unlike the advent of synthetic glycerine. This development caused quite some concern among the natural fatty acid industry about 10–15 years ago. We might draw a parallel between this threat and the synthetic glycerine situation. While, of course, the natural fatty acid industry has never been happy about it, the situation has settled down to a satisfactory status-quo. There are customers for natural glycerine as well as customers for synthetic glycerine. And the big worry on the part of the natural fat splitters has not materialized: expanding markets for glycerine have taken care of almost everyone's products.

We might also mention the threat of tall oil fatty acids which created another crisis as little as five to eight years ago. This development has now been stabilized within the overall fatty acid industry. Not only have tall oil fatty acids grown in volume themselves, but they have provided a number of new uses for some natural fatty acids available from fats and oils, and have also provided the fatty acid derivative manufacturer with a cheaper raw material out of which to produce certain profitable fatty acid derivatives. Things in technological progress are usually good for both sides. I think it is good to keep in mind that this situation is not new. We have gone through a history of new products coming in and perhaps partially replacing older products, and in so doing, stimulating and increasing their growth.

Gentlemen, we shall change the point of view and get down to specific products and talk about them in a little more detail. I should like to turn the microphone over for a little more extended time to Dr. Fefer, who will provide us with more details about Enjay's "Neo Acids."

Neo Acids Chemistry and Applications[1]

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Abstract

Four commercial neo acids (synthetic trialkylacetic acids) C_5, C_7, C_{10}, and C_{13} are synthesized employing an olefin, carbon monoxide, and acidic catalyst and possess the hindered neo configuration around the *alpha* carbon. Esterification using simple alcohols and polyols, and preparation of peroxyesters and metal salts using neo acids as well as toxicity, LD_{50} values of the acids, are discussed. Hydrolytic stability of the esters, and possible end use applications are described.

Introduction

The neo acids are sterically hindered trialkylacetic acids available from the Enjay Chemical Company. They are prepared by reacting an olefin and carbon monoxide in the presence of an acid catalyst and water. The neo acid therefore contains one carbon more than the starting olefin. For example, to prepare trimethylacetic acid (pivalic acid or neo pentanoic acid), isobutylene and carbon monoxide are reacted in the presence of an acid catalyst yielding an isobutylene-carbon monoxide-catalyst complex. This complex is reacted with water to yield the crude carboxylic acid which is then purified. The mechanism for such a reaction using isobutylene as an example would be:

$$\underset{\text{isobutylene}}{CH_2 = C(CH_3)_2} + \underset{\text{catalyst}}{H^{\oplus}} \rightarrow \underset{\text{carbonium ion}}{(CH_3)_3C^{\oplus}} \qquad [1]$$

$$(CH_3)_3C^{\oplus} + C = O \rightarrow \underset{\text{acyl carbonium ion}}{[(CH_3)_3C\text{–}CO]^{\oplus}} \qquad [2]$$

Hydrolysis then leads to the trialkylacetic acid and regenerates the catalyst:

$$[(CH_3)_3C\text{–}CO]^{\oplus} + HOH \rightarrow \underset{\text{neo pentanoic or pivalic acid}}{(CH_3)_3C\text{–}COOH} + H^{+} \qquad [3]$$

For the C_7, C_{10} and C_{13} neo acids, the starting olefins are C_6, C_9 and C_{12} respectively.

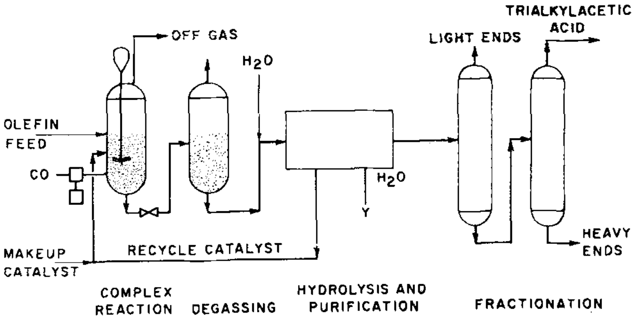

FIG. 1. Flowsheet for trialkylacetic acids process.

The flow diagram shown in Fig. 1 illustrates the basic process steps. Olefin feed and catalyst are pumped to reaction pressure and fed to the complexing reactor while a gas, rich in CO, is compressed and bubbled into the reaction mixture. After degassing, the complex proceeds to a hydrolysis tank where water is added to generate the neo acid and release the catalyst for reuse. The crude acid is then treated to remove the last traces of catalyst and is distilled to remove light and heavy ends.

The C_5 neo acid (trimethylacetic acid) has a purity greater than 99.5% as determined by gas chromatographic analysis and is an isomerically pure compound. Neo heptanoic acid (C_7) is about 95% 2,2-dimethylpentanoic acid with the remainder being 2-methyl-2-ethylbutanoic acid. This latter composition remains liquid below −40C. A typical analysis for alkyl groups on the *alpha* carbon for neo decanoic acid is shown in Table I. This analysis is also typical of the alkyl grouping of the C_{13} neo acid.

In general, reactions which use a mechanism that does not involve the carbonyl group (e.g., metal salt formation) proceed at rates comparable to "normal" fatty acids. If the carbonyl of the neo acid is involved (e.g., esterification) the rate will be slower than with a fatty acid. However, comparable rates can be achieved through using slightly more vigorous reaction conditions.

TABLE I
Neo Decanoic Acid, Analysis of Alpha Carbon Configuration

Alkyl groups	Percentage	Precision
2,2-Dimethyl	31	± 5
2-Methyl-2-higher-alkyl	67	±10
2,2-Di-higher-alkyl	2	±10

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[1] Presented in part at AOCS Meeting, Los Angeles, April 1966.

TABLE II
Physical Properties of Neo Acids

Property	Pentanoic[a]	Heptanoic[b]	Decanoic[c]	Tridecanoic[d]
Color Pt-Co(APHA)	20 (Melted)	10	60	30
Acid value, mg KOH/g	550	424	315	255
Melting Point, C	35 3	<−40	<−40	<−40
Distillation range, C	163–165	204–213	147–152/20 mm.	156–168/10 mm.
Specific Gravity	0.874(70/4C)	0.920(20/20C)	0.906(20/20C)	0.908(20/20C)
Refractive Index n_D^{20}	1.3927	1.4212	1.4385	1.4471
Viscosity, Centistokes				
20C	Solid	7.6	35.7	2.40
60C	1.7	3	7	4
Ionization Constant, $K_a \times 10^{-6}$, 25C	9.3	6.6	4.2	3.7
Flash Point, F (COC)	165	225	305	320

[a] Trimethylacetic acid; pivalic acid.
[b] 95% 2,2-dimethylpentanoic acid + 5% 2-ethyl-2-methylbutanoic acid.
[c] Mixture of C_{10} trialkylacetic acids.
[d] Mixture of C_{13} trialkylacetic acids.

Physical Properties

The physical properties of Enjay neo acids are shown in Table II. With the exception of neo pentanoic acid and neo heptanoic, the neo acids are made from olefin feedstocks which are isomeric mixtures and therefore do not produce single isomerically pure carboxylic acids.

Of particular significance is the physical state of the neo acids at room temperature as compared to their normal fatty acid counterparts. Neo pentanoic acid is a solid, n-valeric acid is a liquid. Neo heptanoic acid like n-heptanoic acid is liquid at room temperature. The higher molecular weight neo decanoic and neo tridecanoic acids are liquids with low freezing points. The corresponding molecular weight fatty acids are solids melting at 31.4C and 41C respectively.

The neo acids are weak carboxylic acids. As shown in Table II, the neo acids have ionization constants about ½ to ⅕ that of acetic acid which has an ionization constant of 1.75×10^{5} (25C).

Chemical Properties

The sterically hindered structures of the neo acids provide them with certain performance advantages over the unhindered fatty acids. Although the structural characteristics of the neo acids in some cases make the preparation of their derivatives more difficult than the straight chain fatty acids, the neo acid derivatives once formed offer superior stability in many cases.

Neo acid esters are readily prepared by carrying out their esterification using conditions slightly more vigorous than conventional. As shown in Table III, the esters can be obtained by using moderately higher temperatures and catalyst concentrations than those for normal-fatty acid esterifications.

Metal salts can be prepared using conventional techniques, such as 1) the reaction of neutral alkali salts (from alkali hydroxides and the free acids) and metal halides, e.g., $BaCl_2$, $CuCl_2$, $Cu(NO_3)_2$; 2) the reaction of metal oxides and the free acid in a refluxing hydrocarbon solvent; 3) the direct thermal fusion of the metal oxide and the acid.

TABLE III
Esterification of Neo Acids by Hexyl Alcohol[a]

Neo acid	Entrainer	Catalyst Wt % on total charge	Max temp, C	Time, hr	% Completion
Pentanoic	Toluene	0.33 (PTSA)[b]	140	4	99.0
Decanoic	Mixed xylenes	2 (H_2SO_4c.)	169	3.5	99.7
Tridecanoic	Mixed xylenes	2 (H_2SO_4c.)	175	3.3	100

[a] Oxo-type hexyl alcohols used. One mole of acid and 1.2 moles of hexyl alcohol are heated using conditions shown in above table.
[b] *p*-Toluenesulfonic acid.

Acid chlorides are readily made using excess thionyl chloride at reflux temperature. Because of the hindered structure of the neo acids the reaction requires heat to maintain the reaction in contrast to the spontaneous reaction of normal fatty acids with thionyl chloride.

Simple amides are generally synthesized from the acid chloride since the simple low molecular weight amine salts reversibly decompose to starting amine and acid when heated. However, high molecular weight amides can be prepared in good yield by pyrolysis of the amine salt, e.g., dodecyl ammonium salts.

The neo alcohols are conveniently prepared in the laboratory by reducing the corresponding acid with lithium aluminum hydride. The ease of reduction decreases with increasing molecular weight. A comparison between neo decyl alcohol and n-decyl alcohol is shown in Table IV.

Applications

Peroxyesters

A current commercial use for neo pentanoic acid (pivalic acid) is in the preparation of *t*-butyl peroxypivalate (Product Bulletin 6.501, Lupersol II, Wallace & Tiernan, Lucidol Div., Buffalo, N. Y.). This perester is a highly efficient source of free radicals at temperatures as low as −40C. The synthesis may be carried out via the acid chloride and the hydroperoxide of *t*-butyl alcohol. It is used as a vinyl polymerization initiator for vinyl chloride, vinyl acetate, styrene, acrylics, etc.

Vinyl Esters

Preparation of vinyl neo pentanoate (pivalate) has been described in a U.S. Patent [Cornthwaite, W. R., and N. D. Scott (E. I. duPont de Nemours & Co.) U.S. Pat. 2,381,388 (Aug. 7, 1955)]. Polymerization of this ester by classical peroxide catalysis yields a polymer with much greater hydrolytic stability than polyvinyl acetate. In addition, the softening point is also higher, 65C for the pivalate vs. 35C for the acetate. The two methods of preparation are:

1. Vapor phase reaction with acetylene

$$(CH_3)_3CCOOH + HC \equiv CH \rightarrow (CH_3)_3CCOOCH = CH_2$$

TABLE IV
Properties of Neo vs. Normal Decyl Alcohol

Property	Neo decyl alcohol	Normal decyl alcohol
Physical state	Liquid	Liquid
Boiling point, C (760 mm)	210–220	233
Melting point, C	<−50	7
Specific gravity	0.8319(20/20C)	0.830(20/4C)
Refractive index n_D	1.4350 (25C)	1.4372 (20C)

TABLE V

Odor Characteristics of Selected Neo Acid Esters

Neo acid ester	Odor	Boiling range C/mm Hg	Neo acid ester	Odor	Boiling range C mm Hg
Methyl neo pentanoate	Citrous	103–105	Benzyl neo pentanoate	Orchid	70–71/0.6
Ethyl neo pentanoate	Thugone	115–117	Methyl neo heptanoate	Camphor	145–148
n-Propyl neo pentanoate	Fruity	138–141	Ethyl neo heptanoate	Winey	159–162
n-Butyl neo pentanoate	Butter ether	163–165	n-Propyl neo heptanoate	Leather	180–183
n-Amyl neo pentanoate	Orchid	69–72/12.0	n-Butyl neo heptanoate	Green leaf	55–58/0.7
oxo-Hexyl neo pentanoate	Fruity	83–86/10.0	Ethyl neo tridecanoate	Vermouth	....

2. Transesterification with vinyl acetate

$$(CH_3)_3CCOOH + CH_3COOCH = CH_2 \leftrightarrows$$
$$(CH_3)_3CCOOC = CH_2 + CH_3COOH$$

Metal Salts

The Pb, Co, Mn, Zn, and Ca neo decanoic acid salts are commercially available (Monney Chemical Co., Cleveland, Ohio) driers used in paint formulations. It is claimed they have the advantage of much shorter drying time vs. the corresponding metal naphthanates. In addition, lighter colors as well as stability are other advantages. Salts of 2-ethyl hexanoic acid (octoates) are also used as driers. With Pb the neo salts are about equivalent in dry time to the octoates. A significant advantage of the neo driers over the octoates is that it is quite easy to prepare a basic lead salt with neo decanoic acid while it is not with 2-ethyl hexanoic acid.

Esters

The low molecular weight monoesters show promise as industrial odorants, masking agents, or as possible hydrolytically stable solvents in extraction processes.

Table V lists some of the low molecular weight esters that exhibit a wide range of unusual and interesting fragrances. Coupled with their excellent stability under both acid and basic pH (Technical Information Sheet C-42A, Enjay Chemical Co., New York), shown in Tables VI and VII for hexyl esters, the fragrant neo acid esters are expected to be useful in such applications as soaps and shampoos where hydrolytic stability can be a problem.

Polyol Esters

Polyol esters of neo acids (neo pentanoic acid) are readily prepared (Technical Information Sheet C-46, Enjay Chemical Co., New York) as shown in Table VIII (see experimental section). These complex esters exhibit properties which should make them interesting for functional fluid and lubricant applications.

Solvents

As solvents for extraction processes, the superior hydrolytic stability of the neo acid esters is expected to decrease solvent losses due to decomposition by hydrolysis. This would be especially significant where the extractions are made under strong acidic or basic conditions. In addition, the neo acid esters might offer better selective extractions than conventional ester solvents. As shown in Table IX, the difference shown between the solubilities of neo decanoic acid and *n*-decanoic acid (capric acid) might be expected to carry through to the esters.

Agriculture

Tributyl tin neo decanoate (Technical Bulletin D-113, Carlisle Chemical Works, Reading, Ohio) is reported to exhibit a broad spectrum of biocidal activity. Potential applications include, inhibition of fungi growth in emulsion paints, control of marine organisms through antifouling paint formulations, wood preservation through control of fungi, termites and marine borers, prevention of mildew and bacterial odor of textiles, and sanitizers in combination with quaternary ammonium compounds and other biocides.

Neo decanoic acid has shown good helminthic properties [Tarjan, A. C., V. J. Yates and J. L. Holmes (Mallinckrodt Chemical Works) U.S. Pat. 2,846,351 (Aug. 5, 1958)]. The helminth problem is particularly important in animals that are fed essentially synthetic diets. When neo decanoic acid was included in synthetic diets, the various helminths were eliminated from the animals. This was followed by a resultant increase in weight and improvements in general condition of the animals.

Experimental

Typical Preparation of Simple Esters

Preparation of hexyl neo tridecanoate. A one-liter, 3-necked flask fitted with a stirrer, thermometer, and Dean-Stark water separator was charged with 214.0 g (1.0 mole) of neo tridecanoic acid, 122.0 g (1.2 moles) oxo hexyl alcohol, and 100 g of xylene. With stirring, 8.7 g of concentrated H_2SO_4 was added, and the reaction mixture was brought to reflex. After 170 min at reflux, the reaction was 96% complete (as determined by titration of residual acid) and after 200 min, the reaction was 100% complete. The mixture was cooled to 100C and washed with water (1 × 100 ml), 5% sodium hydroxide solution (2 × 100 ml) and again with water, until the water washes were neutral. The reaction mixture was then distilled at atmospheric pressure to remove xylene, hexanol and water, and then under vacuum to obtain the desired ester. A total of 249 g (83.5% of theoretical yield) of hexyl neo tridecanoate boiling at about 130C (3mm Hg) was collected. The product had a color of 50 (Pt-Co).

TABLE VI

Rate Constants for Base Hydrolysis of Hexyl Esters at 50C

Ester	k_2 (Liter/Mole/Sec.) × 10^5	Relative rate[a]
Neo pentanoate	55.1	32
Neo heptanoate	8.9	5.2
Neo decanoate	3.2	1.9
Neo tridecanoate	1.7	1.0
Valerate	9260	5400
Pelargonate	2960	1700
Laurate	2285	1300

[a] Neo tridecanoate rate arbitrarily set at 1.00.

TABLE VII

Rate Constants for Acid Hydrolysis of Hexyl Esters at 50C

Ester	k_1 (sec^{-1}) × 10^7	Relative rate[a]
Neo pentanoate	5.2	1.8
Neo heptanoate	1.5	0.5
Neo decanoate	3.8	1.3
Neo tridecanoate	2.8	1.0
Valerate	103	36
Pelargonate	76	26
Laurate	61	21

[a] Neo tridecanoate rate arbitrarily set at 1.00.

TABLE VIII
Polyol Esters of Neo Pentanoic Acid

Polyol	Moles of reagent used		Entrainer	Catalyst Wt % H_2SO_4	Max temp, C	Time, hr	Percent conversion, Wt %	Distillation range, C/mm Hg
	Polyol	Acid						
Ethylene glycol	1.0	2.2	Toluene	1.0	148	2.0	90.2	87– 88/1.8
1,2 Propanediol	1.0	2.2	Toluene	1.0	155	2.0	89.0	105–106/4.0
Glycerine	1.0	3.3	Toluene	1.5	145	1.5	96.0	165–167/5.0
Trimethylol propane	1.0	3.3	Toluene	1.0	168	6.5	100.0	178–180/0.8[a]
Pentaerythritol	1.0	4.4	Benzene	1.0	149	4.0	100.0	225–227/8.0[b]
Dipentaerythritol	1.0	6.6	Toluene	2.5	158	4.5	88.2	........[c]

[a] M.P. 32 C.
[b] M.P. 122 C.
[c] M.P. 146 C (Recrystallized from Isopropyl Alcohol).

Typical Preparation of Polyol Esters

Preparation of pentaerythritol tetra-neo pentanoate. To a one-liter, 3-necked reaction flask equipped with a stirrer, thermometer and Dean-Stark water separator joined to a reflux condenser are added 448.8 g (4.4 moles) neo pentanoic acid, 136.0 g (1.0 mole) pentaerythritol, 1 wt% concentrated sulfuric acid, and 100 ml of benzene. The reaction mixture is heated to 149C and the water of esterification is removed by azeotropic distillation. The conversion to ester is followed by titration of residual acid. After the reaction is completed, the crude product is cooled to room temperature; it is then washed successively with three 200 ml portions of 5% NaOH and with water until neutral. The polyol ester is flash distilled under reduced pressure and then analyzed by gas chromatography.

Preparation of Basic Lead Neodecanoate Drier

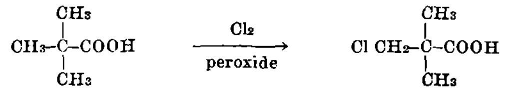
Neo decanoic acid (172 gr; 1.0 mole) and 206 gr of Varsol 3 are charged to a one-liter, 4-necked flask fitted with a condenser, stirrer, water trap and thermometer. Then National Lead Litharge PTX lead oxide (131.7 gr; 0.59 mole) is added *slowly* at 40C with stirring. After complete addition the temperature is raised slowly to 190C and held until a clear solution is obtained. Water and solvent may be removed upon cooling and vacuum stripping (70C). If a somewhat hazy solution results, it may be necessary to add a small amount of magnesium sulfate. The drier is filtered and the metal content adjusted to 24% Pb. Method from Coatings Intermediates News Bulletin, ECL-6605 1448, Enjay Chemical Co., New York.

Preparation of Chloro Neo Pentanoic Acid

To a two-liter round-bottomed reaction flask equipped with a stirrer, a reflux condenser and a thermometer are added 306 g neo pentanoic acid (3.0 moles), 202.5 g sulfuryl chloride (1.5 moles), 0.75 g benzoyl peroxide (0.003 mole) and 462 g carbon tetrachloride (3.0 moles) as solvent. The reaction mixture is then heated in the dark for 3 hr at reflux (approximately 90C). Since sulfur dioxide is liberated as the product is formed, chlorination should be performed in a well-ventilated hood. The crude product is distilled using a 15-plate Oldershaw fractionating column equipped with a liquid dividing head. Monochloro neo pentanoic acid boils at 129–131C/30 mm Hg. A 45% conversion to product is obtained by this procedure. The unreacted neo pentanoic acid is recovered by distillation (86C/25 mm Hg) for subsequent recycle. [Method from Hartman, W. W., and J. B. Dickey, *J. Am. Chem. Soc., 55,* 1228–1229 (1933)].

TABLE IX
Solubility of Decanoic Acids

Solubilities g/100 g Solvent @ 20C	Neo decanoic	Normal decanoic
Isopropyl alcohol	Inf.	360
Benzene	Inf.	398
Carbontetrachloride	Inf.	210
Methyl ethyl ketone	Inf.	318
Ethyl acetate	Inf.	290



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}COOH \xrightarrow[\text{peroxide}]{Cl_2} Cl\,CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}COOH$$

Amination of chloro neo pentanoic acid may be accomplished by passing gaseous ammonia through the product in an inert solvent. After absorption is complete the resulting ammonium salt of amino neo pentanoic acid is taken up in water and is then exhaustively washed with an inert solvent. The free acid is liberated by the addition of hydrochloric acid to the ammonium salt to pH 2–3. The product is extracted with petroleum ether which is then water-washed until neutral. Amino neo pentanoic acid in petroleum ether is dried over sodium sulfate and the solvent is then flash distilled.

Preparation of Neo Heptyl Alcohol

A solution of 456 g (3.50 moles) neo heptanoic acid in 1500 ml of ether was added to a slurry of 114 g (3.00 moles) lithium aluminum hydride in 1,000 ml ether in a nitrogen atmosphere over a period of 3 hr. When the evolution of hydrogen ceased, the mixture was heated at reflux overnight. During the heating period, the reaction mixture set up to a solid mass. The addition of ethyl acetate (to hydrolyze unreacted lithium aluminum hydride) resulted in an exothermic reaction which broke the mass up into a slurry. Methanol was added to the mixture and the mixture was then added to 2 liters of 3 N sulfuric acid. Hydrolysis gave a heterogeneous mixture of ether solution, aqueous solution, and insoluble solid.

The components of the mixture were separated and the solid was boiled in 2 liters of 3 N sulfuric acid. The solid only partially dissolved. The organic materials were extracted with benzene and the benzene and ether layer were combined. This was washed with sodium bicarbonate solution, dried over sodium sulfate, and distilled. Neo heptyl alcohol (2,2-dimethylpentanol-1) was collected at 153-155C, yield = 141 g (34.8% of 406 g theory).

Preparation of n-Dodecyl Neo Tridecanoamide via Pyrolysis

To a one-liter round-bottomed reaction flask equipped with a stirrer, a thermometer, and a reflux condenser connected to a Dean-Stark water trap were added 214 g neo tridecanoic acid (1 M) and 195 g dodecylamine (1.05 M). The temperature of the reaction mixture was raised to 260C and then slowly increased to 320C. After 5.5 hr at these conditions one mole of water was removed. The product was allowed to cool to room temperature and it was then successively washed with three 150 ml portions of 5% NaOH, three 150 ml portions of 5% HCl and finally with water until neutral. The amide was dried over sodium sulfate and then filtered through a bed of Celite and charcoal. The product was distilled through an Oldershaw fractionating column equipped with a liquid dividing head (5:1 reflux ratio) at 190–197C/0.3 mm Hg pressure. The following analytical data were obtained on the pure material: Yield 57%, Elemental Analysis—Found—79.04% C, 13.51% H, 3.62% N, Theory—78.74% C, 13.38% H, 3.67% N, M.W.—Found 381, Theory 381.

Preparation of Neo Tridecanoyl Chloride

To a one-liter, round-bottomed reaction flask equipped with a stirrer, a thermometer, a reflux condenser and a dropping funnel was added 357 g of thionyl chloride (3.0 moles). The reaction flask was heated to 60C, and 210 g of neo tridecanoic acid (1.0 mole) was added dropwise over a period of one hour. The reaction mixture was refluxed for one hour, and the excess thionyl chloride was then stripped at 100 mm Hg pressure. The product was distilled at 81–83C at 1.0 mm Hg pressure through a five-plate Oldershaw fractionating column equipped with a liquid dividing head. Yield 62%, (Chloride analysis theory—15.09%; found—15.19%).

Preparation of Neo Tridecanoamide via Acid Chloride

To a one-liter, round-bottomed reaction flask equipped with a stirrer, a thermometer, a dry ice condenser, and a gas sparger were added 23.2 g neo tridecanoyl chloride (0.1 M) and 250 ml of ether. Gaseous ammonia was bubbled through the reaction system with moderate stirring until ammonium chloride was no longer precipitated (approximately 3 hrs). The solid was removed by filtration and the product was dried over sodium sulfate. The ether was then stripped at 100 mm Hg pressure and the amide distilled through a Vigreaux column at 115C/0.3 mm. The following analytical data were obtained on the pure material: Yield 82%, Elemental Analysis—Found—73.35% C, 12.78% H, 6.84% N, 7.03% O, Theory—73.35% C, 12.70% H, 6.58% N, 7.37% O, M.W.—Found 213, Theory 213, Purity by GC—98.6%.

Preparation of N(2 Hydroxyethyl) Neo Tridecanoamide via Acid Chloride

To a 250-ml, round-bottomed reaction flask equipped with a stirrer, a reflux condenser, a thermometer, and a dropping funnel was added 24.8 g of ethanolamine (0.4 mole). To the reaction flask, cooled in a wet ice bath, was added 45.6 g of neo tridecanoyl chloride (0.2 mole) at such a rate that the pot temperature was maintained at 15–20C. The reaction mass was taken up in ether and the white solid 2-hydroxyethyl ammonium chloride removed by filtration. The ether extract was washed with four 100-ml portions of water, dried over sodium sulfate, and then filtered. The ether was stripped under reduced pressure to yield the desired product. Yield 63%, (elemental analysis theory—70.00% C, 12.10% H, 5.45% N; found—69.23% C, 12.84% H, 6.34% N).

Analysis (Purity) of Lower Molecular Weight Neo Acids

The method of analysis was developed (Basic procedure for separation of carboxylic acids developed by Dr. L. Metcalf of Armour & Co.) with an F & M Model 720 chromatograph. This instrument or an equivalent programmed-temperature chromatograph is suitable. The column consists of a 10 ft, ¼ in. O.D. stainless steel tubing packed with 2/5/100 w/w/w 85% H_3PO_4/Carbowax 20-M/80–100 mesh Chromosorb-W. The required weights of H_3PO_4 and Carbowax were dissolved in the necessary volume of methanol, and this solution was used to coat the solid support in the usual manner. The carrier gas was helium and the rate 50 cc per minute. The starting column temperature was 40C and this was kept for 2 min past the injection time and then programmed to 7.5C per minute up to 200C. The detector temperature and injection port temperature were at 300C. The sample size was between 1 to 5 μl.

Toxicity

Animal exposures to neo pentanoic, neo heptanoic, neo decanoic and neo tridecanoic acids have shown that all four products have a lower order of acute oral and skin absorption toxicity.

The LD_{50} values are as follows:

Neo acid	Oral (rat) g/kg	Dermal (rabbit) g/kg
Neo pentanoic	2.0	3.16
Neo heptanoic	1.86	>3.16
Neo decanoic	2.0	>3.16
Neo tridecanoic	7.05	>3.16

Dr. Sonntag: We are very happy to have had Enjay with us today. I think Dr. Zilch is eager to make a few comments.

Dr. Zilch: Dr. Fefer, you indicated that Neo-Acids could find utilization in the manufacture of esters, metallic salts and peroxy catalysts and that because of their low pour point properties, resulting from the tertiary carbon structure, would show improvements over the same products derived from unsaturated fatty acids. I do not see a direct correlation between these two types of acids. Certainly there will be new uses for the neo-acids as such or their derivatives. They would be a welcomed addition to the family of carboxylic acids to yield products which cannot be produced from other sources.

Dr. Sonntag: You do not see Neo-Acids as a particularly strong threat to natural fatty acids?

Dr. Zilch: No, not at this particular time. They should find new and different uses where presently natural fatty acids are not being used.

Mr. Reck: Part of any threat, or possible threat is wrapped up in the economics. Can you quote any list prices for these synthetic acids?

Dr. Fefer: Yes, Dr. Rutkowski has brought along pricing information.

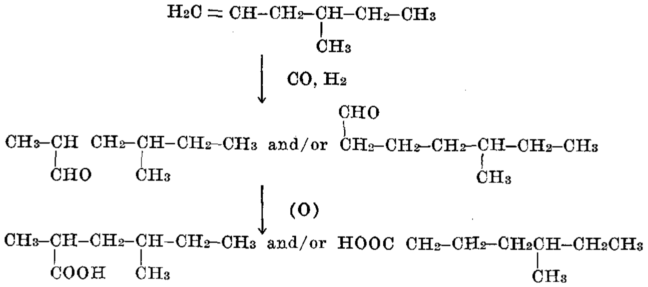
Dr. Rutkowski: Here are the prices for the Neo-Acids. These are delivered, manufacturing point Baton Rouge, Louisiana. There are price differences due to olefin availability, cost, and difficulty of purification.

	Enjay Neo Acid Prices		
	Tank car	Carload drums	LCL drums
Neo Pentanoic	37.5¢/lb	40¢/lb	41.5¢/lb
Neo Heptanoic	45	47.5	49
Neo Decanoic	25.5	28	29.5
Neo Tridecanoic	45	47.5	49

Mr. Reck: If we want, we can compare these prices with some natural fatty acids. Of course, there is nothing in the C-5 range available, similarly, there is very little C-6. The C-8 acids vary, right now it's in short supply priced at 30 c/lb. The C-10 is around 30 cents or so, and the C-12 ranges more than most from 25–30 c/lb. What would you predict about a neo-C-18 acid, Mort?

Dr. Fefer: The neo-C-18 acid we would predict would be a liquid due to the many C-18 isomers present.

Dr. Sonntag: Thank you, gentlemen. I think we have covered the Neo-Acids now in sufficient detail. Let us talk now about a few of the other synthetic acid types. We talked about Neo-Acids because they are now in production; Enpay is making them and they are beginning to be market-developed. Another type of branched-chain synthetic acid had some attention a few years back, but, for one reason or another, it did not make the grade. We are talking about the "oxo-process" acids. These can be made by the carbonylation of a branched-chain terminal olefin (or for that matter, from any olefin). As you can see the products are mixtures of isomers. In the petrochemical industry the producers of oxo-alcohols who have olefins available and practice carbonylation chemistry may always be considered as a potential threat for "oxo-process" acid manufacture. We saw some pilot plant "oxo-process" acids around 1953–55. Dr. Zilch, what was wrong with them?



$$H_2C=CH-CH_2-\underset{CH_3}{CH}-CH_2-CH_3 \xrightarrow{CO,\ H_2} CH_3-\underset{CHO}{CH}\ CH_2-\underset{CH_3}{CH}-CH_2-CH_3 \text{ and/or } \overset{CHO}{CH_2}-CH_2-CH_2-\underset{CH_3}{CH}-CH_2-CH_3$$

$$\xrightarrow{(O)} CH_3-\underset{COOH}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-CH_3 \text{ and/or } HOOC\ CH_2-CH_2-CH_2\underset{CH_3}{CH}-CH_2CH_3$$

Dr. Zilch: It is true that these acids have been investigated in the past, both in this country and abroad. It has also been reported that small plants were designed and dismantled. This type of acid is being extensively studied, and in England products are being marketed. It is difficult to determine what fatty acid market potential manufacturers of oxo type fatty acids will set their sights on. One indication is that they might produce the coconut type acids since alcohols of this chain length are presently being marketed. We certainly can expect to see more work on oxo-acids and it remains to be seen how successfully they can be marketed.

Dr. Sonntag: What about the properties of derivatives of these acids? Are they a threat, in any way, to any natural fatty acid derivatives?

Dr. Zilch: First let me reiterate that most all naturally derived fatty acids are straight chain acids. The synthetic fatty acids which can be produced through oxo-chemistry are mixtures of approximately 70% straight chain and 30% branch chain. To replace natural fatty acids with oxo-acids in a particular end use application it would be necessary to fractionate the straight chain and branch chain acids. Perhaps there will be certain instances wherein the branch chain acid will enhance the usefulness of the product. Normally the branch chain acids have lower melting points than the corresponding straight chain acid which imparts different physical properties in the various derivatives. Generally speaking, branch chain acids also have better solubility in hydrocarbons and their soaps have greater solubility in water. Therefore, a consumer of straight chain acids would have to reformulate his product if he wants to utilize a mixture of oxo-acids.

Dr. Sonntag: I should like to expand your comments a bit further. I think we can illustrate this dilemma by citing, perhaps, the fictitious case of a synthetic lubricant manufacturer who uses, let us say, a C-8, 9 or 10 straight-chain fatty acid to esterify a polyol of some kind or an etherglycol to produce a synthetic ester lubricant or lubricant component. If he replaces his slightly more expensive natural or naturally-derived acid with an "oxo-process" acid containing from 7 to 11 carbon atoms, he gains low temperature performance in his ester. His pour point is depressed, and that is good. He now has a greater liquidus range for his ester lubricant. On the other hand, because his substitute acid has more branched-chain character than the natural acid he used before, he loses oxidation stability, and that is bad. Despite the advantage that the substitute acid might be a little cheaper, he will not use it because he cannot afford the decrease in his oxidation stability for the improvement he gets in low temperature performance.

What about another branched-chain synthetic acid that has been with us for 10–15 years, the C-8 acid made, I believe, by an "aldoling" process, 2-ethylhexanoic acid? There are a number of American producers of this acid. Does this represent a threat to the C-6, C-8 or C-10 natural fatty acids?

Dr. Reck: We at Armour have looked at 2-ethylhexanoic acid a number of times. The economics are not favorable for any derivative production that we can see. Of course, it's chemically possible to synthesize the various types; in some cases, it's a little tricky. I do not think that this acid, by itself, is a significant threat to any fatty acid. We have not looked at this product as an acid for any fatty acid uses.

Dr. Sonntag: I think it is desirable for us to discuss briefly those synthetic acids which, for one reason or another, do not compete with any known natural acid. Compared to a fatty acid they may not be economical and they may not have broad markets, but they may have specialty uses that are not satisfied by any existing natural fatty acids. Since we have exhausted the ones I can think of right now, I should like to give attention to another important aspect of synthetic fatty acids.

We have been reading a lot lately about the advent in eastern Europe of synthetic fatty acids by hydrocarbon oxidation. Karl Zilch, who sits on our panel today, has been very close to these developments. For the past several years he has been surveying and reporting details from Romania, Czechoslovakia, Poland and Russia to the Fatty Acid Producers' Council. We are quite fortunate to be able to hear from Dr. Zilch, who will give us the latest information on developments on synthetic fatty acids in eastern Europe by hydrocarbon oxidation.