saponification no. 280; acid no. 1.2; $n^{30/D}$ 1.4428.

Methyl 9(10)-Butyroxystearate. Methyl 9(10)-hydroxystearate was heated with a four-to-one molar excess of *n*-butyric anhydride, employing the same procedure used for acetylation; b.p. 155°C./0.02 mm.; saponification no. 284; acid no. 1.74; $n^{30/D}$ 1.4428.

Butyl 9(10)-Butyroxystearate. This compound was prepared from butyl 9(10)-hydroxystearate and *n*-butyric anhydride; b.p. 176°C./0.03 mm.; saponification no. 254; acid no. 1.4; $n^{30/D}$ 1.4435.

2-Ethyl-1-Butyl 9(10)-Acetoxystearate. 9(10)-Hydroxystearic acid was esterified with 2-ethyl-1-butanol, then acetylated; b.p. 173°C./0.02 mm.; saponification no. 254; acid no. 2.2; $n^{30/D}$ 1.4455.

n-Octyl 9(10)-Acetoxystearate. 9(10)-Hydroxystearic acid was esterified with *n*-octanol and then acetylated; b.p. 189°C./0.02 mm.; saponification no. 241; acid no. 2.2; $n^{30/D}$ 1.4450.

2-Ethyl-1-Hexyl 9(10)-Acetoxystearate. 9(10)-Hydroxystearic acid was esterified with 2-ethyl-1-hexanol, then acetylated; b.p. 180°C./0.03 mm.; saponification no. 240; acid no. 1.1; $n^{30/D}$ 1.4458.

Isoctyl 9(10)-Acetoxystearate. 9(10)-Hydroxystearic acid was esterified with commercial iso-octyl alcohol, then acetylated; b.p. 178°C./0.02 mm.; saponification no. 242; acid no. 1.2; $n^{30/D}$ 1.4460.

Butyl 9,10(10,9)-Hydroxyacetoxystearate. This was a commercial product prepared by the acetic acid ring opening of butyl 9,10-epoxystearate; saponification no. 223; acid no. 6.5; $n^{30/D}$ 1.4580.

Butyl Polyacetoxystearate. This commercial product is probably a mixture of butyl mono-, di-, and triacetoxystearates. It was used as received; saponification no. 342; acid no. 3.5; $n^{30/D}$ 1.4502.

Isobutyl 9,10-Epoxy-12-Acetoxystearate. The commercial preparation was used as received; saponification no. 265; acid no. 3; $n^{30/D}$ 1.4528.

2-Ethyl-1-Butyl 12-Acetoxystearate. 12-Hydroxystearic acid was esterified with 2-ethyl-1-butanol, then acetylated; b.p. 178°C./0.01 mm.; saponification no. 253; acid no. 1.2; $n^{30/D}$ 1.4453.

Butyl 12-Acetoxystearate. 12-Hydroxystearic acid was esterified with *n*-butanol and acetylated; saponification no. 272; acid no. 1.1; $n^{30/D}$ 1.4430.

Butyl 9(10)-Benzoxystearate. Butyl 9(10)-hydroxystearate (0.4m) was dissolved in a mixture of pyridine (0.5m) and benzene (150 ml.). The solution was added dropwise with good stirring to a solution of benzoyl chloride (0.44m) in benzene (100 ml.) maintained at 25°C. The benzene solution of the product was washed first with water containing enough hydrochloric acid to remove the slight excess of pyridine, then with aqueous sodium carbonate to remove the unreacted benzoyl chloride. Washing with distilled water was continued until the wash water was neutral to litmus. The solvent was removed, and the product was dried by heating in a water bath under a moderate vacuum. Distillation of the crude material gave butyl 9(10)-benzoxystearate; b.p. 206°C./0.08 mm.; saponification no. 241; acid no. 1.4; $n^{30/D}$ 1.4754.

Phenyl 12-Acetoxystearate. 12-Acetoxystearic acid was prepared by acetylation of the corresponding hydroxy acid. Oxalyl chloride (0.6m) (19) was added dropwise with stirring to a solution of 12-acetoxystearic acid (0.32m) in 200 ml. of benzene maintained at 25°C. After the addition the temperature was raised to 65°C. and maintained there for two hours with stirring. The solution was then placed in a hot water bath, and the benzene and excess oxalyl chloride were removed by means of a water aspirator. The 12-acetoxystearoyl chloride (0.32m) was dissolved in 200 ml. of benzene and to this solution phenol (0.32m), dissolved in pyridine (0.40m), was added dropwise with good stirring, maintaining the reaction temperature at 25°C. The mixture was then poured into water containing enough hydrochloric acid to remove the slight excess of pyridine. The benzene solution was washed with distilled water until the washes were acid-free to litmus. The solvent was evaporated, and the crude product was dried under vacuum in a hot-water bath. The phenyl 12-acetoxystearate was vacuum-distilled; b.p. 174°C./0.03 mm.; saponification no. 266; acid no. 4.5; $n^{30/D}$ 1.4730.

Phenyl 9(10)-Benzoxystearate. This was prepared from 9(10)-hydroxystearic acid, phenol, and benzoyl chloride according to the procedures already described in this paper. The high molecular weight of the product made it necessary to purify it by molecular distillation. The distillate obtained at 250°C./20 microns was a light yellow oil; saponification no. 239; acid no. 3.4.

Phenyl-12-Benzoxystearate. This was prepared from 12-hydroxystearic acid, phenol, and benzoyl chloride; saponification no. 230; acid no. 5.2; $n^{30/D}$ 1.4820.

Methoxyethyl 12-Acetoxystearate. This compound was prepared by esterification of 12-hydroxystearic acid with methoxyethanol, followed by acetylation. The vacuum-dried ester had b.p. 170–180°C./0.05 mm., saponification no. 277; acid no 1.9; $n^{30/D}$ 1.4444.

Phenoxyethyl 12-Acetoxystearate. 12-Hydroxystearic acid was esterified with phenoxyethanol, then acetylated; b.p. 207°C./0.04 mm.; saponification no. 234; acid no. 3.0; $n^{30/D}$ 1.4762.

2-Methoxyethoxyethyl 12-Acetoxystearate. 12-Hydroxystearic acid was esterified with methoxyethoxyethanol, then acetylated; b.p. 184°C./0.05 mm.; saponification no. 256; acid no. 3.9; $n^{30/D}$ 1.4472.

Ethylene Glycol Di(12-Acetoxystearate). 12-Acetoxystearoyl chloride was prepared by acetylation of 12-hydroxystearic acid, followed by reaction with a 100% molar excess of oxalyl chloride in benzene solution, as described above. Esterification with ethylene glycol was conducted with pyridine as the condensing agent in benzene solution, also as described above. The product was isolated by molecular distillation at 230°–250°C./4–6 microns; saponification no. 305; acid no. 2.3; $n^{30/D}$ 1.4548.

Diethylene Glycol Di(12-Acetoxystearate). Diethyl-

TABLE I

Properties of Vinyl Copolymer (VYDR) Plasticized with Long-Chain Esters

Long-chain ester	Tensile strength	Elongation	Modulus 100%	Clash-Berg stiffening temperature	Volatility weight loss	Migration weight loss
Group A	*lbs./sq. in.*	%	*lbs./sq. in.*	*°C.*	%	%
Butyl 9(10)-acetoxystearate	2130	410	1060	—67	3.0	33.1
Butyl 9(10)-butyroxystearate	2670	360	1370	—62	5.3	23.4
Isooctyl 9(10)-acetoxystearate	2168	260	1410	—60	....	......
2-Ethyl-1-hexyl 9(10)-acetoxystearate	2330	240	1450	—57	....	......
Butyl 12-acetoxystearate	2600	370	1260	—54	1.9	22.2
2-Ethyl-1-butyl 12-acetoxystearate	2730	320	1450	—54	1.3	22.5
2-Ethyl-1-butyl 9(10)-acetoxystearate	2660	360	1435	—53	2.0	23.2
Butyl 12-acetoxystearate (commercial sample)	2400	310	1090	—46	....	......
Butyl 9(10)-benzoxystearate	2800	300	1650	—43	2.3	16.6
Butyl 2-acetoxystearate	2750	340	1510	—37	5.3	21.4
Ethylene glycol di(12-acetoxystearate)	2970	350	1855	—35	2.2	17.1
Diethylene glycol di(12-acetoxystearate)	2920	295	1870	—35	2.5	15.4
1,2-Propanediol di(12-acetoxystearate)	2940	340	1910	—35	1.5	16.7
1,3-Propanediol di(12-acetoxystearate)	2840	290	1760	—35	0.8	15.8
Group B						
Methyl 9(10)-butyroxystearate	2615	390	1290	—54	3.2	23.4
Methoxyethyl 12-acetoxystearate	2820	370	1140	—51	1.3	20.7
Methyl 9(10)-acetoxystearate	2740	420	1200	—50	4.1	20.4
Methyl 12-acetoxystearate	2515	370	880	—49	3.7	19.4
2-Methoxyethoxyethyl 12-acetoxystearate	2710	360	1180	—46	0.8	18.8
Butyl 12-(methyladipoxy)stearate	2720	360	1300	—44	0.6	15.8
Phenoxyethyl 12-acetoxystearate	2970	370	1480	—33	0.5	13.3
Butyl 9,10-diacetoxystearate	2540	300	1190	—32	2.1	10.3
Isobutyl 9,10-epoxy-12-acetoxystearate	2915	360	1520	—32	1.0	8.4
Phenyl 12-acetoxystearate	2940	390	1360	—28	0.5	13.9
Methyl 9,10-diacetoxystearate	3000	375	1000	—26	0.7	8.3
Butyl polyacetoxystearate	2890	370	1670	—22	2.5	6.3
Butyl 9,10,12-triacetoxystearate	3115	340	1300	—15	....	......
Controls						
Di-2-ethylhexyl sebacate	2670	345	1090	—61	0.7	24.2
Di-2-ethylhexyl azelate	2700	280	1170	—59	1.7	22.6
Di-2-ethylhexyl adipate	2490	345	1000	—58	4.1	23.7
Di-2-ethylhexyl phthalate	2830	350	1480	—29	1.1	6.0

ene glycol was used instead of ethylene glycol in the previous procedure. The product was isolated by molecular distillation at 230°–250°C./6 microns; saponification no. 278; acid no. 4.6; $n^{30/D}$ 1.4548.

1,2-Propanediol Di(12-Acetoxystearate). 1,2-Propanediol was used as the glycol. The product was isolated by molecular distillation at 210°–220°C./4–5 microns; saponification no. 295; acid no. 2.4; $n^{30/D}$ 1.4528.

1,3-Propanediol Di(12-Acetoxystearate). The procedure followed was the same as that for the other glycol derivatives, using 1,3-propanediol. The product was isolated by molecular distillation at 220°–240°C./6–8 microns; saponification no. 297; acid no. 3.5; $n^{30/D}$ 1.4545.

Butyl 2-Acetoxystearate. 2-Hydroxystearic acid was esterified with *n*-butanol, using toluene as an entraining agent for the water and 2% perchloric acid (72%) as the catalyst. The ester was isolated, then acetylated by the procedures already described; boiling range 139°–152°C./0.02–0.07 mm.; saponification no. 286; acid no. 3.0; $n^{30/D}$ 1.4408.

Butyl 12-(Methyladipoxy)Stearate. Butyl 12-hydroxystearate was prepared by esterification of 12-hydroxystearic acid. Monomethyl adipoyl chloride was prepared from monomethyl adipate by the oxalyl chloride procedure and then condensed with the hydroxystearate ester in the presence of pyridine by the described procedure. Molecular distillation gave a product collected at 140°–165°C./6–8 microns; saponification no. 302; acid no. 1.8; $n^{30/D}$ 1.4495.

Plasticizer Evaluation. The resin used for the plasticizer investigations was a commercial copolymer (Vinylite VYDR) containing 95% vinyl chloride and 5% vinyl acetate. The standard recipe for milling and molding was as follows: resin 64.0%, plasticizer 35%, stabilizer ($PbCO_3$) 1.0%. Note that no mold lubricant was used (usually 0.5% stearic acid) since the plasticizers themselves gave good mold release.

The plasticizer was added to the dry mixture of resin and $PbCO_3$ prior to milling. The milling was carried out on a 6 × 12-in. rubber mill at a temperature of 300°F. for approximately 8 min. The sheeted resin was then molded in a standard 6 × 6 × 0.075-in. mold. The mold containing the resin was first heated at 300°F. for 10 min. without pressure, then pressured to 1,000 pounds per square inch and held for an additional 10 min. at the 300°F. molding temperature. The mold was then cooled under pressure to approximately room temperature.

All test procedures were standard ASTM methods, with the exception of heat stability and migration. For determination of tensile strength, ultimate elongation, and 100% modulus, dumbbell specimens were die-cut from the molded sheets parallel to the milling axis (2). The measurements were made on an IP-4 Scott tester at a loading rate of 73 pounds per minute at 73°F. and 50% relative humidity. The specimens were equilibrated to these conditions for at least 24 hrs. prior to testing (3). Torsional modulus as a function of temperature was determined with the Clash-Berg Stiffness tester (4). The results are given in Table I and Figure 1.

Migration of the plasticizers from the resin was measured according to the procedure of Geenty (9) by burying a weighed test specimen in adsorbent powder consisting of a hydrated silica (sold as "silica acid, analytical grade, 100 mesh"), and following the loss in weight as a function of time at 30°C. The basis for this method is the removal of plasticizer as soon as it diffuses to the surface.

Volatility was determined by use of activated carbon (Columbia activated carbon 6- to 14-mesh) (5); the volatilized plasticizer was adsorbed by the activated carbon in a closed container.

Light stability tests were conducted on molded specimens in an Atlas Twin Arc WeatherOmeter. The specimens were also subjected to temperatures of about 75°C. during their exposure. Samples were exposed

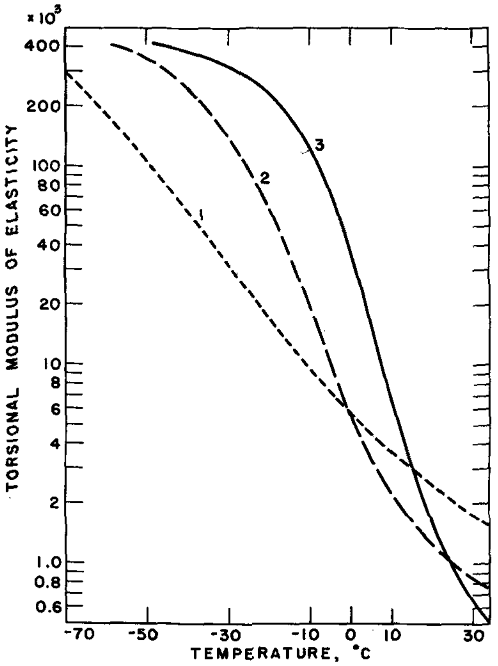

FIG. 1. Change in modulus as a function of temperature of VYDR plasticized with 35% of (1) di-2-ethylhexyl sebacate, (2) di-2-ethylhexyl phthalate, and (3) tricresyl phosphate.

for 24, 48, 72, 96, and 144 hrs. and examined for changes in color and physical appearance.

Heat-stability tests were conducted on molded specimens in an air convection oven at 160°C. for 3 hrs. The samples were observed for changes in color and physical appearance.

Results and Discussion

Mechanical Properties. Table I shows the properties of VYDR plasticized with the esters of hydroxystearic acids. For comparison, the resin plasticized with the di-2-ethylhexyl esters of sebacic, azelaic, adipic, and phthalic acids are also included in the table. Most of the compounds compare favorably with the controls with respect to tensile strength, elongation, and 100% modulus. Table II lists the compounds tested which were incompatible.

TABLE II

Incompatible Compounds

n-Octyl 9(10)-acetoxystearate
n-Butyl 9,10(10,9)-hydroxyacetoxystearate
Phenyl 9(10)-benzoxystearate
Phenyl 12-benzoxystearate

Gradually decreasing the temperature causes plasticized compositions eventually to become stiff and brittle. The stiffness increases gradually and can be measured by observing the change in torsional modulus as a function of temperature, according to the procedure of Clash and Berg (6). These workers arbitrarily selected a torsional modulus of 135,000 lbs. per square inch as the borderline between a rigid and a nonrigid material. The temperature required to reach this modulus is the stiffening or Clash-Berg temperature.

From Figure 1 it is clear that the plotting of torsional modulus as a function of temperature (stiffness-temperature relationship) gives a curve which is characteristic of the plasticizer used (1).

The compatible esters described in this study are divided into two groups in Table I, A and B, according to the shape of the curve obtained from a log plot of torsional modulus *versus* temperature. Figure 2 is a plot of the limits of modulus as a function of temperature for VYDR plasticized with the compounds in Group A. These compounds have modulus-temperature curves similar to that for di-2-ethylhexyl sebacate (curve 1, Figure 1); those in group B, as shown in Figure 3, approximate the characteristic "S" curve of di-2-ethylhexyl phthalate (curve 2, Figure 1). The important fact is that the compounds in group A have a lower rate of change in torsional modulus with decreasing temperature than the compounds in group B. None of the plasticizers tested showed the rapid, undesirable increase in torsional modulus with decrease in temperature exhibited by tricresyl phosphate (curve 3, Figure 1).

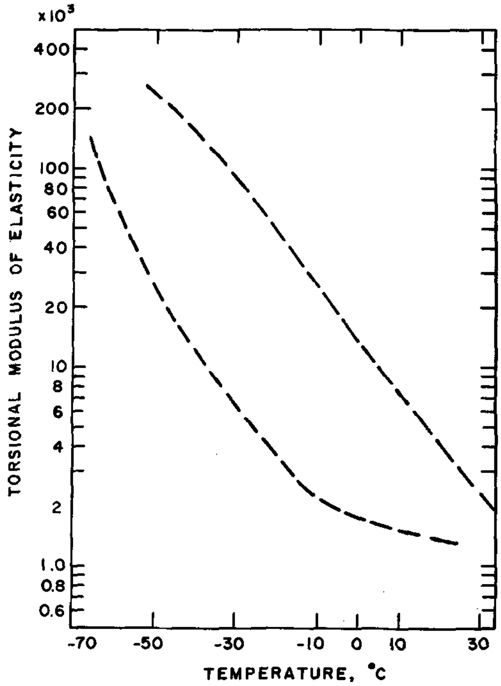

FIG. 2. Limits of modulus as a function of temperature for VYDR plasticized with the compounds in Group "A" of Table I.

Butyl 9(10)-acetoxystearate at the 35% level in the resin has the lowest stiffening temperature we have yet observed (−67°C.). In fact, the first seven compounds in group A, Table I, and the first four in group B, have excellent low-temperature characteristics. With the exception of the last four compounds in group B, all the other long-chain esters are superior to di-2-ethylhexyl phthalate in this respect.

It is interesting to note that all the compounds in Group A of Table I have exactly two ester groups in each stearate portion of the molecule, none of them being a methyl ester. This group shows plasticizer properties similar to those obtained with aliphatic diesters of adipic, azelaic, and sebacic acids. Group B consists of methyl esters, aromatic esters, and esters containing three or more polar centers (or functional groups) in the stearate portion of the molecule.

Permanence. Samples of the milled, molded sheets

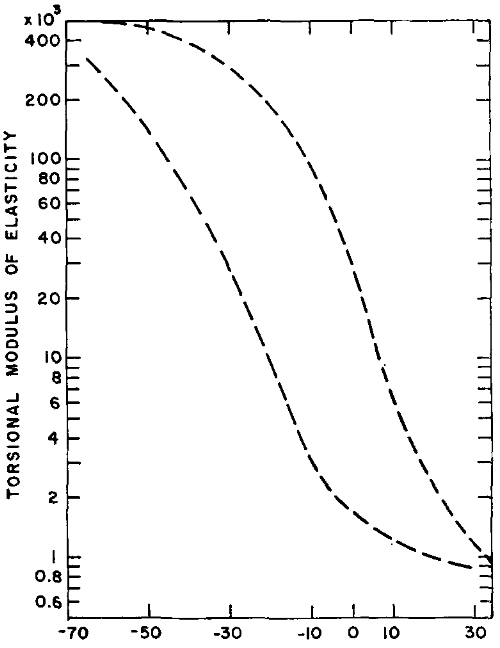

FIG. 3. Limits of modulus as a function of temperature for VYDR plasticized with the compounds in Group "B" of Table I.

of plasticized compositions were stored in a constant temperature room at 73°F. and 50% relative humidity for at least one year. These samples were then examined to determine the permanence of the plasticizer as indicated by the absence or amount of surface exudate. The compounds showing the best results in this test are listed in Table III. This surface exudation after aging has been known for some time to be the principal objection to the use of fatty acid derivatives as plasticizers for vinyl chloride resins. It appears that this objection can be overcome if the fatty acid portion of the molecule contains three or more ester groups, two ester groups one of which is a methyl ester, or a single aromatic structure in the molecule.

TABLE III
Compatible After 1 Year or More

None to Traces of Exudate
Butyl 9,10,12-triacetoxystearate
Methyl 12-acetoxystearate
Methyl 9,10-diacetoxystearate
Butyl 12(methyladipoxy)-stearate
Phenyl 12-acetoxystearate
Butyl 9,10-diacetoxystearate
Butyl 9(10)-acetoxystearate
Methyl 9(10)-butyroxystearate
Methoxyethyl 12-acetoxystearate
Butyl 2-acetoxystearate
Methyl 9(10)-acetoxystearate
Isobutyl 9,10-epoxy-12-acetoxystearate
2-Ethyl-1-butyl 12-acetoxystearate
2-Methoxyethoxyethyl 12-acetoxystearate
1,2-Propanediol di(12-acetoxystearate)
1,3-Propanediol di(12-acetoxystearate)

Butyl 2-acetoxystearate seems to be an exception in many respects. Practically all previous tests show that an unsubstituted chain of over 8 to 10 carbons in length anywhere in a plasticizer molecule gives undesirable properties, but in this compound there is an unsubstituted chain of 16 carbon atoms. The compound has good permanence and compares very favorably with all the compounds tested in its other physical properties.

Volatility. As would be expected, the lower molecular weight compounds have the largest volatilization losses. All of the compounds reported here are high-boiling compounds, and none of them are objectionable in this respect.

Light Stability. The effect of light on the color, flexibility, and surface appearance of the molded specimens was determined. The tests were carried out as described previously in this paper. The following nine samples showed no change after exposure for 144 hrs.: methyl 9(10)-acetoxystearate, butyl 9(10)-acetoxystearate, methyl 9(10)-butyroxystearate, 2-ethylbutyl 9(10)-acetoxystearate, butyl 12-acetoxystearate, methoxyethyl 12-acetoxystearate, phenoxyethyl 12-acetoxystearate, butyl 2-acetoxystearate, and phenyl 12-acetoxystearate. The remainder of the compounds tested showed a darkening in the color of the molded sheets, blistering, and the appearance of exudate on the exposed surface. Under the conditions of this test, samples plasticized with di-2-ethylhexyl phthalate showed a tacky surface, discoloration, and a loss of flexibility after only 24 hrs. of exposure.

Heat Stability. The heat stability of the plasticized specimens was judged by the color change and flexibility after 3 hrs. of exposure at 160°C. Di-2-ethylhexyl phthalate develops an intense brown color during this test but with little or no change in flexibility. The following seven samples showed no change in physical properties and only a very slight color change, from white to light cream: butyl 9,10-diacetoxystearate, butyl 12-acetoxystearate, butyl 9(10)-acetoxystearate, methyl 9(10)-butyroxystearate, butyl 9(10)-butyroxystearate, butyl 2-acetoxystearate, and phenyl 12-acetoxystearate. The remainder of the samples developed a light tan to brown color with some loss in flexibility, but not as pronounced a color change as that of the control sample, di-2-ethylhexyl phthalate.

Migration. It was observed during the work on plasticizer evaluation of epoxy esters (19), as well as in the present study, that compounds which show good low-temperature behavior in plasticized compositions always have high migration. Consideration of the experimental data in Table I suggests that some relationship exists between Clash-Berg stiffening temperatures and loss of plasticizer through migration. This apparent relationship is shown by Figure 4. Seven of the points which do not fall on the curve represent compounds which have major structural differences from the compounds on or closer to the curve. These compounds are butyl 2-acetoxystearate (compound 2), the four glycol esters (compounds 3, 4, 5, and 6), and the two esters containing the phenyl group in the alcohol segment of the molecule (compounds 7 and 9). Butyl 9(10)-butyroxystearate (compound 1) and isobutyl 9,10-epoxy-12-acetoxystearate (compound 8) should probably both be nearer to the curve.

To assume that such a relationship exists between two sets of data obtained in unrelated ways and at different temperatures may at first appear unreasonable. Consideration of the Kinetic or Mechanistic Theory of Plasticizer Action, as discussed by Doolittle (7), Alfrey (1), Fuoss (17), and others, indicates that Clash-Berg temperatures and migration losses may be two different methods of measuring the same property of plasticized resins, that is, plasticization may be dependent on diffusion of the plasticizer molecule through the otherwise rigid plastic mass. Migration is a result of diffusion to the surface of the plastic material, followed by removal by adsorbent.

A rigid, polymeric material consists of a number of polymer molecules (P), each of which possesses spe-

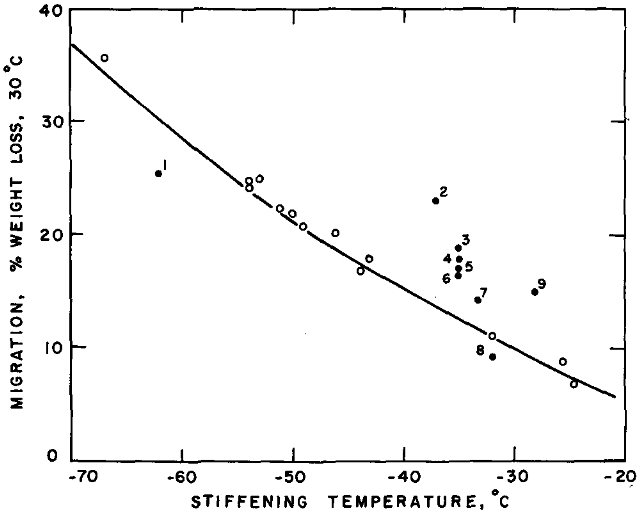

Fig. 4. Relationship between weight loss due to migration and the Clash-Berg stiffening temperature. (1) Butyl 9(10)-butyroxystearate, (2) butyl 2-acetoxystearate, (3) ethylene glycol di(12-acetoxystearate), (4) 1,2-propanediol di(12-acetoxystearate), (5) 1,3-propanediol di(12-acetoxystearate), (6) diethylene glycol di(12-acetoxystearate), (7) phenoxyethyl 12-acetoxystearate, (8) isobutyl 9,10-epoxy-12-acetoxystearate, (9) phenyl 12-acetoxystearate.

cific points or centers which are capable of exerting strong intermolecular forces (localized dipoles). When this interaction is between adjacent polymer molecules, aggregates are formed. As the temperature is raised, thermal agitation tends to break up some of the aggregates and the polymer becomes less rigid. A dynamic equilibrium then exists, which is a function of temperature, and may be expressed,

$$\underset{\text{aggregation}}{\mathrm{P-P}} \rightleftharpoons \underset{\text{disgregation}}{\mathrm{P+P}} \qquad (1)$$

This equilibrium will shift to the right as the temperature is raised and to the left as the polymer is cooled. The plasticizer (S) is a relatively low molecular weight molecule which also contains a localized dipole or a polarizable center. The molecular motion of the plasticizer or its mobility is also a function of temperature and may be represented,

$$\underset{\text{association}}{\mathrm{S-S}} \rightleftharpoons \underset{\substack{\text{nonassociation,}\\ \text{mobile phase}}}{\mathrm{S+S}} \qquad (2)$$

In a binary mixture of plasticizer and polymer there will be an attraction of specific points on the polymer chain for the plasticizer molecule; this interaction is sensitive to changes in temperature and can be designated by

$$\underset{\text{solvation}}{\mathrm{P\cdots S}} \rightleftharpoons \underset{\text{desolvation}}{\mathrm{P+S}} \qquad (3)$$

It is possible then that plasticizer and polymer molecules are engaged in continuous equilibrium involving all three reactions, dependent upon temperature, concentration, the structure of the molecules involved, and the magnitude of the attractive forces.

The elevated temperatures employed during the mixing and milling of the components of the plasticized composition, with the accompanying shift of equilibrium to the right in equation *1*, enables the plasticizer molecules to enter into the polymer lattice and establish the equilibrium indicated in equation *3*. It is evident that to be effective as a plasticizer the relatively low-molecular weight compound must be able to overcome the polymer-polymer interaction (aggregation) and to align itself alongside the polar center of the polymer. Once this interaction has been established and the temperature is lowered to determine the limits of flexibility, then an additional factor may intervene; this has been called "compound formation" (1). The following diagram may then represent the picture for the entire dynamic equilibria of the plasticized system

$$\begin{tikzcd}
\underset{\text{aggregation}}{\mathrm{P-P}} \arrow[rr, shift left] \arrow[rr, leftarrow, shift right] & & \underset{\text{disgregation}}{\mathrm{P+P}} \arrow[d, shift left] \arrow[d, leftarrow, shift right] & (1) \\
\underset{\substack{\text{``compound}\\ \text{formation''}}}{\mathrm{2\,P-S}} \arrow[r, shift left] \arrow[r, leftarrow, shift right] & \underset{\text{solvation}}{\mathrm{2\,P\cdots S}} \arrow[r, shift left] \arrow[r, leftarrow, shift right] & \underset{\text{desolvation}}{\mathrm{2\,P+2\,S}} \arrow[d, shift left] \arrow[d, leftarrow, shift right] & (4) \\
 & \underset{\text{association}}{\mathrm{S-S}} \arrow[r, shift left] \arrow[r, leftarrow, shift right] & \underset{\text{nonassociation}}{\mathrm{S+S}} & (2)
\end{tikzcd}$$

As the temperature is lowered for this system, the shift of equilibria to the left would eventually give a rigid material. This is presumed to be the basis for the Clash-Berg torisonal-modulus *vs.* temperature curves. A good low-temperature plasticizer slows down or resists this shift of the equilibria to the left as the temperature is lowered. At 30°C., the temperature at which migration losses are measured, the equilibria of this system with such a plasticizer are shifted farther to the right. This shift allows the mobile plasticizer to diffuse through the plastic composition, eventually reaching the surface where it is irreversibly adsorbed by the silicic acid used in the migration test.

In the system described in this paper, it is reasonable to assume that in order for a low-molecular weight molecule to be an efficient plasticizer it must have sufficient attraction for the polymer molecule to overcome polymer-polymer interaction. It must also retain enough mobility, by participating in the equilibria shown above, to be able to diffuse through the system if it is to impart good low-temperature flexibility. Unfortunately this diffusion process will eventually bring the plasticizer molecule to the surface of the plasticized mass where it can irreversibly migrate to strongly polar adsorbents.

Summary

Thirty-one acyloxy or aryloxy esters prepared from hydroxystearic acids have been evaluated as plasticizers for a vinyl chloride-vinyl acetate copolymer (95:5). Many of them were found to be primary plasticizers, having outstanding low-temperature performance when employed at the 35% level. Formulations with these compounds compared quite favorably in tensile properties with those containing the di-2-ethylhexyl esters of phthalic, sebacic, azelaic, and adipic acids. Volatility losses were similar to those of the four di-2-ethylhexyl esters. The loss of plasticizer through migration was equal to or less than that from compositions containing the esters of sebacic,

azelaic, and adipic acids but was greater than that of the phthalate ester.

A mechanistic scheme of plasticizer-polymer interaction has been presented, proposing that the rate of diffusion of plasticizer through the polymer mass is a controlling factor in both good low-temperature performance and the resulting high migration losses. Methyl esters, some aromatic esters, and esters containing three or more polar centers have improved permanence but show a more rapid change in torsional modulus as the temperature is lowered during the determination of the Clash-Berg stiffening temperature.

REFERENCES

1. Alfrey, T. Jr., "Mechanical Behavior of High Polymers," Interscience Publishers Inc., New York (1948).
2. Am. Soc. Testing Materials, Philadelphia, Standards, ASTM D 412-51T.
3. Am. Soc. Testing Materials, Philadelphia, Standards, ASTM D 882-56T.
4. Am. Soc. Testing Materials, Philadelphia, Standards, ASTM D 1043-51.
5. Am. Soc. Testing Materials, Philadelphia, Standards, ASTM D 1203-55.
6. Clash, R. F. Jr., and Berg, R. M., Ind. Eng. Chem., *34*, 1218 (1942).
7. Doolittle, A. K., "The Technology of Solvents and Plasticizers," John Wiley and Sons Inc., New York (1954).
8. FIAT Report 861, "Plasticizers for Polyvinyl Chloride," July 23, 1946.
9. Geenty, J. R., India Rubber World, *126*, 646 (1952).
10. Greenspan, F. P., and Gall, R. J., Ind. Eng. Chem., *45*, 2722 (1953).
11. Gruber, W., and Machemer, H., U. S. 2,332,849, Oct. 26, 1943.
12. Hunter, M. J., and Kropscott, E. L., U. S. 2,385,359, Sept. 25, 1945.
13. Kadesch, R. G., Modern Plastics, *29*, No. 12, 111 (1952).
14. Knight, H. B., Koos, R. E., and Swern, Daniel, J. Am. Oil Chemists' Soc., *31*, 1 (1954).
15. Lawrence, R. R., and McIntyre, E. B., Ind. Eng. Chem., *41*, 689 (1949).
16. Magne, F. C., and Mod, R. R., J. Am. Oil Chemists' Soc., *30*, 269 (1953).
17. Mead, D. J., Tickenor, R. L., and Fuoss, R. M., J. Am. Chem. Soc., *64*, 283 (1942).
18. Teeter, H. M., and Cowan, J. C., U. S. 2,652,411, Sept. 15, 1953; Teeter, H. M., Gast, L. E., Bell, E. W., and Cowan, J. C., Ind. Eng. Chem. *45*, 1777 (1953); Gast, L. E., Croston, C. B., Schneider, W. J., and Teeter, H. M., *ibid.*, *46*, 2205 (1954).
19. Witnauer, L. P., Knight, H. B., Palm, W. E., Koos, R. E., Ault, W. C., and Swern, Daniel, Ind. Eng. Chem., *47*, 2304 (1955).

[Received December 8, 1958]

New Reactions of Long-Chain Isocyanides[1]

ERIC JUNGERMANN and FREDERICK W. SMITH, Armour Chemical Division, Chicago, Illinois

THE ISOCYANIDES were discovered about 100 years ago by Gautier, who prepared them by treating an alkyl iodide with silver cyanide (1). In the late nineteenth century Nef (2, 3) investigated reactions of short-chain and aromatic isocyanides with many reagents such as halogens, acid chlorides, sulfur, hydrogen, water, or phosgene. These reactions indicated a peculiar type of unsaturation of the isocyanide group located entirely at the terminal carbon atom; this is nowadays usually presented by the resonance structures:

$$R\ddot{N}{=}C\colon \longleftrightarrow R\overset{+}{N}{\equiv}\overset{-}{C}\colon$$

Addition reactions were reported to take place at the negative carbon atom, giving products with the following structures:

$$R\ddot{N}{=}C\colon + XY \longrightarrow R\ddot{N}{=}C\begin{array}{l}\diagup X\\ \diagdown Y\end{array}$$

In 1920 Passerini (4, 5) re-investigated and confirmed many of the results of earlier workers and also discovered several new reactions. Some typical reactions are shown in Table I.

None of the earlier workers investigated the reactions of fatty isocyanides. In our present studies a series of fatty isocyanides were prepared by the "carbylamine reaction" by heating a primary amine with chloroform and potassium hydroxide in a solvent such as *n*-butanol:

$$C_{12}H_{25}NH_2 + CHCl_3 + 3KOH \longrightarrow C_{12}H_{25}N = C + 3KCl + 3H_2O$$

The reactions of the long-chain isocyanides were studied with three classes of compounds: halogens, alkylating agents (*e.g.*, benzyl chloride, methyl sulfate), and acid chlorides. During our investigation some startling differences were observed between the behavior of the fatty isocyanides and the reported behavior of the corresponding short-chain or aromatic isocyanides. These are the subject of this paper.

TABLE I

Reactions of Isocyanides

	Reference
1. $ArNC + RCHO \longrightarrow RCO.CH = NAr$	(4)
2. $ArNC + RCO.Cl \longrightarrow RCO\overset{Cl\diagdown}{C} = NAr$	(2)
3. $RCN + COCl_2 \longrightarrow RN = \overset{Cl\diagdown}{C} - CO - \overset{\overset{Cl}{\vert}}{C} = NR$	(5)
4. $RNC + R'MgX \longrightarrow RN = \overset{\overset{R'}{\vert}}{C} - MgX$	(6)
5. $RNC + Cl_2 \longrightarrow RN = CCl_2$	(7)
6. $RNC + HCl \longrightarrow RN = \overset{\overset{H}{\vert}}{C} - Cl$	(7)
7. $RNC + H_2 \longrightarrow RNHCH_3$	(7)
8. $ArNC + R'CHO + R''COOH \longrightarrow ArNHCO\underset{\underset{OCOR''}{\vert}}{C}HR'$	(8)

Experimental

Preparation of Isocyanides

All the isocyanides were prepared by the reaction of a primary amine with chloroform and potassium hydroxide. The preparation of dodecylisocyanide is used as a typical example.

Double-distilled dodecylamine (370 g., 2 moles) was dissolved in chloroform (400 g., 3.3 moles). This solution was added slowly from a dropping funnel to a well-stirred solution of potassium hydroxide (400 g. 85% pellets, 6 moles) in 1,400 ml. of *n*-butanol.

After all the amine-chloroform mixture had been added, the resultant solution was refluxed for five to six hours. Water was added to dissolve the salts, the butanol layer was separated and washed with water. The butanol was then stripped under vacuum, taking care to allow the pot temperature to reach no higher than 140°C. An infrared spectrum of the crude iso-

---

[1] Presented at Fall Meeting, American Oil Chemists' Society, Chicago, Ill., October 20–22, 1958.