# Reactions of Carbon Monoxide with Unsaturated Fatty Acids and Derivatives: A Review[1]

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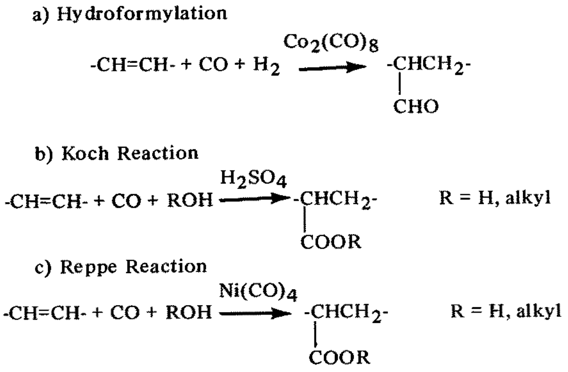
## ABSTRACT

The important reactions of carbon monoxide with unsaturated fatty derivatives that are reviewed in this paper include hydroformylation (the oxo reaction), Koch carboxylation and Reppe carbonylation. With oleic acid as a substrate, the products are $C_{19}$ bifunctional compounds e.g., formyl- or carboxystearic acid. Double bond isomerization before carbon monoxide addition is characteristic of these catalytic reactions; additionally, rearrangement to introduce methyl branching occurs in the Koch carboxylation. Isomerization does not occur when a rhodium-triphenylphosphine catalyst replaces cobalt in the oxo reaction. Properties of the $C_{19}$ dicarboxylic acids differ and depend upon method of preparation. Many areas of application have been reported for $C_{19}$ compounds–lubricants, plasticizers, polyurethanes, epoxy resins, leather and other coatings, unsaturated polyester resins and transparent polyamide plastics.

## INTRODUCTION

Carbon monoxide may react with unsaturated fatty acids–oleic acid in particular–in at least three ways:



a) Hydroformylation

$$-CH{=}CH- + CO + H_2 \xrightarrow{Co_2(CO)_8} -\underset{\substack{|\\ CHO}}{C}HCH_2-$$

b) Koch Reaction

$$-CH{=}CH- + CO + ROH \xrightarrow{H_2SO_4} -\underset{\substack{|\\ COOR}}{C}HCH_2- \qquad R = H, alkyl$$

c) Reppe Reaction

$$-CH{=}CH- + CO + ROH \xrightarrow{Ni(CO)_4} -\underset{\substack{|\\ COOR}}{C}HCH_2- \qquad R = H, alkyl$$

The products of all three reactions are usually mixtures of positional isomers, and with the diacid produced from oleic acid by the Koch process carbon chain rearrangements also occur. Since a specific terminology is difficult to assign to the diacids, the names carboxystearic acid or the $C_{19}$ dicarboxylic acids will suffice. Developmental samples of carboxystearic acid are available commercially from Badische Anilin- & Soda-Fabrik and from Union Camp Corporation.

This review covers synthesis, reactions and uses for hydroformylated and carboxylated fatty products. The reactions involved in the synthesis of the $C_{19}$ dicarboxylic acids have been discussed in greater detail elsewhere (1).

## SYNTHESIS

### Hydroformylation

More than one patent describes the reaction of unsaturated fatty acids and their derivatives with carbon monoxide and hydrogen (synthesis gas) to yield hydroformylated products (2-14). The catalyst is a cobalt hydrocarbonyl, formed in situ from a variety of cobalt compounds. Generally, reaction conditions include a pressure of 2000-4500 psig of synthesis gas and a temperature of about 100-200 C. Benzene or toluene may be the solvent, but one is not necessary. With methanol the acetals of methyl formylstearate are formed (4).

Laï et al. (15) found that the formyl derivative is favored at 150 C with a 2:1 ratio of carbon monoxide and hydrogen at high pressure, but that the hydroxymethyl derivative is favored at 190 C with a 1:2 ratio of carbon monoxide and hydrogen at low pressures. Preparation of hydroxymethyl compounds is complicated because polyesters or estolide condensation products form; however the latter can be saponified to hydroxymethylstearic acid in 90% yield (16). Cobalt (II) acetate is the preferred catalyst; at high concentrations (2% as cobalt) the reaction is faster, but more hydroxymethyl compound is formed than at a concentration of 0.5% (17).

By using dicobalt carbonyl as catalyst, temperatures of 100-110 C and pressures of 3500-4600 psig, Frankel et al. (18) obtained 85% yields of distillable formyl ester from methyl oleate, less with methyl linoleate and linolenate. They prepared the hydroxymethyl derivative of octadecanoate esters at temperatures ranging from 175-200 C (18). Chain-substituted hydroxymethyl isomers were separated from the linear isomer by silicic acid chromatography, and the acetates were suitable derivatives for both gas liquid chromatography (GLC) and thin layer chromatography (TLC) analyses (18).

Various glycerides like camellia, rapeseed, soybean and linseed oils have been subjected to the oxo reaction in the presence of a cobalt-thorium-on-Kieselguhr catalyst (19). With oils containing polyunsaturated fatty acids, hydroformylation occurred only at one double bond, and hydrogenation at the remaining double bonds of the fatty acid chain.

As a consequence of using cobalt compounds, extensive double bond isomerization has been demonstrated to occur before hydroformylation, and the product is a mixture of positional isomers. At least three investigators have demonstrated the presence of $\alpha,\omega$-functionality (in the amount of 10-15%) after conversion of the aldehyde derivative to a diacid or a diester (10,18,20). Distribution of the isomers may be determined as the diesters by mass spectrometry and demonstrated by TLC (18).

Frankel (21) prevented double bond isomerization and prepared exclusively methyl 9(10)-formylstearate by using a rhodium-triphenylphosphine ($Rh/\Phi_3P$) catalyst. This catalyst also had the advantages of higher conversions (90-99%), lower pressures (500-2000 psig) and no reduction of formyl to hydroxymethyl groups compared to conventional cobalt compounds. Also, formyloleate (a mixture of formyloctadecenoate isomers) and diformylstearate esters were formed from polyunsaturated fatty esters (22).

Usually hydroformylation has been applied to unsaturated fatty acids or esters, but it is also applicable to oleyl alcohol (8,23) and oleyl nitrile (23). Conventional hydroformylation at 190 C converts 9-octadecene to hydroxymethyloctadecane (74% yield); methyl 9-octadecenoate to methyl hydroxymethyloctadecanoate (65% yield); 9-octa-

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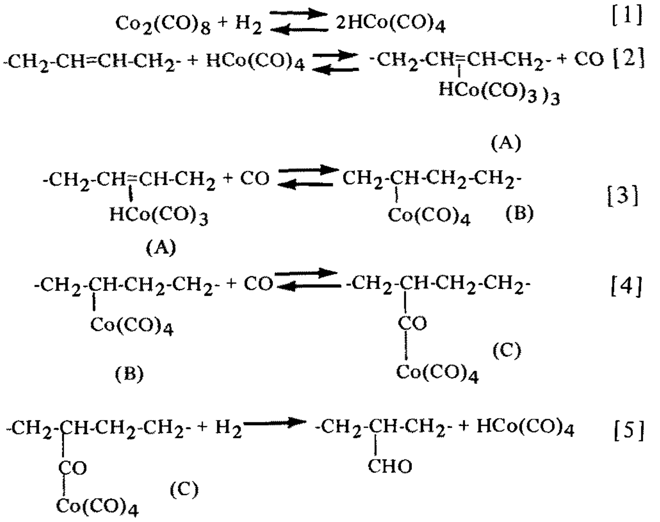
[1] Presented at the AOCS Meeting, Los Angeles, April 1972.

[2] N. Market. Nutr. Res. Div., ARS, USDA.

decenol to hydroxymethyloctadecanol (73% yield, as acetates); and 9-octadecenitrile to hydroxymethyloctadecanitrile (81% yield) (23). Acetate derivatives from the branched hydroxymethyl compounds were liquid, wheras acetate derivatives from the corresponding linear isomers were crystalline. Other important products include formyloctadecanol (75% yield), carboxyoctadecanol (70% yield), carbomethoxyoctadecanol, carboyxoctadecanol acetate, carbomethoxyoctadecanol acetate, formyloctadecanitrile (90% yield) and carboxyoctadecanitrile (65%) (16). Treatment of oleyl amine with cobalt carbonyl forms oleylformamide and N,N'-dioleylurea (16).

The mechanism of conventional hydroformylation of olefins with cobalt corbonyl is complex, and reports on it still appear in the literature. The pathway most generally accepted is summarized in the following scheme (24):



$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \qquad [1]$$

$$-CH_2-CH=CH-CH_2- + HCo(CO)_4 \rightleftharpoons -CH_2-\underset{HCo(CO)_3)_3}{CH=CH}-CH_2- + CO \qquad [2]$$

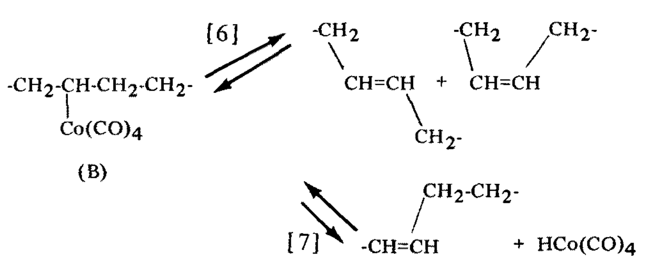
(A)

$$\underset{\underset{(A)}{HCo(CO)_3}}{-CH_2-CH=CH-CH_2} + CO \rightleftharpoons \underset{\underset{(B)}{Co(CO)_4}}{CH_2-CH-CH_2-CH_2-} \qquad [3]$$

$$\underset{\underset{(B)}{Co(CO)_4}}{-CH_2-CH-CH_2-CH_2-} + CO \rightleftharpoons -CH_2-\underset{\underset{\underset{(C)}{Co(CO)_4}}{CO}}{CH}-CH_2-CH_2- \qquad [4]$$

$$-CH_2-\underset{\underset{\underset{(C)}{Co(CO)_4}}{CO}}{CH}-CH_2-CH_2- + H_2 \longrightarrow -CH_2-\underset{CHO}{CH}-CH_2- + HCo(CO)_4 \qquad [5]$$

Key steps in this mechanism involve the formation of the actual catalyst, HCo(CO)$_4$ (step 1), and the inverconversion of $\pi$ to $\sigma$ organo-cobalt intermediate complexes (A and B). The $\sigma$ complex intermediate (B) undergoes CO insertion to form an acyl organo-complex intermediate (C) which reacts with $H_2$ to produce the formyl derivative (step 5). Isomerization occurs as side reactions involving H abstraction and dissociation of intermediate B with change in either configuration or position of the double bond.



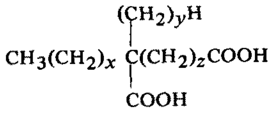
Hydrogenation of B would saturate the double bond and regenerate HCo(CO)$_4$.

## Koch Reaction

In 1955, H. Koch (25) first described a technically feasible route to carboxylic acids by the reaction of olefins with carbon monoxide and water in the presence of a Lewis acid. Koch (26,27) did not describe in detail application to oleic acid. However, Roe and Swern (28-31) give details for obtaining the diacid in good yield. Oleic acid, dissolved in 97% sulfuric acid containing 5 moles water per mole fatty acid, is caused to react at 10-20 C with carbon monoxide at atmospheric pressure. The carbon monoxide may be introduced through fritted glass, or it may be generated in situ from formic acid. Oleyl alcohol may also serve as the starting material (29-31). Ricinoleic and linoleic acid produce the same lactone (32).

Matsubara et al. (33) selected 98% sulfuric acid, because they found that hydration was the main reaction when its concentration was lower than 90%. Even with only a small excess of formic acid, sulfate formation may be avoided when another acid such as phosphoric acid or chloroacetic acid, is present (34). Using hydrofluoric acid as the solvent-catalyst, Miller et al. (35) carried out the reaction on oleic, erucic and 10-undecenoic acids at 30 C and 50-500 psig; they recovered hydrogen fluoride by distillation in 97-99% yield.

The Koch diacid is a mixture of positional and methyl-branched (resulting in a tertiary carboxyl group) isomers. Koch and Schauerte (36) demonstrated that such isomerization occurred,by characterizing products from undecylenic acid. When the reaction was carried out under 180 atm carbon monoxide pressure, the product contained ca. 40% methyl-branched isomers; but when formic acid was used, the product was all methyl-branched. Accordingly a general structure for the Koch diacid from oleic acid may possibly be written:

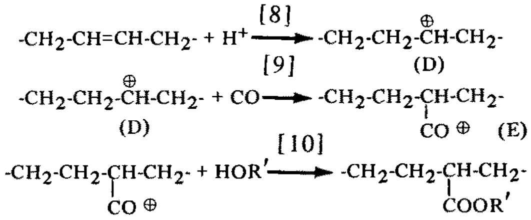


$$CH_3(CH_2)_x\overset{(CH_2)_yH}{\underset{COOH}{C}}(CH_2)_zCOOH$$

$x + y + z = 15$
$y = 0$ or 1

Positional isomerism in carboxystearic acid has been confirmed by mass spectral evidence; maximum concentration of branched carboxyl occurs at about carbon 15 (21). Mass spectra, however, cannot be used to determine methyl branching.

For a mechanism, Koch (26) postulated the formation of a carbonium ion (D) which on reaction with CO produces an acyl cation (E). This intermediate (E) converts to acid or ester by reaction with water or alcohol:



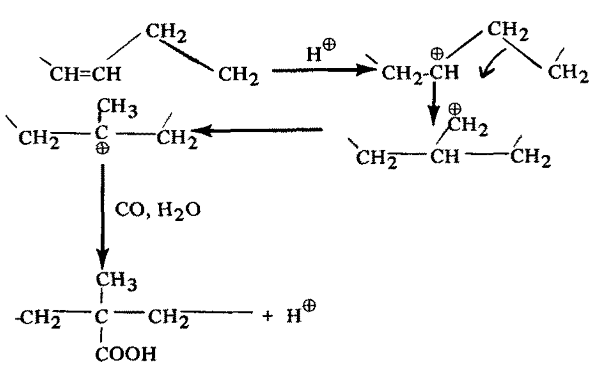
$$-CH_2-CH=CH-CH_2- + H^+ \xrightarrow{[8]} -CH_2-CH_2-\underset{(D)}{\overset{\oplus}{C}H}-CH_2-$$

$$\underset{(D)}{-CH_2-CH_2-\overset{\oplus}{C}H-CH_2-} + CO \xrightarrow{[9]} -CH_2-CH_2-\underset{CO^{\oplus}\ (E)}{CH}-CH_2-$$

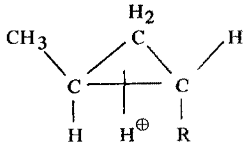
$$-CH_2-CH_2-\underset{CO^{\oplus}}{CH}-CH_2- + HOR' \xrightarrow{[10]} -CH_2-CH_2-\underset{COOR'}{CH}-CH_2-$$

R' = H, alkyl

A probable mechanism for the rearrangement to a methyl-branched system may be indicated as follows:



An alternative is the protonated cyclopropane structure proposed by Brouwer and Oelderik (37) for the $C_6$ system they investigated:

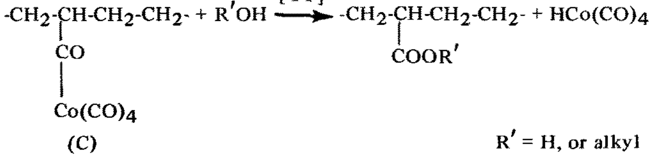


Products from such an intermediate may give rise to methyl branching on the carbon adjacent to the carboxylated carbon.

### The Reppe Reaction

Reppe and Kroper (38,39) carboxylated oleic acid directly in 70% yield with carbon monixide and water by using nickel carbonyl and nickel iodide at 270 C and 200 atm. When this reaction was carried out on methyl oleate in the presence of methanol instead of water, a 36% yield of methyl carbomethoxystearate resulted. A pilot-scale process for the reaction with oleic acid has been described (40). Levering (41) found that the reaction proceeded more quickly with dicobalt octacarbonyl catalyst than with nickel carbonyl. Crowe and Helsler (42) got N-phenyl pentadecylsuccinimide as a major product when the reaction with cobalt carbonyl was carried out in the presence of aniline.

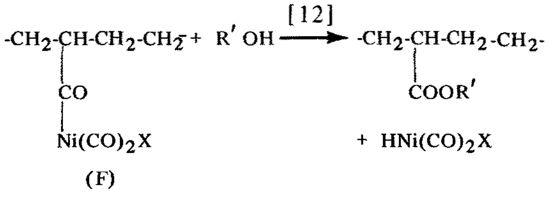
With cobalt catalysts, Heck (43) proposed a mechanism related to that of hydroformylation. The acyl organo-complex intermediate (C) reacts with water or alcohol to form the acid or ester (reaction 11):



$$-CH_2-\underset{\substack{|\\CO\\|\\Co(CO)_4}}{CH}-CH_2-CH_2- + R'OH \xrightarrow{[11]} -CH_2-\underset{\substack{|\\COOR'}}{CH}-CH_2-CH_2- + HCo(CO)_4$$

(C) R′ = H, or alkyl

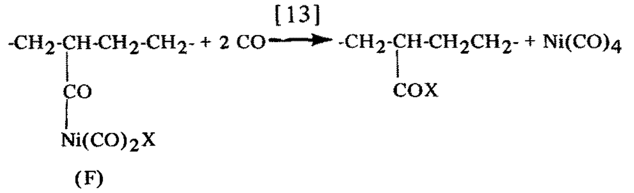
Similarly, with nickel carbonyl and hydrogen halide, Heck proposed the formation of an acyl nickel carbonyl halide F which can produce either acid or ester (reaction 12):



$$-CH_2-\underset{\substack{|\\CO\\|\\Ni(CO)_2X}}{CH}-CH_2-CH_2- + R'OH \xrightarrow{[12]} -CH_2-\underset{\substack{|\\COOR'}}{CH}-CH_2-CH_2- + HNi(CO)_2X$$

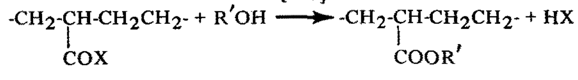
(F)

Alternatively, reaction of intermediate F with CO forms an acyl halide which in turn reacts with water or alcohol (step 14):



$$-CH_2-\underset{\substack{|\\CO\\|\\Ni(CO)_2X}}{CH}-CH_2-CH_2- + 2\,CO \xrightarrow{[13]} -CH_2-\underset{\substack{|\\COX}}{CH}-CH_2CH_2- + Ni(CO)_4$$

(F)



$$-CH_2-\underset{\substack{|\\COX}}{CH}-CH_2CH_2- + R'OH \xrightarrow{[14]} -CH_2-\underset{\substack{|\\COOR'}}{CH}-CH_2CH_2- + HX$$

A summary of the major synthetic routes described in the preceding paragraphs is presented in Table I.

## REACTIONS

### Aldehydes

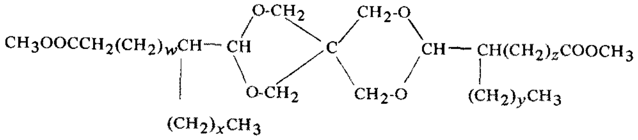
In the conventional oxo process with cobalt catalysts, the initial formylstearate is partially reduced to hydroxymethylstearate at temperatures of 110-150 C and completely reduced at 170-190 C. The selective rhodium-triphenylphosphine system does not catalyze the reduction of the formyl group even at elevated temperatures, but the formyl product can be catalytically hydrogenated with Raney nickel or reduced by sodium borohydride (21). Both the aldehyde and ester groups in formylstearate may be catalytically hydrogenated to obtain hydroxymethyloctadecanol with copper chromite at 275 C and 4000 psig of hydrogen (5), or they may be reduced with lithium aluminum hydride (14).

Methyl formylstearate has been oxidized to the dibasic acid derivative by a variety of ways, including alkali fusion (9,10,12,44,45), air oxidation (3,18,23,46,47) and oxidation by potassium permanganate (21,47) or dichromate (47). Alkali fusion also oxidizes the hydroxymethyl compound to the diacid.

Decamethylenediamine reacts with methyl formylstearate to produce a hard, transparent, amber wax (48).

The dimethyl acetal of methyl formylstearate forms readily in methanol either through the use of dimethoxypropane as a water scavenger and in the presence of HCl catalyst (23) or through the use of methanol•$BF_3$ reagent (18). Although the acetals may be isolated easily, they are cracked to enol (vinyl) ethers if excess alcohol is removed by distillation in the presence of an acidic catalyst. By this means Mertzweiller (6) prepared the isooctyl enol ether-isooctyl ester, then hydrogenated the enol ether to form the saturated ether-ester. Acetals may crack when analyzed by GLC (23). If the injection port, column and packing are free of acidic sites, acetals go through the column unaltered (49).

The reaction of pentaerythritol with methyl formylstearate yields a diester having a cyclic acetal structure (50):



This compound is a viscous liquid that is soluble in acetone, ethanol and benzene and that has been used for preparing poly(ester-acetals) and poly(amide-acetals) (49).

### Acid

Carboxystearic acid prepared from hydroformylated oleic acid can be esterified by the usual procedures (46). Dufek et al. (51) found that the internal carboxyl group was ca. one twenty-fifth to one thirtieth as reactive as the terminal carboxyl group. The carboxystearic acid from the Koch procedure esterifies completely only with difficulty because of the steric hindrance introduced by methyl branching at the internal carboxyl group. Thus total esterification occurs only after 42 hr of reflux with dimethyl sulfate, after 240 hr of reflux in toluene with azeotropic removal of water (28); or at 10-20 C within 1-3 hr if liquid hydrogen fluoride is used as the solvent-catalyst (52). These differences in reactivities confirm the effect of steric factors introduced by methyl and higher alkyl branching in aliphatic carboxylic acids as discussed by Newman (53).

Carboxystearic acid has been converted to the dinitrile by reaction with ammonia at 280-300 C over a catalyst support containing 1% manganese sulfate (54). Hydrogenation of dinitrile to diamine (38) and conversion of the

TABLE I

Reactions of Carbon Monoxide with Oleic Acid and Derivatives

| Reaction | Reactants | Catalyst | Reaction conditions |  | Yield, % | Product | References |
|---|---|---|---|---|---|---|---|
|  |  |  | Temperature, C | Pressure, psig |  |  |  |
| Hydroformylation, oxo (Roelen) | CO, $H_2$ | $[Co(CO)_4]_2$ | 100-150 | 3000-4000 | 70-80 | Isomerized formylstearate | 16,18 |
| Hydroxymethylation, oxo | CO, $H_2$ | $[Co(CO)_4]_2$ | 180-200 | 3000-4000 | 80-90[a] | Isomerized hydroxymethylstearate | 16,18 |
| Hydroformylation, selective | CO, $H_2$ | $Rh/\Phi_3P$ | 100-120 | 1000 | 90-95 | 9(10)-Formylstearate | 21 |
| Hydrocarboxylation (Koch) | CO, $H_2O$[b] | $H_2SO_4$ | 25-50 | 0-50 | 85 | Methyl-branched, isomerized carboxystearate | 28 |
| Hydrocarboxylation (Reppe) | CO, $H_2O$[b] | $Ni(CO_4)$, $NiI_2$ | 270 | 3000 | 80 | Isomerized carboxystearate | 39 |
| Carboalkoxylation | CO, $CH_3OH$ | $[Co(CO)_4]_2$ | 220 | 6000 | 70-80 | Isomerized carbomethoxystearate | 40 |

[a] After saponification of estolide condensation products.

[b] Olefins other than oleic acid have been carboalkoxylated by substituting alcohols for the water.

diamine to a diisocyanate by reaction with phosgene (55-57) have been reported.

## USES

### Lubricants

The viscosity index of the di-*n*-butyl ester of the Koch diacid (169) is higher than that of di-2-ethylhexyl sebacate (145), but the pour point (-54 C) is not so low as that for the sebacate ester (-67 C) (58). Carbomethoxyoctadecyl acetate had a pour point of -47 C and a viscosity index of 100. The diisooctyl ester of carboxystearic acid when added to mineral oil along with polyacrylic acid ester gave a product with a viscosity index of 136 and freezing point of less than -50 C (59).

Hydroxymethyloctadecanol is said to form oil soluble polyesters useful for improving the viscosity index of lubricants (5).

The lithium soap of hydroxymethylstearic acid has gone into formulating grease compositions (60).

### Plasticizers

Esters from both oxo and Koch $C_{19}$ dicarboxylic acids have been found to be effective as plasticizers for poly(vinyl chloride) (PVC). Mixtures of PVC and the dibutyl ester of the oxo diacid have been claimed as novel compositions of matter (46). At a concentration of 40% of the dibutyl esters, low temperature flex was less than -60 C. Other esters said to be compatible with PVC include dibenzyl and ditetrahydrofurfuryl carboxystearates (61).

While testing a number of diesters from the Koch diacid as plasticizers for PVC, Roe et al. (58) found that dimethyl, diethyl and di-*n*-propyl esters were compatible at a 35% level and were efficient, low temperature plasticizers. The dipropyl ester-plasticized PVC had a Clash-Berg $T_{135,000}$ value of -50 C vs. -59 C for the di-2-ethylhexyl sebacate mixture. The dibutyl and diisobutyl esters caused a heavy exudate after 24 hr, and the di-2-ethylhexyl ester/PVC mixture did not fuse on milling. Carbomethoxyoctadecyl acetate was also an efficient plasticizer and had a Clash-Berg $T_{135,000}$ value of -47 C.

The dinitrile from carboxystearic acid is another effective plasticizer for PVC (54).

Either lead or cadmium salt of monobutyl carboxystearic acid stabilizes PVC (62).

Several acetals and an enol ether from methyl 9(10)-formylstearate were extremely low melting (below -80 C) compounds that were generally compatible as secondary plasticizers for PVC (49). When used in 50:50 mixtures with dioctyl phthalate at a total plasticizer level of 32%, they imparted low temperature properties intermediate between those of dioctyl phthalate alone and dioctyl sebacate alone.

PVC has been internally plasticized by converting ethyl hydroxymethylstearate to a coreactive monomer and copolymerizing with vinyl chloride (13). One method transesterified diethyl fumarate with the hydroxymethyl compound, and another converted the hydroxymethyl group to an acrylate. The internally plasticized PVC was greatly superior to conventionally plasticized PVC in migration properties, as well as in heat loss and extractability by soapy water.

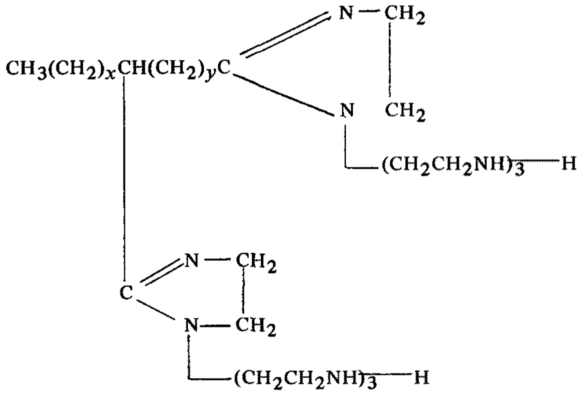
### Polyurethanes

From isomeric hydroxymethyloctadecanols have been prepared polyurethane resins having desirable properties of hardness, flexibility, strength, chemical and moisture resistance suitable for coating electrical wire and encapsulating or potting electrical components and electronic devices (14).

The reaction of phosgene with the hydrochloride salt of aminomethylstearylamine at 50-70 C produced isocyanatomethylstearylisocyanate in more than 90% yield (56). This diisocyanate is characterized by low volatility and consequently low toxicity. Polyurethane coatings and castings made from it are hard, flexible and resistant to degradation by sunlight.

### Epoxy Resins

When caused to react with tetraethylene pentamine, the oxo diacid formed a diimidazoline having the structure (45):



The diimidazolines may serve as coreactants in epoxy resins when present in the amount of 10-30% of total resin weight. Poly(amine-amides) from carboxystearic acid and diethylenetriamine react with epoxy resins to produce clear, hard, tough, abrasion- and solvent- resistant castings or coatings (12). The coatings are said to have exceptional resistance to aviation gas, toluene and oleic acid.

Low molecular weight poly(amine-amides) from carboxystearic acid and diethylenetriamine can be components in varnishes, castings, laminated resins and adhesives from epoxy and phenolic resins (63). Similar poly(amine-amides) when mixed with a copolymer of methacrylamide and vinyl pyrrolidone could be emulsified in water to provide a useful curing agent (64).

The diamine obtainable from tricyclopentadiene, either alone or with diethylenetriamine, also makes polyamides that impart high gloss, excellent hardness and flexibility to the epoxy resin (65). Greater compatibility of the polyamide with epoxy resins for coatings apparently results when another amine, such as 1,3-di(aminomethyl)benzene, is added along with diethylenetriamine (66).

### Leather Coatings

Polyamide coatings for leather have good resistance to rubbing, scuffing and perspiration, but they usually require softeners to improve flexibility and elasticity and are not soluble in the lacquer solvents that are compatible with the bonding nitrocellulose layer. Polyamides containing carboxystearic acid, 4,4′-diaminodicyclohexylmethane, capryllactam and hexamethyldiammonium adipate are transparent, soluble in alcohols and lacquer solvents, and form glossy, smooth and elastic coatings (67). Similar polyamides when mixed with a copolymer of acrylamide, methacrylamide and acrylic acid in water and triethanolamine form stable dispersions, particularly after adding poly(ethylene oxide) (68). Such dispersions are suitable for giving a mat finish to leather goods.

### Unsaturated Polyester Resins

Carboxystearic acid has served as a component of unsaturated polyester resins. After curing, the resin was flexible and moisture resistant and therefore desirable for electrical purposes and as coatings (69).

In comparison to polyesters, polyamides and poly(ester-amides) have improved hydrolytic stability but ordinarily are insoluble in styrene and in common solvents. Poly(ester-amides) from carboxystearic or dimer acid with terminal groups modified by reaction with maleic anhydride were soluble in styrene (70). The hardened poly(ester-amide) resins were said to be extraordinarily resistant to hydrolysis by water or aqueous acid.

### Coatings

Because of strong hydrogen bonding between amide groups of different chains, linear polyamides are highly crystalline, opaque and insoluble in common solvents. Short chain alkyl substitution at the α-carbon of the dibasic acid partially reduces hydrogen bonding, but solution of such polyamides is still difficult, and the polyamide film is opaque. However the longer side chain in carboxystearic acid materially reduces crystallinity to provide greater solubility and transparency. For example a copolyamide made from the salt of carboxystearic acid with 4,4′-diaminodicyclohexylmethane (40 parts), hexamethylammonium adipate (20 parts), capryllactam (20 parts) and caprolactam (20 parts) was soluble in alcohols and produced a transparent film (71).

Ordinarily polyamides do not form stable water dispersions. However mixed copolyamides containing carboxystearic acid are said to be water-dispersible, such dispersions being suitable for transparent films and for coatings for textile fibers or paper (72). For example, a copolyamide from carboxystearic acid, adipic acid, hexamethylene diamine and caprolactam was dissolved in cyclohexanol; to the solution was added water and an aqueous solution of a copolymer of methacrylamide and vinyl pyrrolidone; and finally the cyclohexanol was removed azeotropically. The average particle size of the dispersion was 2 $\mu$. Upon drying at normal temperatures, the dispersion produced a transparent film of high mechanical strength.

Copolyamides containing carboxystearic acid make protective coatings for metal objects that are resistant to salt spray (73). For example the copolyamide was made up from 25 parts of capryllactam and 75 parts of the salt from carboxystearic acid and 4,4-diaminodicyclohexylmethane. The copolyamide was soluble in a mixture of *n*- and isobutyl alcohols and, when mixed with pigments and fillers, made a sprayable lacquer.

Viscous polyacetals were prepared from the reaction of partially hydroformylated linseed oil and various polyols. These polyacetals, related poly(ester-acetals) and the isocyanate-terminated prepolymers derived from them, formed hard films of good chemical and impact resistance (74).

### Transparent Polyamides

Clear and transparent polyamides with good thermoplastic molding properties have been prepared by fusing together two copolyamides, one of which contains carboxystearic acid (75). The latter copolyamide was prepared from capryllactam and the carboxystearic acid salt of 4,4′-diaminodicyclohexylmethane.

Transparent, soluble polyamides from carboxystearic acid and 9,9-bis(aminopropyl)fluorene have a softening point of 120 C and good mechanical strength (76).

### Miscellaneous

The reaction product of carboxystearic acid and hexadecylamine produces a light yellow waxy solid said to have corrosion-inhibiting properties in lubricating oils (77).

Carboxystearic acid apparently is not so effective a corrosion inhibitor as 9(10)-phosphonostearic acid as determined by salt water immersion and humidity cabinet tests (78). Carboxystearic acid has been tested as an air-entraining agent for concrete (79).

The acryloxymethyl stearoyl chloride prepared from 9(10)-hydroxymethylstearic acid has made active polymers that impart shrink resistance properties to wool (80).

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