

Catalytic Hydroformylation and Hydrocarboxylation of Unsaturated Fatty Compounds¹

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ABSTRACT AND SUMMARY

The two catalyst systems rhodium-triphenylphosphine and palladium chloride-triphenylphosphine were investigated for the respective hydroformylation and hydrocarboxylation of oleic acid or ester to produce C-19 bifunctional compounds. Compared to conventional cobalt carbonyl for making formylstearate, rhodium-triphenylphosphine permits lower pressures (1000-2000 psi vs. 3000-4000 psi), higher conversions (95% vs. 80%), and no loss of functionality (vs. 15% hydrogenation with cobalt). Although palladium chloride-triphenylphosphine for hydrocarboxylation introduces the carboxyl function directly into the fatty acid chain, CO pressures of 3000-4000 psi and corrosion-resistant equipment are necessary. When applied to polyunsaturated fatty acids, both rhodium and palladium catalyst systems have the outstanding advantage of introducing functionality at each double bond position to produce polyformyl- and polycarboxystearates. Selected formyl derivatives were converted in excellent yield to acetals, to acids and their esters, to hydroxymethyl compounds and their esters, and also to aminomethyl compounds that could be condensed to polyamides. Several of the esters and acetals were effective primary plasticizers for poly(vinyl chloride) that had outstanding low volatility characteristics. Other applications for these new and highly versatile derivatives included rigid urethane foams, urethane-modified coatings, ester lubricants, and a shrink-resist treatment for wool.

INTRODUCTION

Fats and oils serve a vital function in the United States' economy in both food and nonfood applications as well as in exports. Out of the 16.2×10^9 lb of fats and oils consumed in the United States during 1974, about one third went into nonfood uses and two thirds, into food uses (1,2). Soybean oil, with its 8-9 billion lb annual production, is a major item in both areas of application. For many food uses, soybean oil requires hydrogenation. In the Northern Regional Research Center at Peoria, we have been working for some time in the field of homogeneous catalytic reactions of unsaturated fatty compounds with hydrogen. One logical extension of this work was to examine the catalytic reactions of carbon monoxide. Two important reactions of carbon monoxide include hydroformylation or the oxo reaction and carboxylation. Although both of these reactions are old and well-known industrial processes in the petrochemical field (3), they have not been exploited in the fatty acid field.

Our objective has been to convert unsaturated fatty materials as renewable resources to value-added products of potential economic importance to the chemical industry (2). This objective is becoming ever more realistic, since petrochemical prices seem to be increasing more rapidly than those of fatty materials. Hydroformylation is one reaction that we have investigated in some detail for this purpose. Catalytic hydrocarboxylation was studied in

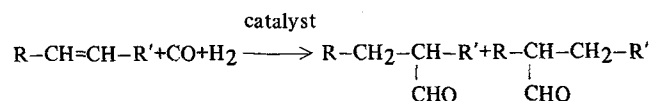
lesser detail. We here review our work on these reactions and on potential applications for the products and several derivatives.

HYDROFORMYLATION

General

The hydroformylation reaction is responsible worldwide for more than 7 billion lb of chemical intermediates for conversion mainly to plasticizer alcohols. For catalyzing this reaction, industry in the past has relied upon cobalt carbonyl. Now, however, intensive research by both industrial and academic scientists on transition metals coordinated with certain ligands has made possible a wider choice of catalysts.

When cobalt is the catalyst, the reaction is carried out with synthesis gas in a 1:1 mixture of carbon monoxide and hydrogen at pressures of 3000-4000 psi and at temperatures above 100 C:



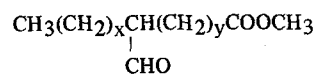
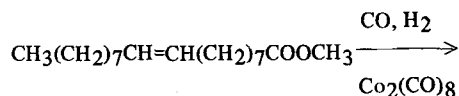
At temperatures higher than ca. 160 C and with cobalt catalyst, hydrogenation of the formyl group to hydroxyl occurs. Conjugated dienes form only the monoformyl product with cobalt carbonyl. Dienes with isolated double bonds do give some diformyl products with cobalt and much more with rhodium catalysts.

Recent reviews are available on the oxo reaction (3), on developments in hydroformylation catalysis (4), on mechanism (5), and on early application of the oxo reaction to unsaturated fatty acids (6). The bulk of reported work emphasizes short chain, monounsaturated olefins and butadiene, since these are the available feedstocks.

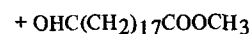
We have investigated the reactions of carbon monoxide with unsaturated fatty compounds in the presence of some of the newly developed catalysts. The investigations included oleic, linoleic, and linolenic acid compounds and their triglycerides. Linoleic acid is a 1,5-disubstituted 1,4-pentadiene and linolenic acid is a 1,8-disubstituted 1,4,7-octatriene.

Formylstearates by Cobalt Catalysis

With cobalt carbonyl, methyl oleate as well as various polyunsaturated fatty esters produced mainly isomeric mixtures of monoformyl compounds as the result of a series of isomerization, conjugation, hydrogenation, and hydroformylation reactions (7).



$$x + y = 15$$



¹Presented at AOCs meeting, New Orleans, April, 1976.

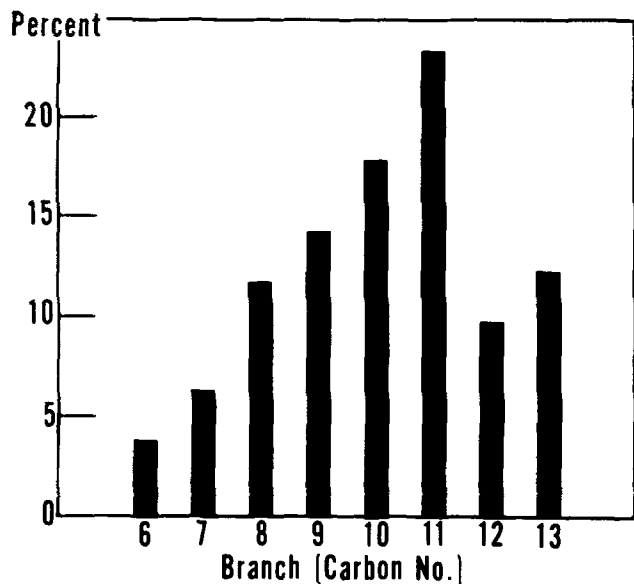
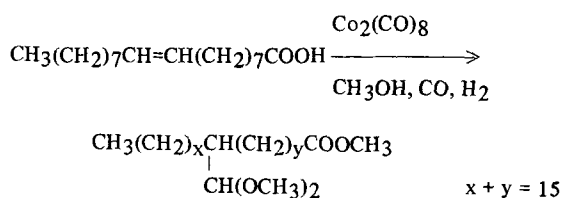


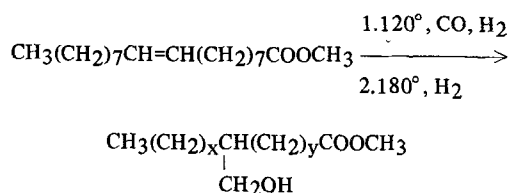
FIG. 1. Distribution of branched C₁₉ diesters (after linear products were removed by preparative gas liquid chromatography as determined by mass spectrometry).

At 100-110 C, aldehydes were produced; at 175-190 C, alcohols were produced. Yields of distillable products varied from 84% for methyl oleate to 42% for methyl esters of linseed oil. The distilled products contained mainly branched chain products and 4 to 16% of methyl 18-formylstearate. The proportion of the linear chain compound increased with increasing temperature and in the presence of triphenylphosphine ligand. Mass spectroscopic analysis of the methyl carbomethoxystearate derivative showed that branching was distributed between C-6 and C-13 of the C-18 chain with a maximum in the C-11 position (Fig. 1). Thin layer chromatography (TLC) was partially successful in separating the various isomers.

Also with cobalt carbonyl, either methyl oleate or oleic acid produced methyl dimethoxymethylstearate when hydroformylated in methanol solution at 120 C (8).



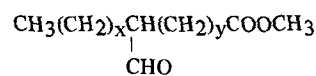
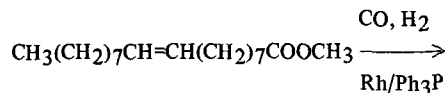
The presence of trimethyl orthoformate helped to drive the acetalation and esterification reactions to completion. In the absence of methanol and with toluene solvent, a two-step procedure consisting of hydroformylation at 120 C followed by hydrogenation at 180 C in the same reactor produced methyl hydroxymethylstearate in good yield from polyunsaturated fatty acid systems, e.g., safflower and linseed methyl esters, as well as from methyl oleate.



Thus, cobalt did not introduce more than one functional group regardless of the number of double bonds in the fatty acid.

Formylstearates by Rhodium Catalysis

Hydroformylation of methyl oleate with rhodium/triphenylphosphine resulted in 90-99% yields of a 1:1 mixture of methyl 9-formylstearate and methyl 10-formylstearate (9).



$$x = 7 \text{ or } 8 \quad x + y = 15$$

$$y = 8 \text{ or } 7$$

methyl 9(10)-formylstearate

Hydroformylation proceeded smoothly at 95-110 C and 500-2000 psi of synthesis gas without or with solvent, such as toluene. The rhodium could be supported on either charcoal, calcium carbonate, or alumina. The actual hydroformylation catalyst is a solubilized rhodium carbonyl/triphenylphosphine complex. Concentrations of 0.05-0.1% of rhodium (based on unsaturated fatty compound) were optimum for complete conversions. At reaction temperatures of 180 C, no reduction of aldehyde to alcohol occurred as it does with cobalt carbonyl and with (Ph₃P)₃RhCl, a weak hydroformylation catalyst. TLC of the methyl 9(10)-formylstearate and mass spectrometry of the diester derived from the aldehyde ester confirmed the absence of any significant amounts of double bond isomerization.

The higher yields and lower pressure requirements with the rhodium/triphenylphosphine catalyst are significant improvements over the conventional cobalt carbonyl catalyst. Furthermore, recovery and recycling of the rhodium catalyst appear to be technically feasible (see Process Studies) (10).

Other homogeneous catalysts studied include ruthenium, platinum, palladium, and iridium, mainly with triphenylphosphine as ligand (10). However, yields of formyl or hydroxymethyl products were low compared to those obtained with rhodium catalyst. A study of ligands used with rhodium revealed the following order of activity: (PhO)₃P, (MeO)₃P, MePh₂P, Ph₃P, Me₂PhP, Bu₃P, Ph₃As, acetylacetone (acac), and Ph₃Sb. The amount of rhodium solubilized from the support into the reaction solution is directly related to the effect of the ligand on catalyst activity. The products obtained with Ph₃As, acac, and Ph₃Sb as ligands contained large numbers of positional isomers, and starting material isolated from the reaction contained appreciable *trans* unsaturation.

Diformylstearates

Hydroformylation of more than one double bond in the same molecule is perhaps the single greatest advantage of the rhodium-triphenylphosphine catalyst. Cobalt carbonyl cannot introduce more than one formyl group, probably because conjugation and hydrogenation are major competitive reactions with this catalyst. Thus, hydroformylation of safflower methyl esters containing 14.3% oleate and 76.0% linoleate produced formyloleate (i.e., formyloctadecenoate), formylstearate, and diformylstearate in various amounts depending upon conditions. Formation of formyloleate was maximum at low pressures; formylstearate was maximum at high temperatures, and diformylstearate was maximum at high pressure (11,12) (Table I).

The structure of the formyloleate esters was deduced from gas liquid and TLC retention data before and after hydrogenation, and from mass spectral analyses. Formyl-

TABLE I

Hydroformylation of Safflower Methyl Esters ^a			
Reaction conditions			
Catalyst	Rh/Al	Rh/Al	Rh/C
Catalyst conc., %	0.5	2.0	2.0
Triphenylphosphine, %	0.25	1.0	1.0
Temperature, °C	110	150	90
Pressure, psi	1000	1500	3500
Time, hr	6	4	6
Product analyses, GLC %			
Unsaturates	26.9	0.0	0.0
Formyloleate	33.0	0.8	0.8
Formylstearate	12.2	36.4	17.7
Diformylstearate	17.7	51.2	71.4

^a14.3% oleate, 76.0% linoleate, 9.7% palmitate and stearate, by gas liquid chromatography (GLC).

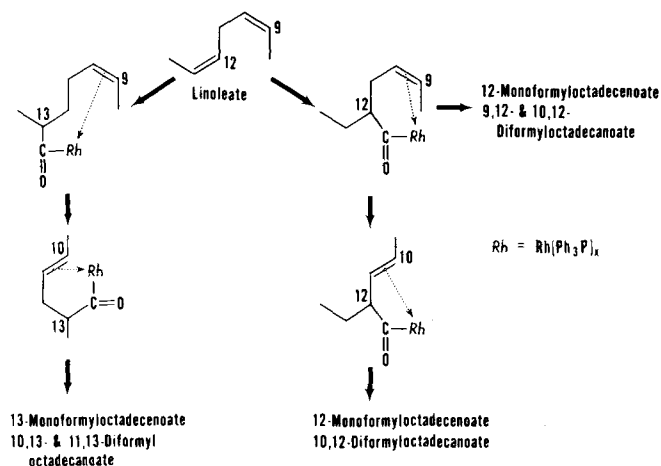


FIG. 2. Mechanism of hydroformylation of methyl linoleate.

oleate was identified as a mixture of methyl 9(10)-formyl-12(13)- and 12(13)-formyl-9(10)-octadecenoate. Dehydroformylation leads to a mixture of 9,12(10,13)- and 10,12(11,13)-diformylstearate (11).

Hydroformylation of methyl formyloctadecenoate isolated from the reaction produced methyl diformyloctadecanoate in 91% conversion (13), and so the unsaturated monoformyl is the most likely intermediate to the diformyl product. Mass spectral analyses of the carbomethoxy derivatives from the unsaturated monoformyl product showed that the branch structure occurred mainly in the 9(10)-positions (36-38%) and in the 12(13)-positions (52-54%).

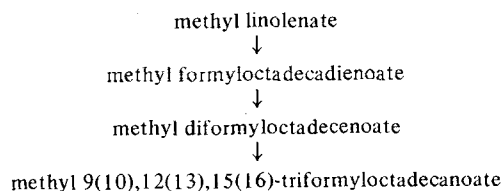
The diformyl product from methyl linoleate consists mainly (68%) of the 1,4-disubstituted (e.g., 9,12-diformyloctadecanoate) and to a lesser extent (19-22%) of the 1,3-disubstituted products (e.g., 10,12-diformyloctadecanoate). The diformyl product from the unsaturated monoformyl compound consisted of 85.6% of the 1,4-disubstituted isomers (i.e., 9,12- and 10,13-diformyloctadecanoate).

Mass spectral analyses of the carbomethoxy derivatives from hydroformylated conjugated linoleate, i.e. methyl 9,11- and 10,12-octadecadienoate, had a greater mixture of isomers and more even distribution of branching between carbon-10 and carbon-13 than the unconjugated products. With 9,15-octadecadienoate, no double bond isomerization occurred, and only the 9(10)-, 15(16)-isomers were formed.

Triformylstearates

Hydroformylation of methyl linolenate with rhodium-triphenylphosphine catalyst takes place in the following sequence, although the intermediates have not been com-

pletely characterized (13):



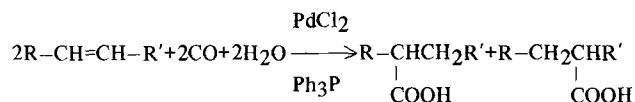
The monocarbomethoxy derivatives made from isolated fractions of the product showed by mass spectral analysis branches centered in the 9,10- (21.8%), 12,13- (29.5%), and 15,16-positions (39.3%). The 1,4-disubstituted dicarbomethoxy derivatives include mainly the 9,12- (11.8%), 10,13- (15.5%), 12,15 (20.8%), and 13,16- (16.6%) isomers. The 1,3-disubstituted isomers have branches between C-9 and C-16. The trisubstituted isomers were isolated chromatographically in 23% yield, but the position of branches could not be established definitely because of the multitude of isomers.

To account for the products obtained from polyunsaturated fatty compounds, we have proposed the mechanism set forth in Figure 2 as applied to methyl linoleate.

HYDROCARBOXYLATION

Monocarboxystearates

Hydrocarboxylation is a reaction of as much interest as hydroformylation, since it produces carboxylic acids in a single step (3) and obviates oxidation of the aldehydes made by hydroformylation.



Hydrocarboxylation of oleic acid produced 9(10)-carboxystearic acid in yields of 85% to 99% depending upon conditions (Table II) (14,15). The isomeric purity determined by mass spectrometry was 87 to 94%. At low pressures and high temperatures, isomerization was more extensive. Another good catalyst system was a mixture of palladium on carbon, triphenylphosphine, and hydrogen chloride. Conversions were higher at 140-150 C than at 160 C and at 4000 psig than at 2000-3000 psig. When PdCl₂ and Ph₃P were used at respective concentrations of 0.5 and 2.0 mole %, conversions were higher at 110-120 mole % of water than at 200-300 mole %. Used catalyst could be recycled, but longer reaction times were required (15).

Hydrocarboxylation of methyl oleate and high oleic safflower methyl esters also produced the carboxy derivative in high yield.

Polycarboxystearates

A mixture of palladium chloride and triphenylphosphine effectively catalyzes carboxylation of linoleic and linolenic acids and their methyl esters with water and carbon monoxide at 110-140 C and 4000 psig (16). Carboxyl groups are introduced at each of the double bond sites. The trifunctional compound from linoleic acid is formed in ca. 80% yield, and the tetrafunctional compound from linolenic acid is formed in ca. 50% yield. The newly introduced carboxyl groups are in a 1,3- and 1,4- relation to each other. By-products include unsaturated, carboxylated intermediates, carbomethoxy esters, and substituted α,β -unsaturated cyclic ketones. Formation of small amounts of conjugated fatty esters also occurs. Monocarboxylated products are formed as the result of saturation of the double bond in an unsaturated, carboxylated intermediate.

TABLE II

Catalytic Hydrocarboxylation of Olive Fatty Acids^a
to Carboxystearic Acid

Variable	Amount ^b			
Reactants, mole % ^c				
Palladium chloride	1.0	1.0	0.5	0.5
Triphenylphosphine	2.0	4.0	2.0	2.0
Water	110	110	110	110
Conditions				
Solvent	Acetone	Acetone	Acetone	Acetic acid
Temperature, °C	140	120	160	140
CO pressure, psig	4250	4100	4000	4000
Time, hr	4	6	6	4.5
Product				
Conversion, %	99.4	92.3	89.8	93.1

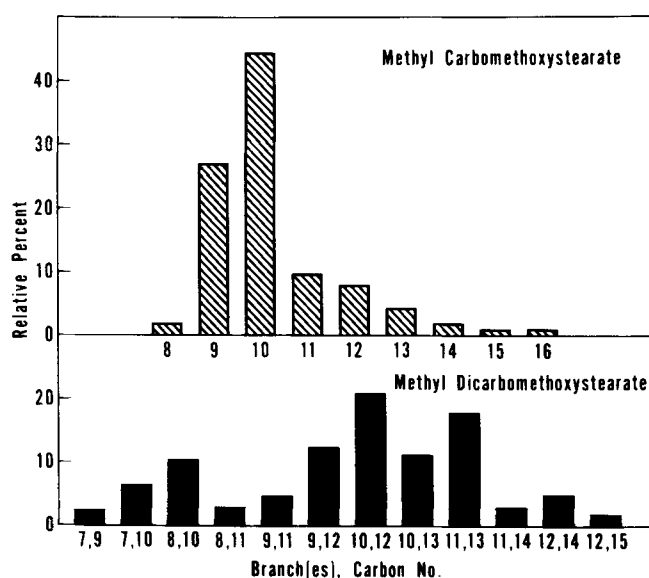
^a81.3% oleic acid by gas liquid chromatography (GLC).^bBlocked figures show major change in variable.^cMole % based on oleic acid.

FIG. 3. Distribution of isomeric methyl carbomethoxy- and methyl dicarbomethoxystearates from linseed esters hydrocarboxylated with palladium chloride-triphenylphosphine catalyst.

Mass spectral analyses of the dicarboxylated products revealed the presence mainly of the 10,12- 11,13-, 9,12-, and 10-13-isomers. 1,3-Dicarboxylated compounds are the principal products of conjugated linoleate. Distribution of isomeric methyl carbomethoxystearate and methyl dicarbomethoxystearate from linseed esters is given in Figure 3 (20).

Catalytic carboxylation proceeds equally well with unsaturated vegetable oils such as linseed, soybean, and safflower oils (20).

Optimum reaction conditions were determined for linseed oil and linseed methyl esters by statistically designed experiments. Yields of total carboxy and tri-carboxy products were maximized at low triphenylphosphine and water levels, low temperatures, and high palladium chloride concentrations. Laboratory experiments indicated that recovery and recycling of the catalyst are feasible (15).

In the mixture of methylene-interrupted and conjugated diene systems from linoleic acid, stepwise carboxylation and formation of cyclic ketone by-product can be explained by the mechanisms shown in Figures 4 and 5.

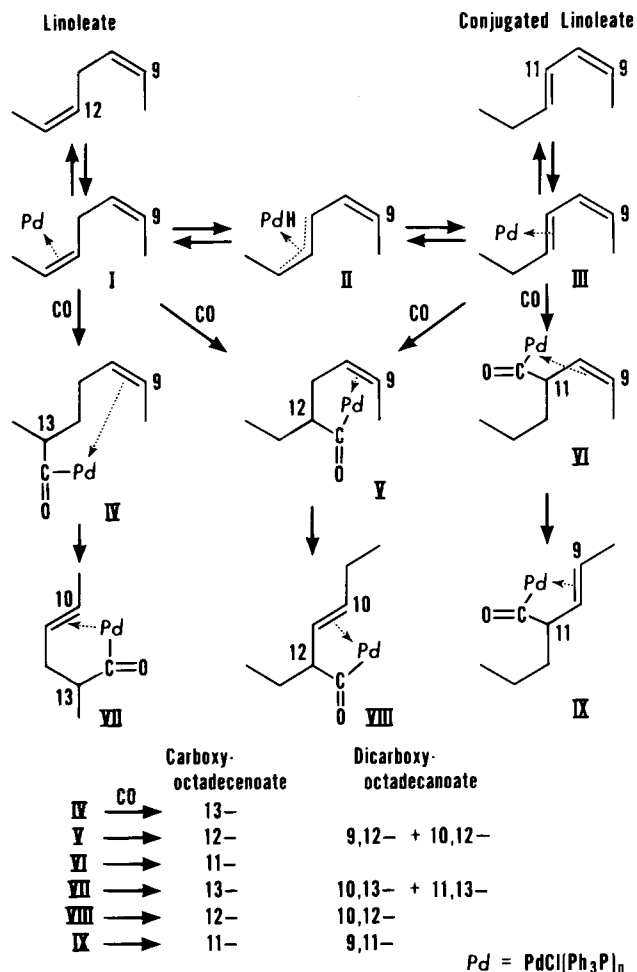
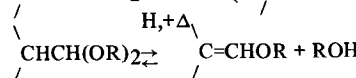
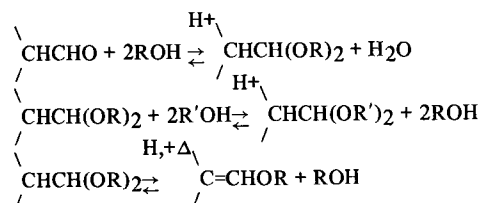


FIG. 4. Mechanism of hydrocarboxylation of methyl linoleate.

REACTIONS OF THE FORMYLSTEARATES

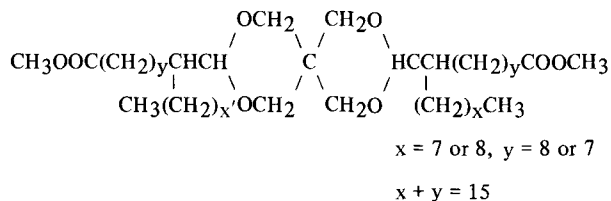
Acetalation

Formylstearates are easily converted into acetals, which are more stable to autoxidation than the free carbonyls. The acetals undergo the potential useful reactions of trans-acetalation and decomposition to enol ethers.



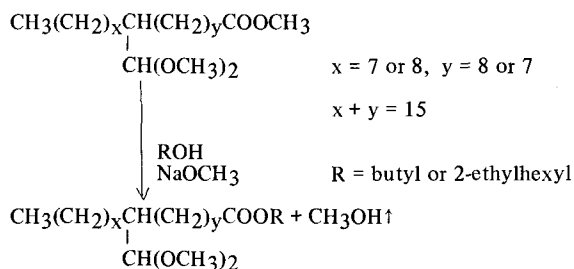
The acetal methyl dimethoxymethylstearate is formed when hydroformylation of methyl oleate is carried out in methanol with cobalt carbonyl, as described earlier (8). It is formed also by letting stand for 4 days a solution of methyl formylstearate in methanol in the presence of HCl and a dehydrating agent such as Drierite (18). The reaction proceeds much more rapidly and is complete within 1½ hr at reflux temperature, but some cracking of the acetal occurs at that temperature when 2,2-dimethoxypropane is the dehydrating agent and KHSO₄, the catalyst. Complete cracking to methyl methoxymethylenestearate occurs when the dimethyl acetal is heated in a vacuum in the presence of KHSO₄ at temperatures up to 150 C or in the presence of rhodium catalyst.

The pentaerythritol acetal:



can be prepared by direct acetalation of methyl 9(10)-formylstearate, by transesterification of methyl 9(10)-dimethoxymethylstearate, or more conveniently by reaction of pentaerythritol with the enol ether, methyl methoxymethylenestearate. Other cyclic acetals prepared include those from ethylene glycol, glycerol, and 3-chloro-1,2-propanediol.

The acetal group is inert and does not react under conditions of basic catalysis. Advantage was taken of this property to convert methyl dimethoxymethylstearate into other alkyl dimethoxystearates by transesterification in an alcohol with sodium methoxide catalyst:



Oxidation

Since dicarboxylic acids have value as chemical intermediates (6,19) investigations were carried out on converting methyl formylstearate to methyl carboxystearate by autoxidation. Autoxidation of methyl formylstearate took place in 95% conversion in the absence of solvent but in the presence of calcium naphthenate in 24 hr at 20 C (20,21). Although the calcium compound was least effective in accelerating oxidation, it was most effective in inhibiting side reactions. Reaction rate was promoted by various metal naphthenates in the following order: $\text{Co} > \text{Pb} > \text{Mn} > \text{Ce} > \text{Fe} > \text{Zr} > \text{Ca}$. The order in suppressing side reactions was: $\text{Ca} > \text{Pb}, \text{Fe}, \text{Zr}, \text{Mn} > \text{Co} > \text{Ce}$. Cobalt and cerium naphthenates were particularly active in producing such by-products as methyl stearate, epoxystearate, hydroxystearate, and ketostearate. Similar results were obtained in the autoxidation of formylstearic acid in place of methyl formylstearate (22). See also Process Studies—Methyl Carboxystearate.

Chemical oxidation of formylstearate with permanganate (9,20,23) or dichromate (20,23) produced carboxystearate in yields of more than 95%. Permanganate oxidation of 9(10)-formylstearonitrile to 9(10)-carboxystearonitrile was equally successful (24).

Carboxystearic acid has aroused industrial interest and is the subject of many patents (6). We have studied some of its properties. For example, rate studies reveal that the terminal carboxy group reacts 26-27 times more rapidly than the internal group and that transesterification of the terminal ester group in methyl carboxystearate is about twice as fast as esterification of the internal carboxyl group (23). The difference in reaction rates made possible selective transesterification to make such mixed esters as 2-ethylhexyl and 2,2-dimethylpentyl-9(10)-carboxymethoxystearate (25). The physical properties of 9-carboxystearic acid (mp, 83 C) and 10-carboxystearic acid (mp 75 C) are sufficiently different to permit separation by fractional crystallization (26).

Methyl di- and tricarbonylstearylates were prepared by permanganate oxidation of the hydroformylated methyl

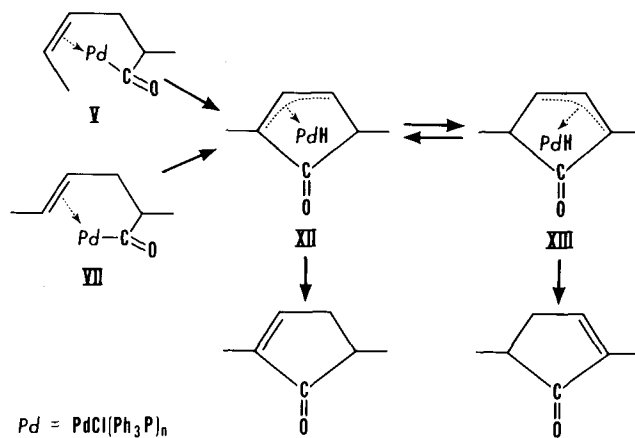


FIG. 5. Formation of cyclic ketones based on a cyclic mechanism.

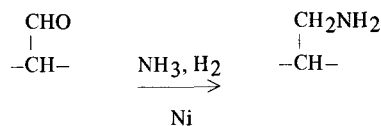
esters of safflower and linseed oils, respectively (25). Isolation of di- and tri-carboxystearic acids was accomplished by stepwise extraction with aqueous potassium bicarbonate (25) or with sodium hydroxide or bicarbonate (27).

Reduction

Preparation of hydroxymethylstearate by hydrogenation is particularly easy to do when cobalt is the hydroformylation catalyst (7). However, rhodium does not promote hydrogenation; when it is used for hydroformylation, some other means of hydrogenation must be sought. Hydrogenation of formylstearates with Raney nickel proceeds readily at 100-110 C and 500-1000 psig of hydrogen (9). Reduction with sodium borohydride is also satisfactory (7,9).

Reductive Amination

Reductive amination of 9(10)-formylstearic acid with ammonia and Raney nickel at 100 C and 1000 psi of hydrogen for 2 hr produced 9(10)-aminomethylstearic acid in ca. 50% yield (24):



Considerable effort was required in removing last traces of nickel from this amino acid.

The structurally isomeric 9(10)-carboxyoctadecylamine was made in 85% yield by hydrogenation of 9(10)-carboxystearonitrile with Raney nickel at 125 C and 2000 psig hydrogen pressure in the presence of ammonia and in methanol solvent for 4 hr (24). Removal of nickel was also necessary, but ease of purification by recrystallization was better than for aminomethylstearic acid.

Polycondensation

Condensation polymers were prepared from the pentaerythritol acetal of methyl 9(10)-formylstearate by reaction with diamines and ethylene glycol (I, Fig. 6) (28). A poly(ester-acetal) was made from the glycerol acetal of methyl 9(10)-formylstearate, a hydroxy ester (II, Fig. 6). The glycerol acetal monomer was also copolymerized with caprolactam (III, Fig. 6). These polymers have latent cross-linking sites at the cyclic acetal groups that are activated at elevated temperatures in the presence of certain metal oxide or acidic catalysts. This reaction was applied to preparation of several bonded stationary phases for gas chromatography (See Potential Applications).

The linear poly(amide-acetals) were amorphous, low melting (40-50 C) materials of molecular weights ranging

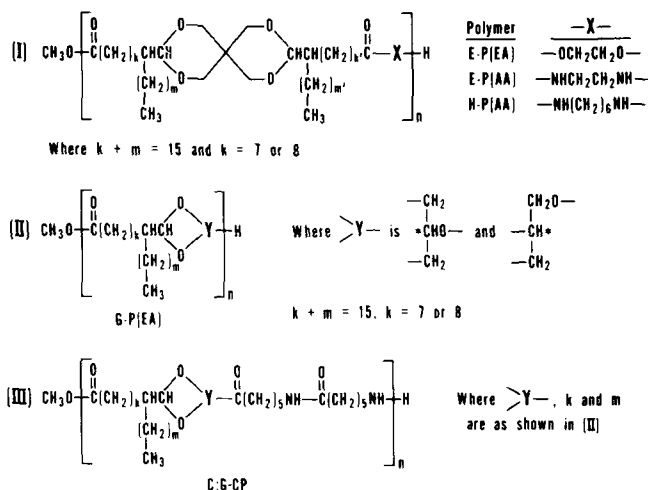


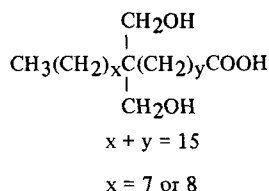
FIG. 6. Polymer structures: (I) Poly(ester-acetal) or poly(amide-acetal) from polycondensation of methyl formylstearate pentaerythritol acetal with ethylene glycol, ethylenediamine, and hexamethylenediamine; (II) poly(ester-acetal) from self-condensation of the glycerol acetal; (III) poly(ester-acetal-amide) copolymer from polycondensation of caprolactam with the glycerol acetal.

from 6000 to 11,000. The poly(ester-acetals) were viscous liquids (melting points of -30 to -50 C) of molecular weights ranging from 3000 to 7200. The amorphous nature of the polymers can be attributed not only to the disorder or entropy effects from the C_8 and C_9 alkyl side chains but also to the isomeric complexity (both geometrical and positional) of the main chain. Because of the low degree or lack of crystallinity, the poly(amide-acetals) as well as the poly(ester-acetals) were soluble in ordinary solvents such as chloroform and tetrahydrofuran.

A novel step-growth, addition polymerization was developed in which reaction of ethylene bis[9(10)-methoxymethylenestearate] with pentaerythritol occurred to make a poly(ester-acetal) similar to that formed by polycondensation. The first step is the addition of hydroxyl to the enol ether followed by a ring-closing condensation of a second hydroxyl from pentaerythritol to form the spiro acetal.

Tollens Condensation

In the Tollens condensation, formaldehyde is caused to react with the α hydrogen atoms of another aldehyde to form a hydroxymethyl aldehyde, which in turn reacts with excess formaldehyde in a crossed Cannizzaro reaction to form a polyhydroxymethyl product (29). Pentaerythritol and trimethylolpropane are examples of commercial application of the reaction to acetaldehyde and butyraldehyde, respectively. When applied to 9(10)-formylstearic acid, the reaction produced 9,9(10,10)-bis(hydroxymethyl)octadecanoic acid in essentially quantitative yields (30):



This compound is a trimethylene glycol with no hydrogen *beta* to the hydroxyl groups. A series of ester acetal derivatives have been prepared that are characterized by high temperature stability and extremely low freezing points (<-70 C).

PROCESS STUDIES

Methyl Formylstearate

Recovery of the precious metal rhodium and its

recycling are essential for an economic hydroformylation process. In commercial processes, with either cobalt or rhodium catalysts, recovery is simplified by the high volatility of the olefins involved. With the higher molecular weights and lower volatilities of the fatty acid derivatives, the problem is more complex. Nevertheless, a practical process was demonstrated for recovering and recycling rhodium for the hydroformylation of methyl oleate to make methyl formylstearate (31,32).

Roughly 50-80% of the supported rhodium is solubilized into the reaction product. The solubilized rhodium was recovered as residue from distillation of methyl formylstearate at 185 C and 0.3-0.5 mm of mercury. The residue was combined with the spent catalyst recovered from the initial crude product mixture by filtration. Roasting the combined catalyst residues in a specially designed kiln produced a catalyst in which the rhodium is presumably in an oxide form and which was more active than the original catalyst. The loss of rhodium over 10 cycles was less than 2% per cycle (31-33).

A preliminary cost estimate was made for a hypothetical plant having an annual capacity of 2 million lb of methyl formylstearate and operating as an adjunct to an existing vegetable oil processing plant (31). With a fixed capital investment of \$630,000, estimated processing cost was 13.7 cents per lb for a plant producing 105 lb of methyl formylstearate (95% purity) from 100 lb of methyl oleate (98% purity), including 2% catalyst makeup at \$180 per lb. Triphenyl phosphite took the place of triphenylphosphine because of its lower cost and was not recovered.

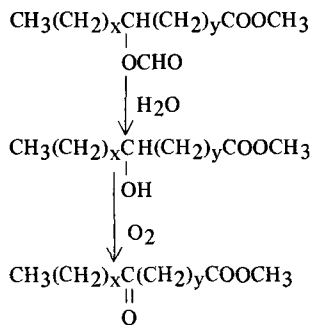
Methyl Methoxymethylenestearate

Since oleic acid is available at a lower cost than its methyl ester, the acid was used as the starting material in another process study (34). To recover catalyst, conversion of the formylstearic acid product to a more volatile and distillable compound was necessary. Simultaneous conversion of the formyl and carboxyl groups to the respective acetal and ester with methanol was accomplished by use of a strong acid ion exchange resin to catalyze both reactions and by use of a molecular sieve to water. Distillation then produced methyl methoxymethylenestearate as the final product as the result of the acetal being cracked by soluble rhodium catalyst, still present in the solution. In a typical run, 900 g of oleic acid produced about 1000 g of methyl methoxymethylenestearate containing 5-10% methyl formylstearate. The filterable resin catalyst was necessary to avoid introduction and buildup of mineral salts that would result if a mineral acid were used. Triphenylphosphine was the preferred ligand since the phosphite or its decomposition products apparently caused problems in catalyst recovery.

Methyl methoxymethylenestearate is even more attractive than formylstearate as an intermediate because it is not susceptible to autoxidation and is more easily converted to a variety of acetals.

Methyl Carboxystearate

Our investigations indicate that the most attractive route to carboxystearic acid is air oxidation of methyl formylstearate. The oxidation is carried out in the same reactor after hydroformylation is complete, at 20-25 C in the presence of either air or oxygen at 1-3 atmospheres, the formylstearate being in an emulsified state brought about by vigorous agitation with about 26% water (35). Conversion to methyl carboxystearate is 87-89% in 2-3 hr. Methyl formoxystearate is also formed in small amounts (7-10%) and is the major by-product, along with some hydroxystearate resulting from hydrolysis of the formoxy compound and some ketostearate resulting from oxidation of the hydroxystearate.



Formation of formoxystearate was minimized (4-6%) if catalytic amounts of calcium acetate were added, but calcium salt buildup would soon burden the catalyst recycle process. Furthermore, the calcium salt depressed rates of both hydroformylation and oxidation. Rhodium apparently has some activity as an oxidation catalyst. The recycled rhodium catalyst, as before, showed enhanced activity for hydroformylation in the absence of calcium salt. Again, triphenyl phosphite performed well as the catalyst ligand but was not recovered.

POTENTIAL APPLICATIONS

Bonded Stationary Phases

Diesters from the reaction product of methyl 9(10)-formylstearate with pentaerythritol were condensed with diols and diamines to produce the respective linear poly(ester-acetals) and poly(amide-acetals). Like those derived from methyl azelaaldehyde, these polymers have latent crosslinking sites at the acetal bond and, when cross-linked on an acidic diatomaceous support, form useful stationary phases bonded to the support surface for gas chromatography (36). Unlike that derived from methyl azelaaldehyde, the linear poly(amide-acetal) from methyl 9(10)-formylstearate is soluble, so that column packings are more easily prepared and advantage can be taken of the more polar nature of the poly(amide-acetal). The stationary phases derived from the formylstearate have a continuous operating range from at least -60 C to 190-220 C with no detectable amount of phase bleed, and only slight bleed up to 290 C.

Coatings

Partial hydroformylation of linseed oil introduces new functionality into the molecule but leaves sufficient unsaturation to permit air drying. Hydroformylated linseed oil

samples containing different amounts of aldehyde were used to make several different types of resins, viz. poly-acetals, poly(ester-acetals), and diisocyanate modified poly(ester-acetals) (Table III) (37,38). The urethane coatings had the best properties, but these resins had a relatively short pot life and tended to gel upon storage. However, coatings from the polyacetals and the poly(ester-acetals), as exemplified in Table III, had better storage properties and still had better film properties than a commercial soy alkyd. Resistance to xylene and hydrochloric acid was excellent, and resistance to alkali was superior to that of commercial alkyds.

Lubricants

Several esters of mono-, di-, and tricarboxy stearic acid had good properties as aircraft turbine engine lubricants, having high viscosity indices and low ASTM slopes (25). 2,2-Dimethylpentyl 9(10)-carboxymethoxystearate had an extremely low pour point of below -70 C, exceeding Mil-L-23699 specifications.

Plasticizers

The methyl, butyl, and 2-ethylhexyl esters of 9(10)-dimethoxymethylstearic acid are compatible with poly(vinyl chloride) to a limited extent only, but could serve as useful secondary plasticizers in conjunction with bis(2-ethylhexyl) phthalate (18). These acetal-esters are about equivalent to bis(2-ethylhexyl) sebacate in many of the properties imparted, except that migration weight loss is desirably less.

Although the monoacetal derivatives are useful only as secondary plasticizers, di- and triacetal derivatives are more compatible and can serve as primary plasticizers (Table IV) (39). Compared to bis(2-ethylhexyl) phthalate, triacetal esters gave less migration, at least equivalent volatility characteristics, comparable compatibility numbers and strength, but somewhat less desirable low temperature and heat stability properties. The diacetal esters also had good compatibility, equivalent strength, somewhat better low temperature flexibility, but less desirable migration and volatility properties.

Mixed acetoxyglycerol acetals from hydroformylated safflower and linseed methyl esters also were good primary plasticizers for poly(vinyl chloride) (Table IV) (40).

Various esters of mono-, di-, and tricarboxystearic acids are also effective plasticizers (Table IV) (27). As with the acetals, one functional group in the hydrocarbon chain was not sufficient to obtain maximum compatibility. Two or three functional groups did impart excellent compatibility

TABLE III
Comparative Film Properties^a

Item	Developmental resin		Commercial soy alkyd
	TDI-modified	Polyacetal	
Composition			
Partially hydroformylated LSO, meq aldehyde/g	2.10	1.36	--
Polyol	PE	HEMA:MMA:EA (16:45:45)	--
OH/CHO ratio	2	0.5	--
NCO/OH ratio	2	--	--
Film properties			
Touch dry time, min	25	65	90
Sward hardness at 7 days	24	24	30
Impact resistance, in./lb			
Direct	>160	>160	>160
Reverse	>160	60	>160
Chemical resistance, min			
5% NaOH	>1440	720	38

^aLSO = linseed oil, TDI = toluene diisocyanate, PE = pentaerythritol, HEMA = hydroxyethyl methacrylate, MMA = methyl methacrylate, EA = ethyl acrylate.

TABLE IV

Properties of Poly(Vinyl Chloride) Plasticized with 32% Oxo-Derived Compounds

Compound	Torsional stiffness T _f , °C	Migration wt loss, %	Volatility wt loss, %
Methyl 9(10),12(13),15(16)-tris[acetoxymethyl octadecanoate] ^a	-1	0.04	2.0
Methyl 9(10)-carboxymethyloctadecanoate	-47	18.7	4.1
Methyl 9(10),12(13),15(16)-triacetoxymethyloctadecanoate	-20	2.8	0.4
Acetoxymethyl derivative of hydroformylated linseed oil	-14	0.8	0.3
2-Methoxyethyl 9(10)-acetoxymethyloctadecanoate	-46	16.2	1.4
Trichloroacetoxymethyl derivatives of hydroformylated linseed oil	-5	1.3	3.1
bis(2-Ethylhexyl) phthalate	-25	3.0	1.5
bis(2-Ethylhexyl) sebacate	-57	19.3	1.6

^aFrom linseed methyl esters.

and improved migration and volatility properties, although at the expense of poorer low temperature flexibility.

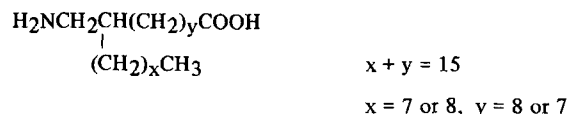
Acetoxy esters of various hydroxymethylated derivatives, formed by hydrogenation of hydroformylated unsaturated esters, followed a similar pattern in the plasticization of poly(vinyl chloride) (Table IV) (41). However, linseed oil, after hydroformylation, reduction, and acetylation, made an excellent plasticizer having outstandingly low migration and volatility properties and still having fair low temperature properties. An unusual combination of good compatibility and low flex temperature was obtained with 2-methoxyethyl 9(10)-acetoxymethyloctadecanoate. The use of trichloroacetoxy groups offers the possibility of reduced flammability in plasticized poly(vinyl chloride).

Polyamides

Studies were made on the condensation polymers that could be prepared from the bifunctional compounds, 9(10)-carboxystearic acid and its isomers, as well as the C-19 amino acids 9(10)-carboxyoctadecylamine and 9(10)-aminomethyloctadecanoic acid.

Polyamide resins were prepared readily from 9(10)-carboxystearic acid and aliphatic diamines by conventional melt polymerization techniques (42). The polyamides were clear, ethanol-soluble, glassy resins having flow properties that were affected markedly by carboxystearic acid purity and, in copolyamides, by the proportion of adipic acid comonomer. Addition of 24 mole % adipic acid for a copolymer made with 95.3% 9(10)-carboxystearic acid or of 21 mole % of adipic acid to a copolymer from 99.5% material was sufficient to achieve the 160 C flow temperature required for major hot-melt adhesive applications. Without adipic acid, the respective flow temperatures were 105 C and 130 C.

The two structurally isomeric amino acids prepared, viz. 9(10)-carboxyoctadecylamine and 9(10)-aminomethyloctadecanoic acid, are monomers for modified polyamides with lateral substitution (24).



Each of the structural isomers as prepared is a 50:50 mixture of positional isomers, and all structural and

positional isomers are racemic mixtures of optical isomers.

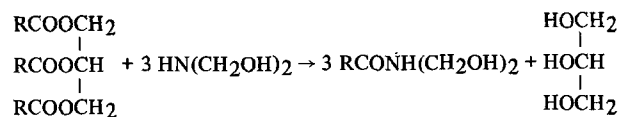
Although there are several types of isomerism in effect, our investigations on the polyamides made from these amino acids indicates that structural isomerism has the greatest importance. One isomer has an alkyl substituent *alpha* to the carboxyl, whereas the other isomer has an alkyl substituent *beta* to the amine group.

9(10)-Carboxyoctadecylamine was relatively easy to prepare and purify by crystallization, and it melted about 35 C higher than 9(10)-aminomethyloctadecanoic acid (155-158 C vs. 119-125 C). Polyamides from the former had higher molecular weights and were transparent, hard, and somewhat brittle. Polyamides from the latter were soft and rubbery and flowed slowly at room temperature. Similar properties were carried over into copolymers of the two C-19 amino acids with nylon-66 salt, caprolactam, and 9-aminononanoic acid, although 9(10)-aminomethyloctadecanoic acid had a disproportionate softening effect. The copolymer of 9(10)-carboxyoctadecylamine with 25 mole % nylon-66 salt was transparent and elastic, and could be either drawn into fibers or made into a coherent film. The properties of the two C-19 amino acids and of their polymers and copolymers agreed with those expected from simpler alkyl-substituted amino acids.

Urethane Foams

Hydroxymethylated linseed oil and its polyol esters when blended with Quadrol® [N,N,N',N'-tetrakis(2-hydroxypropyl)ethylene diamine] can be used to make rigid polyurethane foams meeting the requirements of commercial products with respect to density, compressive strength, and dimensional stability (43). These foams were superior to analogous foams made with castor oil. At any given hydroxyl equivalent weight, more of the hydroxymethylated linseed oil can be incorporated than can castor oil to reduce the amount of Quadrol necessary. Another advantage of the hydroxymethylated oils is the higher reactivity of the primary hydroxyl groups compared to that of the secondary hydroxyl in castor oil, thereby reducing the amount of catalyst required. Indeed, less catalyst was required than is generally used for polyether foams.

To increase the hydroxyl number, several of the hydroxymethylated oils were converted to diethanolamide derivatives (44,45):



R = hydroxymethylated fatty acid chain

TABLE V

Rigid Polyurethane Foams from Hydroxymethylated and Carboxylated Fatty Compounds

Components	Hydroxymethylated linseed oil	Castor oil	Hydroxymethylated linseed diethanolamides	Carboxylated linseed oil diethanolamides
Polyol component, g	33.2	25.8	40.3	39.3
Quadrol ^a , g	26.8	34.2	19.7	20.7
Hydroxyl equivalent	110	110	110	110
PAPI ^b , g	76.2	76.2	76.4	76.4
Evaluation				
Density, lb/ft ³	1.91	1.89	1.94	1.81
Compressive strength, psi				
Parallel	32.1	25.4	27.7	30.1
Perpendicular	12.9	12.1	21.4	15.2
Open cells, %	4	4	7.5	6.3
Humid aging at 150 F, % volume change				
Days: 1	2.9	2.4	5.4	4.8
28	5.1	3.0	7.2	8.8 ^c
Weight change, % @28 days	-3.5	-6.2	---	---
Dry aging, % volume change @212 F				
7 days	2.9	2.1	2.4	9.0

^aN,N,N',N'-tetrakis(2-Hydroxypropyl)ethylenediamine.

^bPolymethylene polyphenylisocyanate.

^cAfter 14 days.

The diethanolamide derivatives made foams equally as good as those from the hydroxymethylated oils and required even less Quadrol (Table V).

Rigid urethane foams from hydroxymethylated castor, safflower, and oleic safflower oils also showed good properties, with polyol esters of hydroxymethylated castor acids showing the best properties in this series (46). However, these polyols required considerably more Quadrol than the hydroxymethylated diethanolamide derivatives described above.

Shrink-resist Wool Treatment

9(10)-Hydroxymethylstearic acid can be used to impart durable shrink resistance to wool without much loss of "hand" or feel (47). To incorporate a polymer coating to the fabric, the following procedure was used. Acryloyl chloride was copolymerized with n-butyl acrylate in a 1:4 ratio to make a prepolymer, which was then allowed to react with 9(10)-hydroxymethylstearic acid (or 12-hydroxystearic acid). The pendant carboxyl groups were converted to acid chloride groups by treatment with thionyl chloride. Wool fabric, treated with this polymer to the extent of 7.4% uptake, had only 1% shrinkage and had a hand of 3+ out of a possible 5. The improved hand results from internal plasticization of the polymer coating. 9(10)-Hydroxymethylstearic acid seemed to have a slightly better effect than 12-hydroxystearic acid.

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