

Liquid C-18 Saturated Monocarboxylic Acids— Their Preparation, Characteristics, and Potential Uses

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IN 1942 Bradley and Richardson (7) reported that in the alkaline isomerization of linseed oil in water, ethylene glycol, or diethylene glycol, triene conjugation reaches a max and then decreases upon continued heating. Kass and Burr (16) showed that the triene formed in the alkaline isomerization of linseed oil is at least partly 10-,12-,14-octadecatrienoic acid. These observations led to further investigation at this laboratory, and in 1959 Scholfield and Cowan (22) reported that prolonged alkaline isomerization of linolenic acid in ethylene glycol leads to the formation of cyclic monomeric acids in good yield along with smaller amounts of dimeric acids and other products. Aromatization followed by oxidation and isolation of phthalic acids furnished proof of the cyclic nature of the monomeric acids. Since the disappearance of the previously mentioned conjugated triene coincides with the formation of cyclic monomeric acids, it appears that a trienoic acid of this type is an intermediate in the cyclization reaction.

Cyclic compounds have been postulated previously to explain a liquid product produced by heat treatment of alpha- and beta-eleostearic acids (19–21,23). Rossmann (21) was among the first to report such a product and postulated a 5,6-disubstituted 1,3-cyclohexadiene structure; however Sunderland (23) could not obtain the C₁₆ tricarboxylic acid that should have resulted from the alkaline permanganate oxidation of this material. He did obtain a polycarboxylic acid or mixture of acids of lower mol wt, the presence of which he accounted for by suggesting that hydrogen migration within the molecule could result in a shifting of the relative positions of the double bonds. This possibility was also suggested by Rivett (20).

More recently it was reported (14) that the monomeric acids produced by prolonged alkali isomerization of linseed and tung oil in ethylene glycol, followed by complete hydrogenation and careful separation of the straight chain saturates, yield liquid C₁₈ saturated monocarboxylic acids hereafter designated "cyclic acids" that have an extremely low pour point (about -45C). Interest in this unique material resulted in extensive research at this laboratory on methods of preparation of these liquid acids and their derivatives for possible industrial application.

The effects of time, temp, catalyst type, catalyst concentration, solvent type, and solvent concentration have been studied (9,13). Production of cyclic acids from linolenic acid has also been investigated (10). Cyclic acids have been produced by continuous as well as by batch processes (4). The effect of ethylene vs. nitrogen as the head-space gas for batch operations has also been determined as well as the nature of the products formed (5,12).

A number of nitrogenous derivatives of the cyclized acids have been prepared and evaluated as plasticizers for polyvinyl chloride and as surface active agents (8). Vinyl esters of the cyclized acids have been prepared and evaluated as internal plasticizers for polyvinyl chloride (15). Alkyd resins modified with cyclic acids have been prepared and partially evaluated (18).

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The purpose of this report is to review the work on cyclic acids to date.

Preparation of Cyclic Acids by Alkaline Isomerization in a Nitrogen Atmosphere

Batch Process. The isomerizations were carried out in a 2 l stainless-steel autoclave equipped with a stirrer and capable of withstanding 1,000 psi. The substrate (linseed oil, linolenic acid, or tung oil), solvent (ethylene glycol, diethylene glycol, glycerine, t-butanol, or water), and catalyst (NaOH, KOH, potassium t-butoxide, or the sodium salt of ethylene glycol) were placed in the autoclave, which was subsequently sealed and flushed with nitrogen. The vessel was then heated rapidly to a predetermined temp and samples were taken at various time intervals for analysis.

The samples were diluted with approx three volumes of water and acidified with dilute H₂SO₄. The crude cyclized acids were extracted with either diethyl or petroleum ether, washed and dried, and then the solvent was removed under vacuum.

Distillation of these acids under vacuum yielded monomeric liquid acids and a polymeric residue. When the monomeric acids were subjected to hydrogenation in the presence of a Pd-C catalyst, the I.V. was reduced to essentially zero.

Semisolid hydrogenated acids containing straight-chain saturates, as well as hydrogenated cyclic acids, were then dissolved in 10 volumes of acetone. The catalyst was removed by filtration, the filtrate was cooled to -50C, and the saturates were removed by filtration in the apparatus previously described (11). Removal of the solvent yields liquid C₁₈ saturated monocarboxylic acids, the physical constants of which are shown in Table I.

With ethylene glycol solvent, and particularly at low catalyst concentrations and high temp, an appreciable loss in total acid equivalents occurred during distillation of the crude acids as indicated by a carboxyl balance. Subsequent investigation showed that the residues had neutralization equivalents ranging from 450 to more than 1,000. Saponification of these residues (polyesters) reduced the neutralization equivalent to slightly more than 300.

To make an accurate determination of the extent of the cyclization the crude acids were esterified before distillation to prevent polyesterification.

Yields of cyclic acids were determined by gas chromatography of the methyl esters (6) as well as by crystallization from acetone. The cyclic yield as determined from the chromatograms of the hydrogenated monomer esters (40.5%) (Fig. 1) agrees with that determined by crystallization; however resolution of

TABLE I
Physical Const of Hydrogenated Cyclic Acids and Methyl Esters (I.V. <1)

Hydrogenated derivative	n _D ²⁵	Sp. Gr. at 25C	B. P. at 0.075 mm Hg	F. P. to -70C
Cyclic acids.....	1.4698	0.936	159-166C	No cryst.
Methyl esters of cyclic acids.....	1.4609	0.918	125-131C	No cryst.

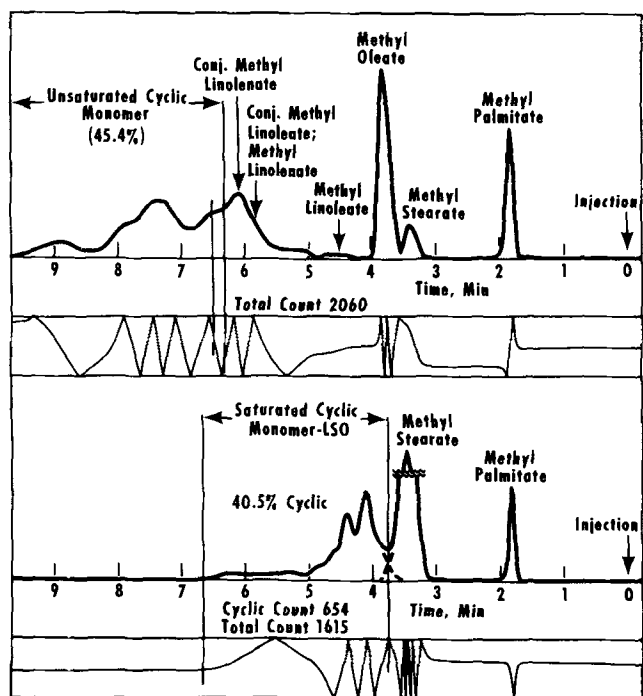


FIG. 1. Gas chromatograms of hydrogenated and unhydrogenated cyclized monomer methyl esters from a Beckman GC2A chromatograph, 6' x 1/4" column, stationary phase 10% DEGS, temp 220C.

conjugated linoleate and conjugated linolenate from the unsaturated cyclic was not effected.

Effect of Variables on Yield. Because the variables are so interrelated, the number of experiments required to completely interpret this relationship would be prohibitive; however certain limits can be established and generalizations drawn.

Temperature. Although isomerization takes place below 200C, formation of the cyclic structure is very slow. At temp above 320C side reactions take place leading to high neutral equivalents and excessive polymeric residues. From 220C-295C is the best temp range for carrying out the cyclizations (Figs. 2 and 3).

Time. The time required to reach maximum cyclic acid yields depends on temp (Fig. 3) and catalyst concentration (Fig. 4).

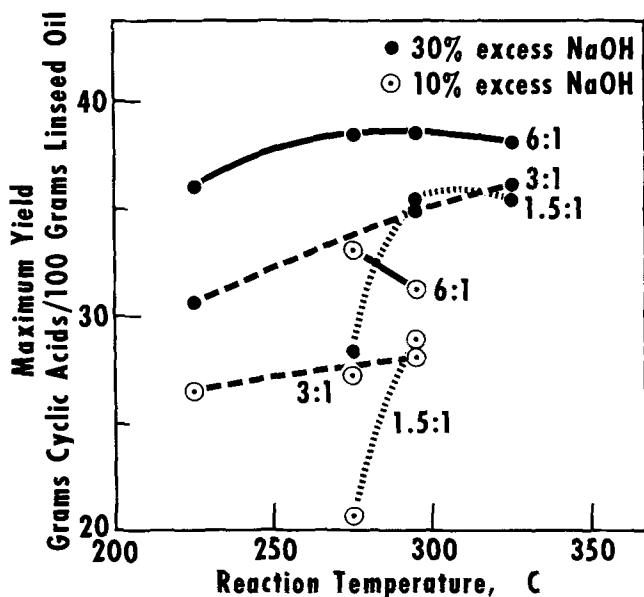


FIG. 2. Effect of reaction temp and solvent concentration on cyclic acid yields at two different catalyst levels.

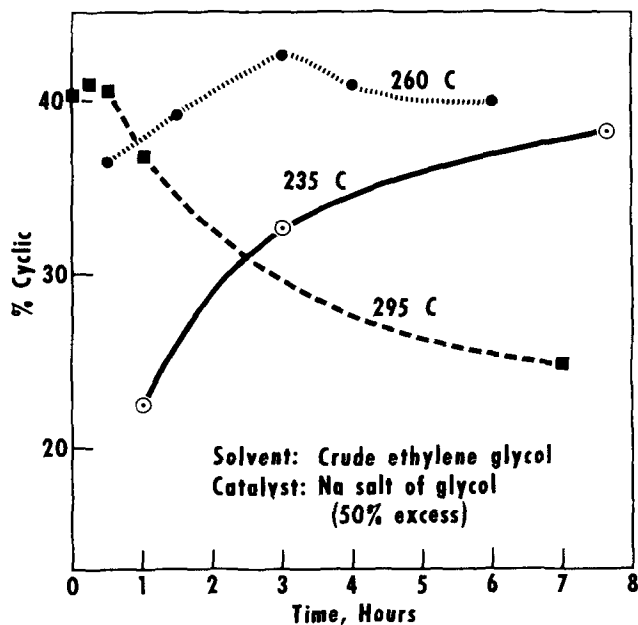
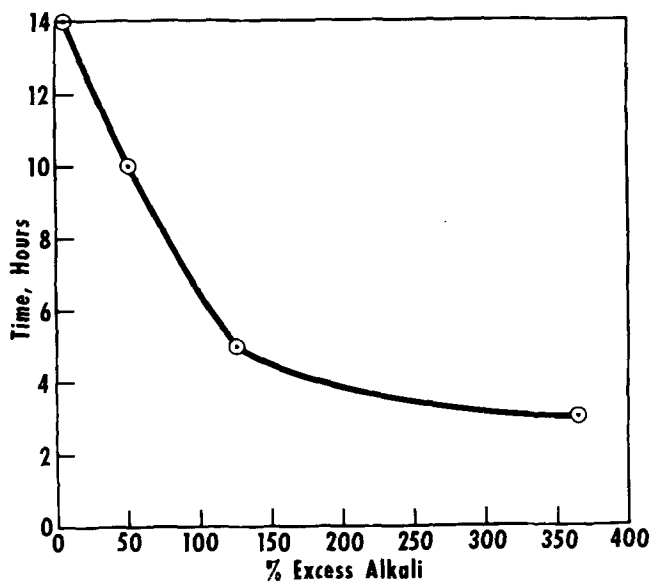


FIG. 3. Effect of reaction time on cyclic acid yield at three different temp.

Solvent and Concentration. Solving the several requirements that a solvent has to meet has been the most difficult problem. First, this material must be a good solvent for fatty acids, soaps, and the excess catalyst at the temp and concentration desired. It must be high boiling to prevent excess pressures at the high temp required. It must be stable at these temp and environment, and it must be easily separated from the reaction products. The following solvents were tried: water, glycerine, t-butanol, ethylene glycol, and diethylene glycol. Water and t-butanol are low boilers and require high pressure vessels. Use of water results in high polyester residues and low cyclic acid yields. T-butanol is satisfactory in combination with its potassium salt as catalyst. Glycerine is apparently unstable under the conditions of the reaction and leads to large residues. Ethylene



* At a temp of 295 C with 25% X's alkali one hr is required for the maximum yield

FIG. 4. Effect of percentage excess catalyst on reaction time required for max cyclic acid yield. Solvent: Ethylene glycol. Temp.: 220C.

glycol and diethylene glycol both appear to be satisfactory solvents. The effect of solvent ratio is shown in Figure 2. The upper curve in each pair represents the higher alkali concentration. Since the formation of polymeric acids is a bimolecular reaction, increasing the solvent ratio would be expected to decrease polymer formation and consequently increase cyclic acid yields. The figure indicates that this solvent effect results at low, but not at high, temp.

Catalyst. Initially it was not known whether the alkali used in this reaction was actually a catalyst for cyclization or merely served as a conjugation catalyst and whether cyclic acids were subsequently formed by a thermal mechanism.

The best conversion of eleostearic acid to a cyclic product by purely thermal means was about 25%, whereas alkali treatment of tung oil (about 80% eleostearic) resulted in about 70% conversion based on the eleostearic acid present. Since neither the alpha nor beta form contains a *cis*-11 bond, it could be argued that the configuration is unfavorable for thermal cyclization.

To further determine the necessity of alkali for cyclization, a sulfur-poisoned Ni isomerization catalyst was used. The results were inconclusive. Under the best reaction conditions, i.e., 1 part linseed fatty acid, 3 volumes heptane, 4.5% catalyst at 180C for 3 hr then 260C for 3 hr, a yield of 14% liquid C₁₈ saturated acid was obtained after hydrogenation. This material has a different GLC pattern than that obtained by the alkaline treatment. MacDonald (17) also noted that the cyclic material formed from heat-treated linseed oil showed no absorption above 255 m μ as do the alkaline-treated linseed fatty acids. This absorption is characteristic for cyclohexadienes (24). If these liquid acids produced in the presence of Ni catalyst are cyclic acids, they must then be formed by a different mechanism than those produced by alkaline isomerization. Although the data do not constitute unequivocal proof that alkali catalyzes cyclization as well as conjugation, the data certainly lend strong support to this contention.

The following alkaline catalysts were employed: sodium hydroxide, potassium hydroxide, the potassium salt of t-butanol, and the sodium salt of ethylene glycol. Sodium and potassium hydroxides appear to be equivalent. As mentioned previously, if the crude cyclized acids are distilled without first making their methyl esters, larger amounts of polyester residues result. The sodium and potassium hydroxides contain some water as does the solvent, ethylene glycol, and since the use of water itself as a solvent gave rise to excessive polyester residues, it was decided to try a catalyst that would act as a water scavenger (Table II). High temp and extended reaction times give rise to polyester formation and reduction in cyclic acid yield even with a hydroscopic catalyst as indicated by Figures 3 and 5. This result may occur because ethylene glycol dehydrates.

TABLE II
Effect of Different Solvent-Catalyst Systems on Cyclic Acid Yields

Solvent 3:1	Catalyst 50% Excess	Atm	Time	Temp	Max yield %
			hr	C	
Crude glycol	NaOH	N ₂	3	260	37.3
Dry glycol	NaOH	N ₂	3	260	39.4
Crude glycol	Na salt of glycol	N ₂	3	260	42.5
Dry glycol	Na salt of glycol	N ₂	3	260	43.5
Dry glycol	Na salt of glycol	C ₂ H ₄	4	260	46.3
t-Butyl alcohol	K salt of t-Butyl alcohol	N ₂	5	237	44.0

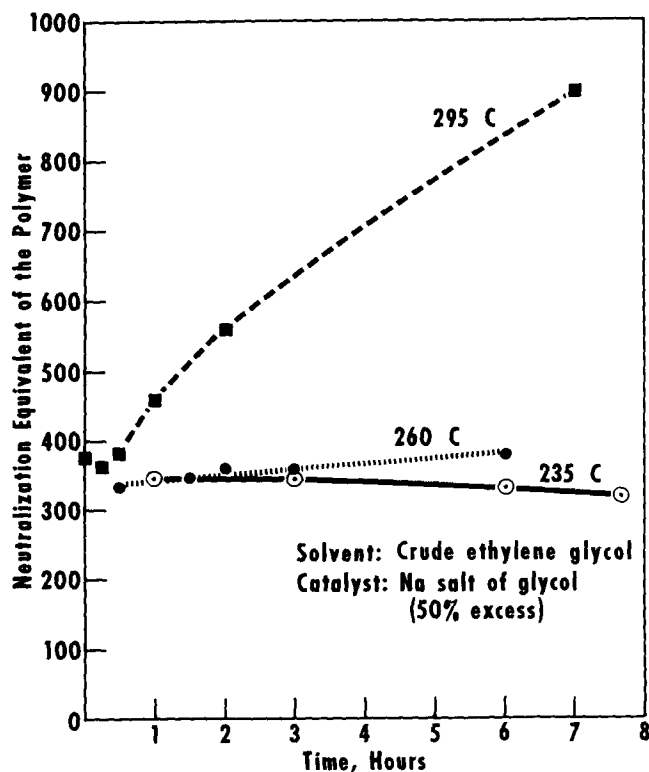


FIG. 5. Variation of the neutralization equivalent of the polymer with time at three different temp.

If alkali does catalyze cyclization, a mechanism that would account for the hydroxylation, as well as the cyclization, is shown in Figure 6. It is believed that this mechanism, if proved accurate, constitutes a new type of general reaction, which could be applied to various other unsaturated systems.

Compounds of type I are known to be formed by the alkaline isomerization of linolenic acid (16). Furthermore a compound of type IV is formed if the alkaline isomerization is continued at elevated temp (14). One cannot explain the presence of hydroxyl in the reaction products on the basis of a thermal mechanism for cyclization. On the other hand, if a nucleophilic attack by the catalyst on the conjugated system is postulated, intermediates of type II and III could exist that could give rise to structures IV, V, or VI. Although hydroxyl has been found in the reaction products both by spectrophotometry and

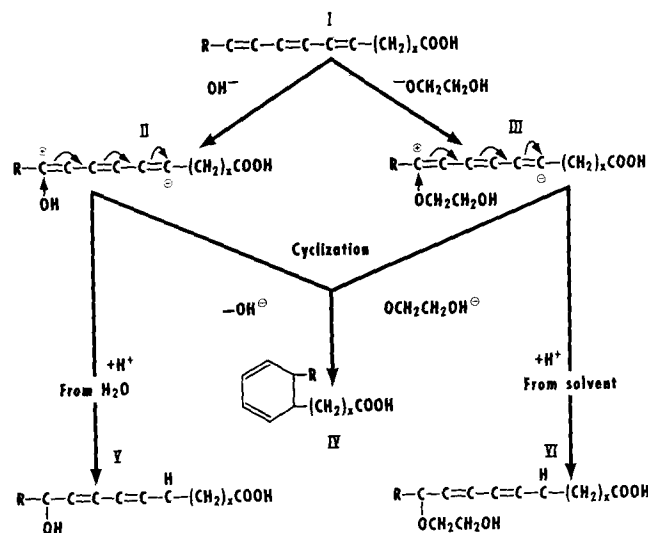


FIG. 6. Proposed mechanism for the formation of cyclic acid.

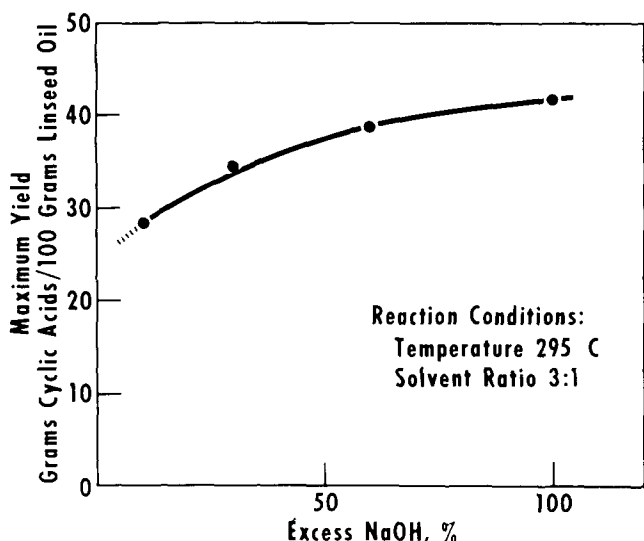


FIG. 7. Effect of excess catalyst on cyclic acid yields.

by acetylation with acetic anhydride, no amount of ether linkage was detectable. Route I → III → VI is therefore improbable. In the presence of water, if the reaction proceeds through an intermediate of type II, the large increase in polymer due to hydroxylation and subsequent polyester formation could be explained. In the absence of water, if the reaction proceeds through intermediate III, an increase in IV should result since the alternate route I → III → VI has been ruled out.

Increasing the catalyst concentration improves the cyclic acid yields (Fig. 7). Since at any given temp the rate of cyclization is increased with increased catalyst concentration and since the formation of polyacids is not catalyzed by alkali, this observation would be predicted.

Preparation of Cyclic Acids by Alkaline Isomerization in a Nitrogen Atmosphere

Continuous Process. Cyclic acids have also been prepared by a continuous process (4). The equipment used for this work is shown in Figure 8. Typical results are shown in Table III.

Preparation of Cyclic Acids in an Ethylene Atmosphere

Beal and co-workers (3,5) were the first to employ ethylene as the headspace gas in an autoclave for

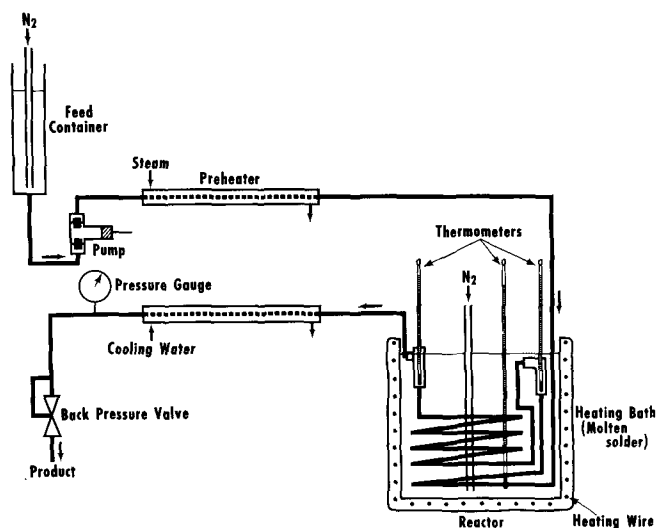


FIG. 8. Apparatus for continuous cyclization process.

TABLE III
Results of Continuous and Batch Cyclization Reactions

Solvent: oil ratio	Excess NaOH %	Reaction pressure psi	Reaction temp C	Retention time min	Yield, g/100 g linseed oil		
					Polymeric acids	Cyclic acids ^a	Polymer + cyclic
6	25	400	332	4.0	3.5	29.8	33.3
6	100	400	300	4.3	4.3	32.0	36.3
6	100	400	300	9.2	5.0	35.6	40.6
6	100	400	320	4.0	5.6	30.1	35.7
6	100	400	320	10.8	6.7	37.5	44.2
3	100	400	312	4.2	4.9	32.1	37.0
3 ^b	100	295	30.0	5.5	39.3	44.8

^a Determined by GLC.
^b Batch reaction.

batch operations. They reported an increase in cyclic acid yield as determined by low-temp crystallization from acetone.

Later the gas chromatogram of the methyl esters of cyclic acids prepared in the presence of ethylene showed material with a retention time greater than that exhibited by those prepared in the presence of nitrogen. Assuming this material was an ethylene adduct of the fatty material, studies (Fig. 9) were conducted on the addition of ethylene to 9,11-t,t-octadecadienoic acid (Curve II), linoleic acid (Curve III), and soybean fatty acids (Curve IV) (12). Good yields of C₂₀ adduct were obtained in each reaction. Thus, it is believed that the increase in cyclic acid yield experienced in the presence of ethylene is partly due to the addition of ethylene to the various conjugated systems present. The effect of ethylene, under 500 psi initial pressure, on the yields of cyclic acids from linseed oil is shown in Table IV. Increasing the ethylene pressure increases the cyclic acid yields from

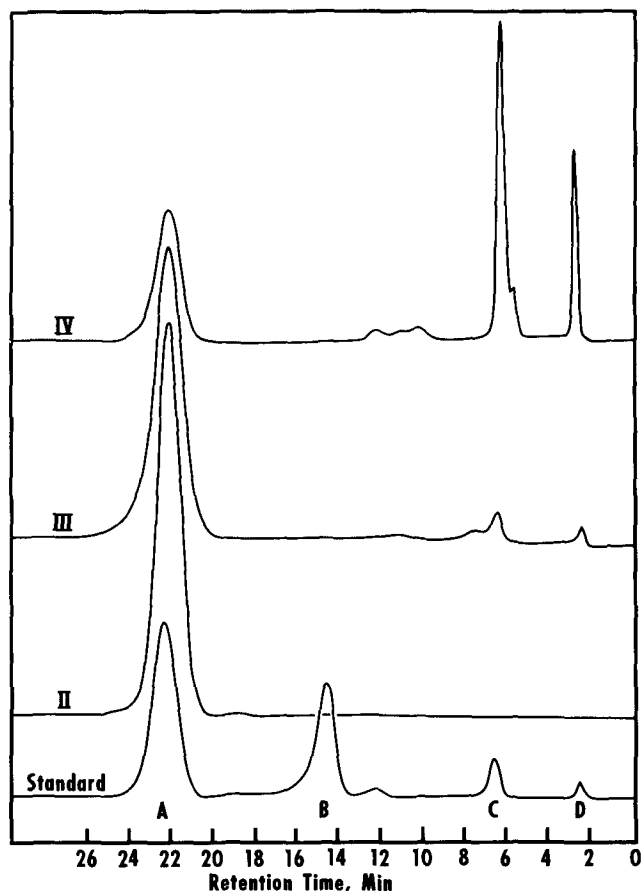


FIG. 9. Gas chromatograms of ethylene adducts from a Pye-Argon chromatograph, column 4' x 1/4", stationary phase 10% DEGS, temp 184C. A = ethylene adduct of methyl 9,11-t,t-octadecadienoate, B = methyl 9,11-t,t-octadecadienoate, C = methyl stearate, D = methyl palmitate.

TABLE IV
 Effect of Ethylene on Cyclic Acid Yield

Reactor head-space gas	Solvent ratio	Excess NaOH	Reaction temp	Reaction time	Cyclic acid in monomer	Product yield	
	Glycol: oil	%	C	hr	%	Polymeric acids ^a	Cyclic acids
Nitrogen	6	30	295	1	44.0	11.4	36.8
Nitrogen	3	100	295	1	47.5	7.6	41.8
Ethylene	6	30	295	3	55.0	11.4	46.0
Ethylene	3	100	295	1	58.0	11.5	49.5

^a At maximum cyclic acid yield.

linolenic acid as well as from linseed oil as shown in Figure 10. The effect of time, temp, catalyst concentration, and solvent ratio on the yield of cyclic acids closely parallels the data obtained with nitrogen.

Potential Uses of Cyclic Acids

Alkyd Resins. Three different forms of cyclic acids have been used in alkyd resin formulations (18). All these forms are unhydrogenated and will be designated as crude, flash-distilled, and pure cyclic acids. The crude acids are those obtained by acidifying isomerized linseed oil; flash-distilled acids are obtained by distilling the crude acids under vacuum to remove the polymer. Both of these products contain saturates, monoene, and diene, present in the oil. The so-called pure cyclic is obtained by urea separation of the flash distilled acids. Straight-chain unsaturates are not completely removed by this separation. This final concentrate contains 78% cyclic by hydrogenation and crystallization.

Resins modified with the three previously mentioned forms to 50% oil length were compared with ones modified with naturally occurring fatty acids and with vegetable oils. Alkyds modified with cyclic acids process more rapidly than those prepared with linseed, safflower, or soybean fatty acids, and they also have good nonyellowing properties (Fig. 11).

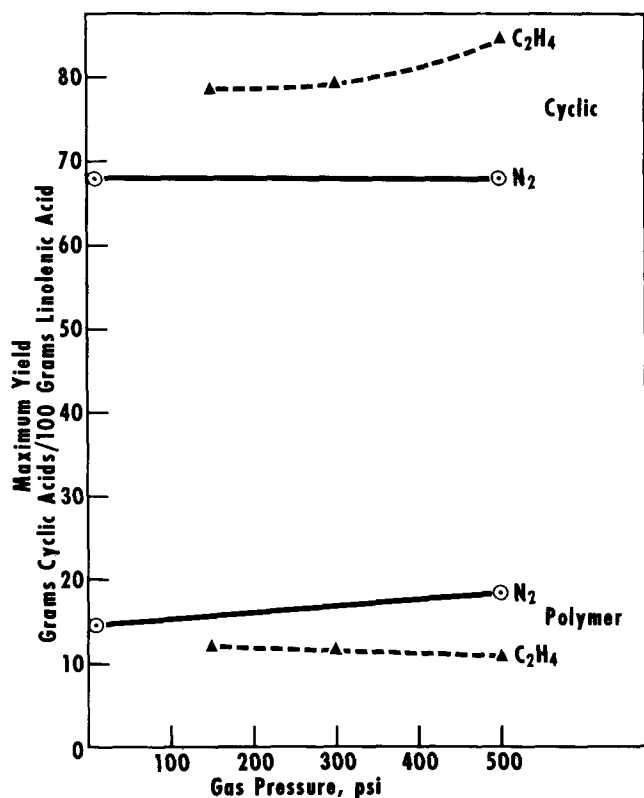


FIG. 10. Effect of increasing ethylene and nitrogen pressure on the yield of cyclic and polymeric acids from linolenic acid.

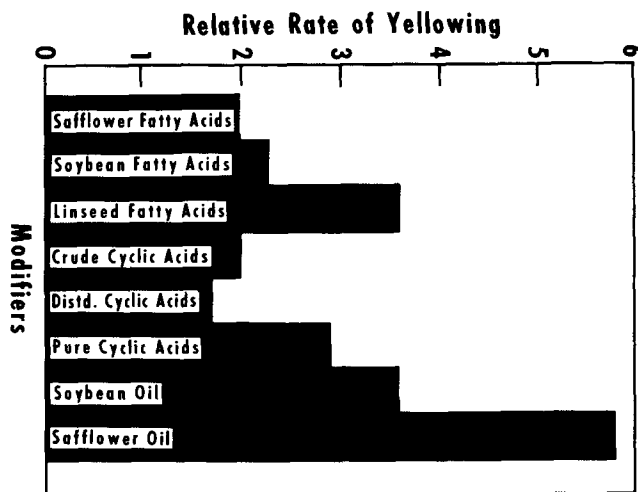
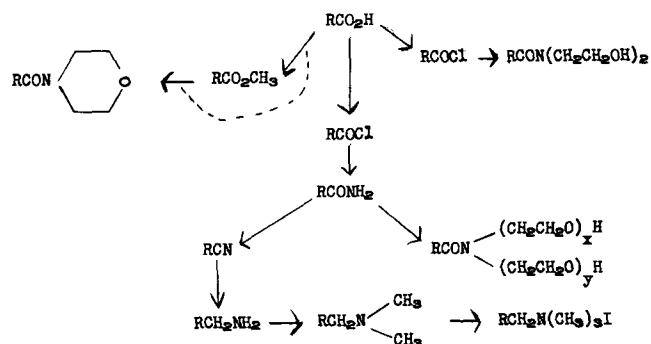


FIG. 11. Relative yellowing rates of modified alkyd resins.

Resins modified with 78% pure cyclic acids show definite improvement in drying time, hardness, and chemical resistance in air-dried films and an almost equal improvement in baked film over resins obtained with the other modifiers, Table V. Distilled cyclic acids also improve alkyd resins although not to the extent that pure acids do. Both give resins superior to commercial oil-modified resins under the test conditions. Resins with crude cyclic acids are as good in air-dried films as are the others but are poorer in baked films.

Nitrogenous Derivatives of Cyclic Acids. Several nitrogenous derivatives were prepared from: a.) the pure hydrogenated cyclic acids and b.) the flash-distilled or monomeric unhydrogenated acids obtained from the crude isomerized mixture. The derivatives and their general methods of preparation are:



The amides of the hydrogenated cyclic and monomer acid mixtures had melting points of 33 and 43C, respectively.

Because the two amide mixtures have low mp, one might anticipate they would have good solubility in organic solvents, which is shown in Table VI where a comparison is made between the two amide mixtures and the amides of hydrogenated tallow acids. Fatty amides generally show good solubility in ethanol and

TABLE V
 Cumulative Rankings of Modified Alkyd Resins—Drying Times, Hardness, Solvent Resistance

Modified	Air-dried	Baked
Pure cyclic acids.....	1	2
Distilled cyclic acids.....	5	3
Crude cyclic acids.....	4	5
Linseed fatty acids.....	3	3
Safflower fatty acids.....	2	1
Soybean fatty acids.....	7	3
Safflower oil.....	6	4
Soybean oil.....	6	5

TABLE VIII
 Properties of Nitriles and Morpholides as Plasticizers^a

Plasticizer	Tensile strength (psi)	Modulus at 100% elong. (psi)	Elongation, %	Clash-Berg		Migration after 14 days, % loss	Volatility at 70C, % loss
				T _{135,000} C	T _{110,000} C		
Monomer acid nitriles.....	2340	920	255	-43	-12	16.5	14.0
Hydrogenated cyclic acid nitriles.....	2270	985	255	-42	-8	13.1	13.3
Monomer acid morpholides.....	2500	1200	210	-27	0	6.6	0.6
Hydrogenated cyclic acid morpholides.....	2550	1450	220	-12	+6	1.4	0.5
Control							
Di-2-ethylhexyl phthalate.....	2590	1350	250	-27	+2	4.3	1.7

^a Carried out at 33% level of a commercial polyvinyl chloride resin (Geon 101).

methanol; however the two amides of the cyclic acids show much higher solubility in benzene and carbon tetrachloride than in alcohols. Apparently the cyclic structure, whether hydrogenated or not, contributes to the solubility and mp phenomenon since the monomer acid amides, which contain the much lower percentage of cyclic structure, have a higher mp and lower solubility than do hydrogenated cyclic acid amides. Hydrogenated cyclic amide exhibits compatibility with acrylic and vinyl resins, whereas oleamide does not. The hydrogenated cyclic acid amides are also compatible with vinyl resin (Table VII).

 TABLE VI
 Amide Solubilities at 30C

Solvent	Amides		
	Monomer acid	Hydrogenated cyclic	Hydrogenated tallow ^a
Ethanol (95%).....	0.3 ^b	0.9	1.0
Methanol.....	0.1	1.1	0.8
Acetone.....	<0.1	0.1	0.6
Ethyl acetate.....	0.2	0.4	0.6
Benzene.....	37.2	>237	0.4
Carbon tetrachloride.....	8.5	>254	0.1

^a Data from Armour Chemical Division booklet "Armids," p. 3.

^b Figures are g of amide per 100 ml of solvent.

 TABLE VII
 Amide-Resin^a Compatibility

Resin	Amides		
	Monomer acids	Hydrogenated cyclic	Oleic
Acrylic ^b	C	C	I
Cellulose acetate ^c	C	C	C
Cellulose acetate butyrate ^c	C	C	C
Ethyl cellulose ^c	C	C	C
Nitrocellulosealkyd ^b	C	C	C
Polystyrene.....	I	I	I
Vinyl ^b	I	C	I

^a Amides 5% of total solids.

^b Commercial resin solutions. C = compatible, I = incompatible.

^c Solvents were: chloroform for cellulose acetate and cellulose acetate butyrate, 80% toluene-20% ethanol for ethyl cellulose, and toluene for polystyrene.

Nitrile mixtures prepared from the monomer acids and hydrogenated cyclic acids also have low mp, -21 and -25C, respectively. Again, one would anticipate certain advantages in compatibility of these nitriles as compared with other fatty nitrile mixtures.

The properties of the nitriles and morpholides as plasticizers for polyvinyl chloride are shown in Table VIII. These data show the superiority of the nitriles with respect to Clash-Berg temp as compared to the control (di-2-ethylhexyl phthalate); but they also show the high volatility and migration of the nitriles. The last two properties are greatly improved in the morpholides and are indeed superior to the control. The morpholides show Clash-Berg temp higher than the control. The greatest weakness of all of these nitrogenous derivatives as plasticizers are their poor light and heat stability. All the cyclic derivatives failed in light stability within 216 hr, whereas the

control had not failed after 600 hr. Similarly, the cyclic acid derivatives showed a very rapid drop in light transmission at 600 m μ after exposure at 160C as compared to the control. After 3 hr the control had dropped to ca. 50% transmittancy, whereas all the cyclic acid derivatives were virtually opaque.

The amine prepared from the hydrogenated cyclic acid exhibited a low freezing point (-34C) as did its N,N-dimethyl derivative (-54C). It is noteworthy that the amines derived from soybean, coconut, tallow, and hydrogenated tallow acids had mp greater than 20C (2). Even commercial octyl amine had a mp of -13C.

Vinyl Esters of Cyclic Acids (15). The vinyl esters of flash-distilled linseed derived cyclic acids (unhydrogenated) and vinyl esters of pure hydrogenated cyclic acids were prepared by the method of Adelman (1). Crude reaction products were stripped of vinyl acetate diluted with 2.5 parts of petroleum ether (pentane-hexane) and passed through alumina to remove fatty acid. After removal of the solvent the vinyl esters were distilled rapidly under vacuum.

The vinyl esters of pure hydrogenated cyclic were also prepared by the direct addition of acetylene at 500 psi and 165C to the fatty acid in the presence of zinc stearate as catalyst. After 5 hr an acid value of 6 was obtained. This product was worked up in the same way as the material prepared by ester exchange.

These vinyl esters were homopolymerized and copolymerized with vinyl chloride. The vinyl esters of the pure hydrogenated cyclic acids show some promise as an internal plasticizer for polyvinyl chloride.

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