Acyl Esters from Oxo-Derived Hydroxymethylstearates as Plasticizers for Polyvinyl Chloride[1]

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ABSTRACT

Hydroxymethylstearates were made by hydroformylation or oxo reaction of mono- and polyunsaturated fats and esters with either rhodium-triphenylphosphine or cobalt carbonyl catalysts. Rhodium-oxo products were hydrogenated with nickel catalyst, whereas, cobalt-oxo products were heated directly under hydrogen pressure. Hydroxymethyl fatty alcohols also were prepared by a two-step copper-chromite hydrogenation of hydroformylated linseed fatty esters. Of these hydroxymethyl compounds, 39 were converted to their acetates and other acyloxy derivatives and then evaluated as primary plasticizers for polyvinylchloride. For compounds with good compatibility, methyl 9(10)-acetoxymethylstearate and 9(10)-acetoxymethyloctadecyl acetate gave the lowest flex temperature (-47 C). An unusual combination of good compatibility and low flex temperature was obtained with 2-methoxyethyl 9(10)-acetoxymethylstearate. Addition of more than one acetoxymethyl group in the fatty acid molecule, made possible by rhodium hydroformylation, imparted good compatibility and outstanding permanence (low migration and volatility) but raised flex temperature. Butyl diacetoxymethylstearate, methyl triacetoxymethylstearate, and polyacetoxymethyloctadecyl acetate from linseed esters displayed good compatibility, strength, and volatility characteristics. As glycerides, acetoxymethylated safflower and linseed oils produced good compatibility and outstanding permanence, better than esters commonly used as commercial plasticizers.

INTRODUCTION

Research at the Northern Center on catalytic reactions of vegetable oils with carbon monoxide and hydrogen has led to ways of introducing polar functional groups into known positions on the unsaturated fatty acid chain. By catalytic hydroformylation or oxo reaction one or more formyl groups have been substituted into polyunsaturated fats and esters (1-4). From these aldehyde products, several new and unusual derivatives of industrial interest have been made. Oxo fatty derivatives made as plasticizers for polyvinylchloride (PVC) include acetal esters (5,6), esters of mono-, di-, and tricarboxystearic acid (E.J. Dufek, unpublished data), and acetoxyglycerol acetal esters (W.E. Neff, unpublished data). This paper deals with another series of oxo-derived PVC plasticizers with acyloxymethyl functionality that are of particular interest because of their permanence.

Various fatty derived plasticizers are commercially used. Acetylated monoglycerides and aliphatic esters of dihydroxystearic acid reportedly serve as plasticizers for PVC (7,8), and alkyl esters of 12-acetoxystearic acid as plasticizers for ethyl cellulose (9). Many acyl or aryl esters of mono-, di-, and trihydroxystearic acid are efficient low-

temperature plasticizers when formulated with a vinyl chloride-vinyl acetate (95:5) copolymer (9). Acetylated castor oil and esters are suitable secondary plasticizers, but epoxidation of their unsaturation improves their compatibility and thermal stability (10). Similarly, epoxidized soybean and linseed oils, epoxy stearate, and epoxy esters of tallow fatty acids are used both as plasticizers, and as heat and light stabilizers. These esters also exhibit good low temperature properties (11).

More than 4 billion pounds of PVC is produced per year, and a large share of this market is found in flexible products containing as much as 50% plasticizer (12). Production of plasticizers in 1971 was ca. 1.5 billion pounds, dominated by di-2-ethylhexyl phthalate (DOP) (13). Because of its volatility, migration, and incomplete biodegradability, DOP is suspect as an environmental contaminant (14,15). Any new plasticizer to be superior to DOP would have to show lower volatility, migration, and solvent extractability, as well as better biodegradability. Some of these requirements are met by several of the oxo-derived acyloxymethyl esters described in this paper.

EXPERIMENTAL PROCEDURES

Hydroxymethylated Oils and Esters

Soybean, linseed, safflower, and castor oils and their alkyl esters, as well as oleic esters, were hydroformylated with a rhodium-triphenylphosphine catalyst under standard conditions (110 C and 2000 psi H_2 + CO) (2,18). A modified procedure giving higher yields of polyformyl products from polyunsaturates consisted of hydroformylating first at 90 C and then at 110 C until gas absorption ceased at each temperature. By this modified hydroformylation procedure, 10% more diformyl esters (75% vs 65%) were produced with safflower methyl esters. The filtered hydroformylated products were converted to the hydroxymethyl derivatives by hydrogenation with Raney nickel in ethanol at 100 C and 1000 psi H_2 (16).

Hydroxymethyl derivatives also were made directly from soybean and linseed esters by conventional hydroformylation with cobalt carbonyl (1) at 120 C and 3500 psi H_2 + CO until gas absorption ceased. The synthesis then was gas vented and replaced with H_2 at 2500 psi. Hydrogenation was carried out with the same cobalt carbonyl oxo catalyst at 175-180 C until H_2 uptake ceased.

Acyloxymethyl esters. Methyl 9(10)-hydroxymethylstearate (16) of 98% purity by gas liquid chromatography (GLC) (OH value, 167.1) was esterified either directly with the acid anhydrides (C_2-C_4) or with short chain fatty acids (C_5-C_{10}) by refluxing under N_2 in xylene solution with 1% concentrated H_2SO_4. Esterification was continued until the theoretical amount of water was collected azeotropically in a Dean-Stark trap. After workup, the esters were distilled and bleached by percolating a petroleum ether solution through a carbon black filter aid column. Analyses of the methyl acyloxymethyl esters by GLC column (JXR, dimethyl silicone Stationary Phase (Applied Science Labs, State College, PA) programmed from 180 to 250 C at 4 C per min (2) were as follows: C_2:98.0; C_3:96.7; C_4:98.8; C_5:98.2; C_6:97.4; C_7:98.6; C_8:95.6; C_9:89.7; and C_{10}:98.6% (impurity:alkyl stearate).

TABLE I

Analyses of Acetoxymethyl Esters and Oils

Acetoxymethyl compounds[a]	Gas liquid chromatographic analyses,[b] (%)					Hydroxyl value[c]		Saponification equivalent[d]	n_D^{20}	D_{25}^{25}
	Pal	St	Mono-	Di-	Tri-	Before acetylation	After			
Me oleate		3.2	95.5	1.3		(167)	---	---	---	---
Mol distilled		1.5	98.5			168	0.6	184	1.4502	0.9344
Me safflower esters	6.6	2.5	16.5	74.4		259	---	---	---	---
Mol distilled			2.4	97.6		310	0.5	151	1.4536	0.9835
Me linseed esters	4.5	3.4	19.8	22.4	49.9	(320)	---	---	---	---
Mol distilled				9.3	90.7	422	0.6	134	1.4609	1.0193
Bu soybean esters	11.1	4.7	36.8	45.7	1.7	213	6	189	1.4536	0.9446
Bu soybean esters (Co)	13.2	8.8	78.0[e]			133	1	226	1.4564	0.9273
Me castor esters	1.0	1.1	13.0	84.9[f]		330	0.1	145	1.4522	0.9835
Oleic safflower oil	4.5	4.4	91.1			174	2	182	1.4636	0.9591
Safflower oil	4.6	2.4	23.9	69.1		249	2	158	1.4660	0.9898
Linseed oil - A	5.4	3.2	19.4	21.2	50.8	320	2	145	1.4677	1.0087
B	5.0	3.6	23.7	24.8	42.9	301	---	---	---	---
C	4.1	3.4	18.1	18.8	55.6	331	---	---	---	---
Castor oil	1.0	1.0	18.9	79.1[f]		310	2	145	1.4642	1.0041
Octadecyl alcohol		3.3	96.7			379	1	197	1.4496	0.9223
Linseed alcohol	6.7	5.6	21.2	25.8	40.7	391	2	174	1.4570	0.9697
Mol distilled			8.8	37.4	53.7	419	---	---	1.4578	---
Mol distilled residue			4.0	20.3	75.7	428	---	---	1.4665	---
Linseed alcohol (Co)	8.9	9.6	81.5[e]			245	6	207	1.4614	0.9497

[a]Samples labeled (Co) are hydroformylated with cobalt carbonyl (1); all others are hydroformylated with rhodium-triphenylphosphine (2).

[b]By gas liquid chromatographic (GLC) analysis of acetylated esters on JXR column (2); Pal = palmitate, St = stearate.

[c]Values in parenthesis are calculated on basis of GLC analysis (monohydroxymethyl:171, dihydroxymethyl:313, trihydroxymethyl:433).

[d]Calculated on basis of GLC analysis (monoacetoxy:188, diacetoxy:149, triacetoxy:128).

[e]Includes several peaks.

[f]9(10)-Hydroxymethyl-12-hydroxystearates.

Alkyl 9(10)-acetoxymethyl esters. Alkyl 9(10)-hydroxymethyl esters were made by hydroformylation followed by hydrogenation of the corresponding alkyl oleate (16). Each ester (130 g) was acetylated by refluxing 1 hr with 150 ml acetic anhydride and N_2 bubbling in the presence of 2 drops concentrated H_2SO_4 (17). Excess acetic anhydride was hydrolyzed with water to acetic acid and removed in vacuo on a rotating evaporator. The solvent stripped ester was decolorized on a carbon black filter aid column. The acetoxymethyl esters were > 97-98% pure by GLC (impurity:alkylstearate). Molecularly distilled (2) methyl 9(10)-acetoxymethylstearate was 98.5% pure by GLC (calcd. for $C_{22}H_{42}O_4$: C, 71.29; H, 11.45; found:C, 71.32; H, 11.53) (Table I).

Polyacetoxymethyl esters and triglycerides. Methyl and butyl hydroxymethyl fatty esters were either acetylated with acetic anhydride:H_2SO_4 as above or refluxed 4 hr with 100% excess acetic anhydride:pyridine (1:3, v/v) based on the OH value of the starting material. After cooling, the reaction mixture dissolved in diethyl ether was acidified and then washed repeatedly with a dilute $NaHCO_3$ solution and water until neutral. The dried solution (Na_2SO_4) was stripped of solvent on a rotating evaporator. The acetoxymethyl esters and triglycerides were analyzed directly for OH content. Analyses by GLC were done on the methyl and butyl esters directly, and on the triglycerides after saponification, esterification with diazomethane, and re-acetylation. Methyl and butyl di- and triacetoxymethylstearates were prepared from the respective esters of safflower and linseed oils by repeated molecular distillation. Analyses of representative samples are given in Table I. Molecularly distilled methyl diacetoxymethylstearate was 97.6% pure by GLC (calcd. for $C_{25}H_{46}O_6$: C, 67.82; H, 10.50; found:C, 67.32, H, 10.54); methyl triacetoxymethylstearate was 90.7% pure by GLC (calcd. for $C_{27}H_{50}O_8$: C, 64.50; H, 10.04; found:C, 65.72; H, 10.02).

Acetoxymethyl fatty acetates. Hydroxymethyloctadecyl alcohol and the hydroxymethyl linseed fatty alcohols were prepared by catalytic hydrogenation of hydroformylated oleic and linseed methyl esters with a copper-chromite

catalyst (10% Cu lot 1106-P, Harshaw Chemical Co., Cleveland, OH). The formyl groups were first hydrogenated to hydroxymethyl at 150 C and 3000 psi H_2 for 1 hr and then the carboxy methyl esters, into alcohols by heating to 280 C and keeping this temperature and pressure for 3-4 hr. The hydrogenated products dissolved in ether were filtered, solvent stripped, and concentrated by molecular distillation (2). The purified hydroxymethyl fatty alcohols then were acetylated with acetic anhydride-pyridine as above. One sample of linseed methyl esters hydroformylated with cobalt carbonyl (1) was hydrogenated with copper-chromite successively at 150 and 280 C and then acetylated as above. Analyses of these products are given in Table I. Molecularly distilled acetoxymethyloctadecyl alcohol was 96.7% pure by GLC (calcd. for $C_{23}H_{44}O_4$: C, 71.81; H, 11.55; found: C, 72.07; H, 11.72).

Acetylated oligomers. Methyl hydroxymethylstearate (100 g) was homopolymerized partially by heating at 240 C under N_2 in the presence of 0.05% CaO for 1 and for 1.5 hr. Extent of polymerization was followed by refractive index and disappearance of OH estimated by infrared (IR) (absorbance at 3500 cm⁻¹ of a CCl_4 solution). Polymerization reduced the OH content in the starting material to ca. half (n_D^{20} 1.4603) after 1 hr and to ca. one-third (n_D^{20} 1.4633) after 1.5 hr. Mol wts, determined by osmometry, of acetylated oligomers were 408 (1.1 monomeric units) and 686 (2.1 monomeric units), respectively. These low degrees of polymerization suggest cyclization or estolide formation. However, preliminary studies showed that acetylated oligomers of higher mol wt were not compatible with PVC.

Trichloroacetoxy acetates. Hydroxymethyl linseed alcohol (50 g; OH value, 391) was refluxed with trichloroacetic acid (25% excess based on OH value) in dry xylene. Water formed azeotropically was collected in a Dean-Stark trap. The products were worked up in the same way as those acetylated with acetic anhydride:H_2SO_4. IR analyses on crude product showed no OH; saponification value, 441.

Benzoyloxymethyl linseed oil. Hydroxymethylated linseed oil (50 g; OH value, 320) was cooled in ice water with
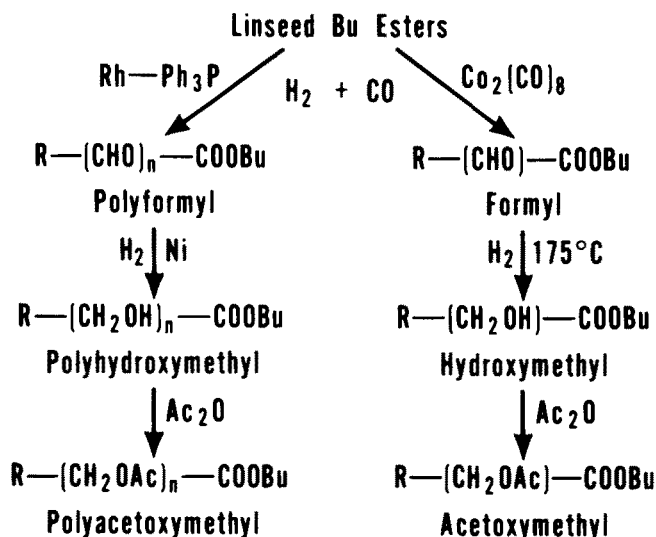
Linseed Bu Esters

Rh—Ph$_3$P   H$_2$ + CO   Co$_2$(CO)$_8$

R—(CHO)$_n$—COOBu   R—(CHO)—COOBu

Polyformyl   Formyl

H$_2$ | Ni   H$_2$ | 175°C

R—(CH$_2$OH)$_n$—COOBu   R—(CH$_2$OH)—COOBu

Polyhydroxymethyl   Hydroxymethyl

Ac$_2$O   Ac$_2$O

R—(CH$_2$OAc)$_n$—COOBu   R—(CH$_2$OAc)—COOBu

Polyacetoxymethyl   Acetoxymethyl

FIG. 1. Preparation of acetoxymethyl linseed butyl esters (n = 1, 2, or 3).

Linseed Me Esters $\xrightarrow[\text{Rh-Ph}_3\text{P}]{\text{H}_2 + \text{CO}}$ R'—(CHO)$_n$—COOMe $\xrightarrow[\substack{\text{CuCrO}_3 \\ 150°\text{C}}]{\text{H}_2}$ R'—(CH$_2$OH)$_n$—COOMe

Polyformyl   Polyhydroxymethyl

R'—(CH$_2$OH)$_n$—COOMe $\xrightarrow[\substack{\text{CuCrO}_3 \\ 280°\text{C}}]{\text{H}_2}$ R'—(CH$_2$OH)$_n$—CH$_2$OH $\xrightarrow{\text{Ac}_2\text{O}}$ R'—(CH$_2$OAc)$_n$—CH$_2$OAc
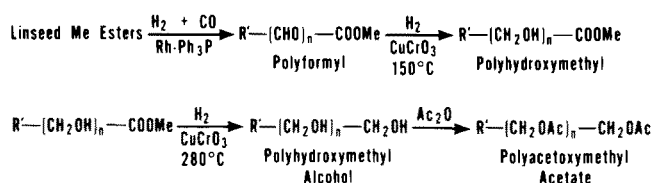
Polyhydroxymethyl Alcohol   Polyacetoxymethyl Acetate

FIG. 2. Preparation of acetoxymethyl linseed acetate (n = 1, 2, or 3).

vigorous stirring and reacted with benzoyl chloride (50% excess based on OH value) added dropwise. When evolution of HCl was completed, the reaction mixture was heated to 50 C and then cooled. The product was worked up by washing an ethyl ether solution of it with dilute NaHCO$_3$, followed by water and drying (Na$_2$SO$_4$). IR analysis of this product showed no OH.

Control samples. Acetylated alkyl 9(10)-hydroxystearate, 9,10-dihydroxystearate, and trihydroxystearate were described previously (9). Commercial samples were acetyl derivatives of ricinoleates and castor oil (NL Industries, Inc., Bayonne, NJ), di-2-ethylhexyl phthalate (DOP, Union Carbide, Charleston, WV), dioctyl sebacate (DOS), dioctylazelate (DOZ), Plastolein 9720 (Emery Industries, Inc., Cincinnati, OH), and tricresyl phosphate ("Kronitex," Ohio Apex, Nitro, WV).

Plasticizer evaluations. Procedures used were described previously (18,19).

RESULTS

Plasticizer Synthesis

Plasticizers were prepared by either a 3-step process involving rhodium-triphenylphosphine catalyzed hydroformylation, hydrogenation, and acylation, or a 2-step process involving cobalt carbonyl catalyzed hydroxymethylation and acylation. Hydroformylation or oxo reaction with rhodium catalyst gave formyl products, which were hydrogenated to hydroxymethyl derivatives with Raney nickel (16). Hydroformylation with cobalt carbonyl gave hydroxymethyl products directly by heating the reaction mixture with H$_2$ at 175-180 C. To increase the hydroxyl content, further hydroxymethylated fatty alcohols were prepared by using copper-chromite as a hydrogenation catalyst. Both rhodium- and cobalt-oxo derived methyl esters were hydrogenated with copper-chromite in two steps to minimize estolide formation. The formyl sub-

stituents were first reduced at 150 C and then the carbomethoxy ester group at 280 C.

Acetates proved to be the most useful derivatives of hydroxymethyl fatty esters, triglycerides, and alcohols. The various reaction steps taken to prepare acetoxymethyl linseed butyl esters and polyactoxymethyl linseed acetate are shown in Figures 1 and 2.

The 3-step rhodium oxo process gave monoacetoxymethylstearate with monounsaturates, diacetoxymethylstearate mainly with diunsaturates, and a mixture of mono-, di-, and triacetoxymethyl esters with linseed and soybean oils and esters. Acetoxymethyl components totaled between 84 and 98% (Table I). The two-step cobalt carbonyl oxo process gave only monoacetoxymethyl esters with polyunsaturated starting materials. This oxo product was a complex isomeric mixture of 78-81.5% monosubstituted esters. The rhodium oxo-derived castor oil and ester products consisted of a mixture of 9(10)-acetoxymethyl-12-acetoxy fatty esters or triglycerides (20). Methyl and butyl mono-, di-, and triacetoxymethylstearates were purified by molecular distillation of rhodium-oxo derived fatty esters. Purity estimated by GLC varied from 90.7 to 98.5%. Acetoxymethyl acetates from molecularly distilled alcohols were not so pure and consisted mainly of mixtures of di- and triacetoxymethyl components which were concentrated further in the distillation residue (Table I).

Plasticizer Evaluation

An ideal plasticizer for PVC should produce the following properties: a stiffness temperature (T$_f$) below -40 C; a compatibility number (T$_4$-T$_f$) below Δ30; a tensile strength above 2800 psi; an elongation above 290%; 100% modulus below 1200 psi; a migration loss below 3%; and volatility loss below 1%. Migration and volatility losses approaching zero are desirable requirements for a permanent plasticizer.

None of the commercial samples evaluated as controls have all the desired characteristics of an ideal plasticizer. On the one hand, DOP and the polymeric plasticizer (Plastolein 9720) are compatible with PVC but do not have good low-temperature properties (Table II, samples 49, 50, and 54). On the other hand, DOS and DOZ are good low-temperature plasticizers but are not too compatible with PVC (samples 51-53). Except for tricresyl phosphate (sample 55), which is thermally unstable, all commercial samples tested do not have good permanence characteristics. The polymeric plasticizer Plastolein 9720 had low volatility loss, but its migration loss in one sample was as high as that of DOP. Criteria for an ideal PVC plasticizer are considered in discussing evaluations in Table II in the light of the characteristics of commercial plasticizers used as controls.

Methyl acyloxymethyl esters. All methyl 9(10)-acyloxymethylstearates prepared showed good low temperature properties, but only the acetoxymethylstearate had satisfactory compatibility with PVC (sample 1, Table II). Compatibility decreased with increasing acyl chain length. Tensile strength was in the same range as the DOP control for acetoxymethylstearate, but undesirably low for the other members of the series. Elongation was equivalent or better than that of DOP in the first 5 members of the series (C$_2$-C$_6$) but was too low in the higher members of the series. Only the acetoxymethyl ester showed better modulus than DOP; all other esters were inferior. Migration loss was higher than that of DOP for all esters. Volatility loss was low for the first 5, and then became too high for the higher esters. Heat stability was good for all esters, except for the octyl and nonyl compounds (samples 8 and 9).

Compared to methyl 9(10)-acetoxystearate control (sample 40), methyl 9(10)-acetoxymethyl ester (sample 1) was similar in mechanical properties, but slightly better in permanence and superior in heat stability.

Alkyl acetoxymethyl esters. Because the acetoxymethyl-

stearate was the best plasticizer in the previous series, another set of esters was made to test the effect of the alkyl ester group. Going from C_1 to C_4 improved the low temperature property, but compatibility, tensile strength, elongation, and volatility loss were decreased, and other properties were not noticeably affected. The best member of the branched alkyl series was the 2-methoxyethyl 9(10)-acetoxymethylstearate (sample 12) which showed the unusual combination of good low temperature property and compatibility with PVC. Mechanical properties also were good, and volatility loss was low. Although the other members of this series had even better low temperature characteristics, they were less compatible and in the same order of magnitude as that of DOS. A similar lowering of T_f was observed in esters of dicarboxystearate when the size of the alkyl group in the internal ester was increased (E.J. Dufek, unpublished data).

Compared to butyl 9(10)-acetoxystearate control (sample 41), butyl 9(10)-acetoxymethylstearate (sample 11) displayed better elongation and only slightly lower volatility loss.

Polyacetoxymethyl esters. When one, two, or three acetoxymethyl substituents were introduced in the stearate chain, T_f rose, compatibility improved markedly, and elongation, migration, and volatility losses decreased. Methyl triacetoxymethyl and butyl diacetoxymethyl esters (samples 16 and 17) were the best plasticizers in this set. The methyl and butyl triacetoxymethyl esters (samples 16 and 18) displayed outstanding permanence.

The acetoxymethyl derivative of castor methyl esters (sample 19) was also a good plasticizer candidate and its migration loss, although higher than that of DOP, was lower than that of either methyl or butyl acetyl ricinoleate (samples 45 and 46). Compared to the acetyl ricinoleates, the acetoxymethyl castor esters have a higher T_f, are similar in plasticizing efficiency, but are more compatible with PVC, more permanent, and more thermally stable.

The acetoxymethylated linseed butyl esters (sample 22) had better compatibility, elongation, and permanence characteristics than the corresponding derivatives of soybean butyl esters. The cobalt carbonyl-oxo-derived acetoxymethylated soybean butyl esters (sample 21) were unsatisfactory in all properties evaluated. Their poor performance reflected not only the absence of more than one acetoxymethyl substituent, which is scattered throughout the fatty acid chain, but also the high content of saturated fatty esters due to some double bond hydrogenation catalyzed by cobalt carbonyl (1) (Table I). Although removal of these objectionable saturated fatty esters should have improved their performance, such a step would negate the economic advantage of their preparation.

Compared to the polyacetoxy ester controls, methyl diacetoxymethylstearate (sample 15) was not so good in tensile strength and migration loss as methyl 9,10-diacetoxystearate (sample 42). However, butyl diacetoxymethylstearate (sample 17) was more compatible, more efficient (lower modulus), and displayed lower volatility loss than butyl 9,10-diacetoxystearate (sample 43).

Acetoxymethyl triglycerides. The oleic safflower oil (sample 23) was an exception in this series by its poor performance. The other acetoxymethyl oils were very compatible by comparison, had good tensile strength, and outstanding permanence characteristics. Although the linseed oil samples were best in overall properties, they displayed lower thermal stability.

Acetoxymethylated safflower, linseed, and castor oils were all much superior to the castor-derived acetyl triglycerides (samples 47, 48) in all properties evaluated and were more permanent than the commericial control samples 49-54. In this respect, tricresyl phosphate (sample 55) was an exception, but it had poor thermal stability.

Acetoxymethyl fatty acetates. 9(10)-Acetoxymethyl-octadecyl acetate (sample 29) had the best low temperature characteristic in this series. The acetoxymethylated linseed acetates (samples 30-32) were more compatible, imparted low volatility losses, but were not so thermally stable. Acetoxymethyl linseed acetates derived from molecularly distilled alcohols (sample 31) had improved compatibility and were more efficient plasticizers (higher elongation and lower modulus). The acetoxymethyl linseed acetate made with cobalt carbonyl catalyst (sample 33) was the poorest plasticizer in the lot, and molded PVC sheets made with it had a moderate exudate after 10 days. This result re-emphasizes the importance of polyacetoxymethyl functionality in these types of plasticizers.

Miscellaneous compounds. Benzoyloxymethyl linseed oil (sample 34) was compatible with PVC, and like other polysubstituted triglyceride samples (no. 24-28) had outstanding permanence characteristics. However, the PVC sheet made with the benzoyloxymethyl oil had poor thermal stability.

Low mol wt acetylated oligomers of methyl 9(10)-hydroxymethylstearate had poor compatibility decreasing with increased mol wt. The more compatible lower mol wt sample 35 was also a more efficient plasticizer (higher elongation and lower modulus). Both acetylated oligomers had good low temperature properties, but their performance was inferior to that of the commercial polymeric plasticizer (sample 54).

Trichloroacetoxymethyl acetates of linseed alcohols were made as potential fire retardant plasticizers. The samples tested (no. 37-39) showed poor compatibility with PVC, high tensile strength, and low migration loss, but they imparted low heat stability to PVC.

DISCUSSION

One basic requirement for a plasticizer is that all intermolecular forces be of the same order of magnitude between plasticizer and plasticizer, between polymer and polymer, and between plasticizer and polymer (21). To be an efficient plasticizer, a low mol wt compound must have sufficient affinity for the polymer to overcome polymer-polymer interactions (9). To impart good low temperature flexibility, the compound also must retain enough mobility to participate in the equilibria of the plasticized system, and must be able to diffuse through the system. PVC, containing polar groups, requires polar plasticizers to achieve good compatibility, which depends on the proper kind, number, and arrangement of polar groups in the plasticizer (22). Ester groups are notable effective polar functions in plasticizers producing compatibility with PVC. The esters we describe have a sufficient number of polar substituents to mask polar sites in the PVC polymer chain and to reduce attraction forces between polymer molecules, giving them freedom of movement as requied for desriable flexibility (23).

The choice of an external plasticizer involves a compromise, because different requirements cannot be met simultaneously for compatibility (size, shape, and chemical composition), efficiency (compatibility, size, and diffusion rate), and permanence (boiling point, compatibility, and diffusion rate) (24). Increasing the length or size of either the acyloxy substituent or the alkyl group in the hydroxymethyl esters we investigated did not decrease their mobility in the PVC polymer sufficiently to affect adversely low temperature flexibility. Apparently, their solvent power decreased and caused decreased compatibility. This decreased compatibility (samples 5-9, Table II) results in greater loss of volatilization (23) despite increased mol wt. The 2-methylethyl 9(10)-acetoxymethylstearate (sample 12, Table II) displayed the unusual combination of good compatibility and low temperature property.

TABLE II

Properties of Polyvinylchloride Plasticized with Oxo-Fatty Derivatives

Sample number	Plasticizer[a] (32%)	Torsional stiffness Tf (C)	Torsional stiffness T4 (C)	Compatibility No. (Δ) (T4-Tf)	Performance Tensile strength (psi)	Performance Elongation (%)	Performance 100% Modulus (psi)	Performance Heat stability (hr)	Permanence Migration loss (%)	Permanence Volatility loss (%)
Me 9(10)-(CH₂OCOR) stearates					**Methyl acyloxymethyl esters**					
1	R = methyl	-47	-12	35	2725	380	905	12	15.5	2.3
2	R = ethyl	-50	-4	46	2540	330	1175	9.0	17.3	1.9
3	R = n-propyl	-52	-10	42	2500	330	1025	9.5	17.8	1.5
4	R = n-butyl	-53	-1	52	2610	340	1240	10	17.8	2.0
5	R = n-pentyl	-55	-1	54	2595	290	1270	8.0	19.2	1.7
6	R = n-hexyl	-55	9	64	2545	285	1275	9.0	18.3	6.1
7	R = n-heptyl	-54	12	66	2515	265	1320	8.0	19.4	8.1
8	R = n-octyl	-55	20	77	1645	320	1335	7.5	18.3	11.3
9	R = n-nonyl	-35	47	82	2355	120	1515	7.0	14.1	12.6
R 9(10)-(CH₂OAc) stearates					**Alkyl acetoxymethyl esters**					
10	R = ethyl	-49	-12	37	2700	360	920	12	16.7	2.2
11	R = n-butyl	-51	-6	45	2680	325	1070	8.0	17.6	1.3
12	R = 2-methoxyethyl	-46	-15	31	2660	310	880	7.5	16.2	1.4
13	R = 2,2-dimethylpentyl	-49	5	54	2600	320	1180	10	16.8	1.3
14	R = 2-ethyl-1-hexyl	-55	8	63	2590	260	1195	8.5	18.5	2.5
R (CH₂OAc)₁₋₃ stearates					**Polyacetoxymethyl esters**					
15	Me diacetoxymethyl	-33	8	25	2610	335	835	7.0	8.1	0.8
16	Me triacetoxymethyl	-20	0	20	2900	280	1040	7.0	2.8	0.4
17	Bu diacetoxymethyl	-33	-7	26	2820	345	935	9.5	8.0	0.5
18	Bu triacetoxymethyl	-23	-1	22	2680	260	1095	6.5	3.3	0.5
19	Me castor	-31	-6	25	2695	300	980	11	7.2	1.2
20	Bu soybean	-38	-2	36	2695	350	1230	8.0	11.0	2.3
21	Bu soybean (Co)	-36	12	48	2280	175	1425	5.5	12.6	3.6
22	Bu linseed	-32	0	32	2646	335	1270	5.5	6.5	1.7
					Acetoxymethyl triglycerides					
23	Oleic safflower oil	-32	20	52	2415	200	1640	8.5	6.9	2.4
24	Safflower oil	-18	10	28	2910	315	1590	6.5	1.5	0.3
25	Linseed oil A	-12	18	30	2805	245	1855	4.0	0.6	0.4
26	Linseed oil B	-14	12	26	2890	245	1855	4.5	0.8	0.3
27	Linseed oil C	-14	12	26	3075	310	1765	4.5	0.7	0.3
28	Castor oil	-14	12	26	3030	265	1715	8.5	0.8	0.3
					Acetoxymethyl fatty acetates					
29	9(10)-Octadecylacetate	-47	-10	37	2460	310	1080	4.0	17.4	2.0
30	Linseed	-32	-5	27	2630	325	1105	2.5	5.4	1.0

No.	Compound									
31	Linseed—mol distilled	-25	- 6	19	2585	340	965	3.5	5.7	0.7
32	Linseed—mol distilled residue	-23	7	30	2690	260	1355	5.0	3.2	0.5
33	Linseed (Co)	-30	12	42	2500	265	1420	2.5	9.3[b]	2.9
	Miscellaneous									
34	Me benzoyloxymethyl linseed oil	-2	32	30	2900	210	2675	0.75	0.2	0.5
	Acetylated oligomers: $AcO-(-OCH_2-C_{17}H_{34}CO-)_nCOCH_3$									
35	Mol wt, 408 (n = 1.1)	-46	-2	44	2545	320	1130	10	14.9	2.0
36	Mol wt, 686 (n = 2.1)	-45	18	63	2770	255	1455	9	12.6[c]	7.3
	Trichloroacetoxymethyl acetates									
37	Linseed	-5	37	42	3050	215	2580	0.5	1.3[b]	3.1
38	Linseed—mol distilled	-10	30	40	2975	265	2260	1.5	1.2[b]	1.4
39	Linseed—mol distilled residue	15	50	35	2930	150	2890	2.0	0.6	4.6
	Acetoxystearate controls									
40	Me 9(10)-acetoxy	-46	-11	35	2795	370	980	9.5	16.0	3.6
41	Bu 9(10)-acetoxy	-50	- 8	42	2620	270	1020	11	17.0	1.5
42	Me 9,10-diacetoxy	-25	- 1	24	2840	335	975	11.5	4.5	1.1
43	Bu 9,10-diacetoxy	-33	2	35	2785	450	1295	14	8.0	1.7
44	Bu triacetoxy	-14	9	23	3000	320	1335	10	1.3	0.7
	Acetyl ricinoleate controls									
45	Methyl	-47	-10	37	2675	330	985	8.0	13.6	5.0
46	n-Butyl	-49	- 2	47	2795	320	1190	7.5	15.1	2.2
	Acetyl triglyceride controls									
47	12-Acetoxystearate	-37	25	62	1420	40	----	11	5.7	10.5
48	Acetyl ricinoleate	-35	22	57	2455	200	1630	9.0	9.1	7.6
	Di(2-ethylhexyl) ester controls									
49	Phthalate (DOP)	-25	4	29	2835	290	1165	6.5	3.0	1.5
50	Phthalate (DOP)	-29	1	30	2770	280	1115	10	3.9	1.3
51	Sebacate (DOS)	-57	-11	46	3570	315	925	10	19.5	1.2
52	Sebacate (DOS)	-57	-7	50	2355	295	1045	----	19.3	1.6
53	Azelate (DOZ)	-56	-12	44	2615	470	1020	10	18.7	1.5
	Polymeric control									
54	Plastolein 9720	-21	8	29	2830	305	1345	7.5	3.9	0.9
	Phosphate control									
55	Tricresyl	-1	18	19	2950	205	1860	1.5	0.3	0.3

[a]See Table I for analyses of selected acetoxymethyl derivatives. See references 18 and 19 for formulations. DOP = di-2-ethylhexyl phthalate; DOS = dioctyl sebacate; DOZ = dioctyl azeleate.
[b]Moderate exudate after 10 days.
[c]Moderate exudate after 2 weeks.

The plasticizing characteristics of 5 acetoxymethyl fatty esters from primary hydroxyl groups (samples 1, 15-18) can be compared directly with those of corresponding acetoxy fatty esters from secondary hydroxyl groups (samples 40-44). Significantly superior characteristics observed in the acetoxymethyl derivatives included T_f in two samples, modulus in four samples, and volatility in all five samples. Compatibility was the same in two samples and only slightly better in three. Less desirable characteristics noted in the acetoxymethyl esters included migration losses in three samples and thermal stability in four. Although no overall generalization can be made, the methylene oxy side chains ($-CH_2O$) of the oxo-derived fatty acid plasticizers appears to increase migration and flexibility of their molecules in the polymer matrix. Mainly, they improve low volatility characteristics.

Although the cobalt cabonyl-oxo process would be expected to be more economical than the rhodium-oxo process, which requires an additional hydrogenation step, the products from the latter are markedly superior in having polyhydroxymethyl functionality and no increase in saturated fatty esters. Introduction of more than one acetoxymethyl substituent in fatty acid molecules imparts good compatibility at the expense of poorer low temperature properties. However, this adverse effect is more than made up by the resulting outstanding permanence characteristics, i.e., low migration and volatility losses, of the polyacetoxymethyl esters and especially the triglycerides. In general, the superior permanence properties of the acetoxymethyl compounds assumes particular importance today because phthalate and other petroleum derived plasticizers may volatilize or be leached from plastic materials and can become ubiquitous environmental contaminants (14,15).

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