

# Nitrogenous Derivatives of Cyclic Fatty Acids<sup>1</sup>

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## Abstract

A number of nitrogenous derivatives of cyclized acids derived from C-18, triene-containing fatty acid sources, were prepared. Mixed amides (mp 33C), nitriles (fp -25C), and amines (fp -34C), prepared from the hydrogenated cyclic acids, have uniquely low mp for fat-derived substances of their mol wt. Compatibility with synthetic resins and solubility in organic solvents of the mixed amides are high compared to common fatty-amide mixtures. The nitriles and morpholides are compatible with polyvinyl chloride and may have potential as plasticizers for it. The hydrogenated cyclic fatty acid amines have an approximate fp of -34C. The diethanolamides, ethenoxyated amides, and quaternary amines were prepared and their surface-active properties compared with similar fat-derived substances.

## Introduction

PROLONGED TREATMENT of linseed oil or other triene-containing oils or fatty acid mixtures with alkali in a suitable solvent produces cyclic monocarboxylic acids (1). Although the exact structures of the cyclic acids are not known, from a study of the absorption spectra and the isolation of phthalic acids by aromatization and subsequent oxidation, Scholfield and Cowan (1) concluded that the acids must be ortho-disubstituted cyclohexadienes. Friedrich et al. (2) found that catalytic hydrogenation produced saturated acids of very low pour point. Furthermore, neither the cyclic acids nor their saturated derivatives would crystallize at temp down to -70C.

Because of the unique properties of these two acid mixtures, we have prepared some of the common nitrogen-containing derivatives and examined their properties.

## Experimental

Hydrogenated cyclic acids were obtained by the procedure previously described (2). Experiments with the cyclic acids were performed using the mixture separated from the cyclization reaction mixture by distillation (2). This mixture is referred to as the "monomer acid mixture." The cyclic acids may be concentrated by urea-adducting the straight chain acids, a tedious and time-consuming procedure. The monomer acid mixture contains about 47% cyclic acids, 28% stearic and oleic, 17% linoleic isomers, and 8% palmitic. This mixture typically has I.V. 119,  $n_D^{20}$  1.4816, sp gr 20/20 0.9364, equivalent wt 284.

*Monomer Acid and Hydrogenated Cyclic Acid Amides.* The amides were prepared by adding the respective acid chloride mixture, obtained by the method of Youngs et al. (3) and diluted with ether, to a stirred mixture of liquid ammonia and ether in an indented flask equipped with a dry ice cooled reflux condenser. The mixture was allowed to stand

TABLE I  
Amide Solubilities at 30C.

Solvent	Amides		
	Monomer acid	Hydrogenated cyclic	Hydrogenated tallow <sup>c</sup>
Ethanol(95%).....	0.3 <sup>a</sup>	0.9	1.0
Methanol.....	0.1	1.1	0.8
Acetone.....	I <sup>b</sup>	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

<sup>a</sup> Figures are grams of amide per 100 ml of solvent.  
<sup>b</sup> I = insoluble, i.e. solubility estimated to be less than 0.1 g per 100 ml of solvent.  
<sup>c</sup> Data from Armour Chemical Division booklet "Armids" p. 3.

while the ammonia evaporated. The residue was dissolved in ether and filtered to remove salts. The filtrate was extracted with alkali to remove acids. Evaporation of the ether after drying gave the amide mixtures substantially free of acids.

The hydrogenated cyclic amides were light tan solids, having a fp of +33C, negligible acid content, and I.V. 5.5. Distillation of the amides *in vacuo* results in partial decomposition to nitrile and acid.

The monomer acid amides were tan solids, containing 1.5% free acid, with I.V. 121.2 and fp of 43C.

Approximate solubilities of the two amide mixtures in some common solvents are shown in Table I. Solubilities of hydrogenated tallow fatty-acid amides are included in the table for comparison.

Compatibility of the amides with a number of common resins is shown in Table II. Compatibility was determined by adding the respective amide to the resin solution so that the resulting solution contained 5% amide on a total solids basis. Films were then drawn employing a doctor blade at 40 mil wet-film thickness on tin plate, and, when dry, the films were examined for haziness and/or surface extrusion of amide. For comparison, similar data for oleamide were obtained. The possibility that traces of solvent remain in the films cannot be excluded.

*Diethanolamides, Morpholides, and Ethenoxyated Amides.* The diethanolamides of the monomer and hydrogenated cyclic acid mixtures were prepared by reacting the respective acid chloride with diethanolamine according to the procedure of Trowbridge, Falk, and Krems (4). The monomer acid diethanola-

TABLE II  
Amide-Resin\* Compatibility

Resin	Amides		
	Monomer acids	Hydrogenated cyclic	Oleic
Acrylic <sup>b</sup> .....	C	C	I
Cellulose acetate <sup>c</sup> .....	C	C	C
Cellulose acetate butyrate <sup>c</sup> .....	C	C	C
Ethyl cellulose <sup>c</sup> .....	C	C	C
Nitrocellulose-alkyd <sup>b</sup> .....	C	C	C
Polystyrene.....	I	I	I
Vinyl <sup>b</sup> .....	I	C	I

\* Amides 5% of total solids.  
<sup>b</sup> Commercial resin solutions. C = Compatible, I = Incompatible.  
<sup>c</sup> Solvents were: chloroform for cellulose acetate and cellulose acetate butyrate, 80% toluene - 20% ethanol for ethyl cellulose and toluene for polystyrene.

<sup>1</sup> Presented at AOCs meeting in St. Louis, Mo., 1961.  
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TABLE III  
 Surface Active Properties (25C)

Substance	1.0% Solutions	0.1% Solutions		Emulsion stability Time-sec.
	Surface tension <sup>a</sup>	Interfacial tension <sup>a</sup>	Surface tension <sup>a</sup>	
Diethanolamides of hydrogenated cyclic acids.....	32	1.3	32	1040
Diethanolamides of monomer acids.....	31	0.8	31	660
Diethanolamides of coconut acids.....	27	0.5	27	880
Diethanolamides of technical stearic acids.....	1 <sup>b</sup>	....	1	....
Ethenoxylated amide of hydrogenated cyclic acids.....	38	6.8	37	410
Trimethyl hydrogenated cyclic alkyl ammonium iodide.....	32	0.8	31	420
Trimethyl soya-alkyl ammonium chloride.....	....	....	34 <sup>c</sup>	....

<sup>a</sup> Surface and interfacial tensions are in dynes per cm.

<sup>b</sup> I = Insoluble.

<sup>c</sup> Data from Armour Chemical Division bulletin "Arquads" p. 4 (1956).

mides were tan, greaselike substances. They had I.V. 98.6, 5.1% free acid, and approximate mp 87C.

The hydrogenated cyclic acid diethanolamides were tan semisolids having I.V. 4.0, 3.5% free acid, and mp 63C. Surface-active data are included in Table III. Solubility data are shown in Table IV.

The morpholides of the hydrogenated cyclic acids were prepared by the method of Dupuy et al (5). This method was extremely slow. For the preparation of the morpholides of the monomer acids the method of Magne et al. was followed (6).

The morpholides of the hydrogenated cyclic acids had the following properties:  $n_D^{30}$  1.5025, sp gr 30/30 0.9917, bp 185–195C/0.05 mm, becomes glass at –30C.

The monomer acid morpholides had  $n_D^{30}$  1.4920, sp gr 30/30 0.9540, I.V. 99.7, fp 16C.

The ethenoxylated-hydrogenated cyclic amides were prepared by placing 70.6 g of amide and 0.35 g of sodium carbonate in a 500-ml indented flask equipped with stirrer, thermometer, and gas-dispersion tube. The flask was swept with nitrogen, and the contents were heated to 110C. Ethylene oxide was introduced for 2 hr at 110–125C, then for 8.5 hr at 185–200C. When about 180 g of oxide had been absorbed, the addition was discontinued. There were then about 16 moles of ethylene oxide reacted for each mole of the amide. The product had a Gardner color 13 and Gardner-Holdt  $\eta$  I.

The approximate miscibilities of the ethenoxylated amide were estimated in g per 100 ml of solvent as follows: water, > 120 g; methanol, > 123 g; acetone, > 104; ethyl acetate, > 92; and benzene, > 96.

**Nitriles.** In a 250-ml flask were placed 52.6 g (0.14 mole) of hydrogenated cyclic amide and 150 ml of acetic anhydride. The mixture was heated at reflux for ½ hr. The clear yellow solution was poured into 1 l. of water. The upper phase was separated and washed with 5% carbonate solution, dried, and distilled. There were obtained 31.8 g (86%) colorless

nitrile having bp 130–138/0.25 mm, sp gr 30/30 0.8886,  $n_D^{30}$  1.4688, and approximate fp –25C.

In a similar manner the nitriles of the monomer acids were prepared. These nitriles had b.p. 122–153/0.1 mm,  $n_D^{30}$  1.4783, sp gr 30/30 0.8896, I.V. 94.3, and approximate fp –21C.

**Evaluation of Morpholides and Nitriles as Plasticizers.** A commercial (polyvinyl chloride) resin (Geon 101) was used employing the following recipe (all parts by wt): Geon 101, 65 parts; plasticizer-stabilizer combination, 35 parts. Stabilization was at the 2% level of the total mix, employing 1 part epoxidized oil (G60) and 1 part liquid barium-cadmium phosphite system (Mark M). No attempt was made to determine the stabilizer system necessary to obtain max heat and light stability. The plasticizer was added to the mixture of Geon 101 with the stabilizers and dry blended in a beaker with a spatula until a uniform mixture was obtained. The mixture was then placed on the moving rolls of a 4 x 8 in. rubber mill at a temp of approximately 160 C and milled for approximately 8 min during which time the material was repeatedly cut and worked.

Test sheets were molded in a standard 6 x 6 x 0.075 in. mold. The mold containing the milled sheet which had been cut into 3 in. sq and stacked in the mold was preheated in the press, without pressure, at about 160C for 10 min and then pressured to 1000 psi and held for an additional 10 min at 160C. The mold was then cooled under pressure until it was about room temp and removed from the press. All formulations were milled and molded at 160C. The specimens were equilibrated at 23C and 50% relative humidity for at least 24 hr prior to testing.

All test procedures are standard ASTM methods with the exception of heat stability and migration. For the determination of tensile strength, ultimate elongation and 100% modulus, specimens were die-cut from the molded sheets parallel to the milling axis. The measurements were made on an Instron tester at a jaw separation rate of 20 in. per min. Torsional modulus as a function of temp was determined with a stiffness tester (ASTM D 1043–51).

Migration and volatility were studied on sheets of approximately 10 mils thickness by previously reported methods (7). Heat stability tests were conducted on the molded specimens in an air convection oven at 160C. Samples were removed periodically and the relative heat stabilities were determined by measurement of the color change at 600  $m\mu$   $\lambda$  with a visible range spectrophotometer. The percent transmittance at a  $\lambda$  of 600  $m\mu$  was chosen as it provided the best quantitative measure of the development of color in the specimens.

Light stability tests were conducted by exposing the molded specimens to the light emitted by the twin carbon arcs of a weatherometer. During exposure the samples were necessarily subjected to temperatures in the range of 65–85C. Specimens were examined at 24-hr intervals for four signs of degradation: spotting, discoloration, stiffness, and tack formation. These factors were evaluated as follows: no degradation, slight degradation, moderate degradation, severe degradation, and very severe degradation. The failure of a compound was arbitrarily chosen as the length of exposure needed for moderate degradation to occur by any one of the preceding modes of breakdown, or for slight degradation to occur in any three modes of breakdown.

 TABLE IV  
 Approximate Solubilities of Diethanolamides (30C)<sup>a</sup>

Solvent	Diethanolamide origin			
	Hydrogenated cyclic acids	Monomer acids	Coconut acids	Stearic acids
Water.....	I <sup>b</sup>	I	0.2	I
Methanol.....	1.5	3.3	110	12
Ethyl acetate.....	I	I	0.7	1.5
Acetone.....	0.1	0.1	0.6	3.6
Benzene.....	3.0	0.4	45	0.2

<sup>a</sup> Figures are g per 100 ml of solvent.

<sup>b</sup> I = Insoluble, meaning solubility less than 0.1 g per 100 ml solvent.

**Hydrogenated Cyclic Amine.** In an indented flask equipped with mechanical stirrer, reflux condenser, nitrogen atmosphere, and dropping funnel were placed 70 g (3 moles) sodium and 1 l. xylene. The sodium was melted and dispersed with stirring in the xylene. A mixture of 161.6 g (0.62 mole) hydrogenated cyclic acid nitrile, 143.0 (1.4 mole) methyl isobutyl carbinol, and 250 ml xylene was then added to the sodium. The excess sodium was destroyed by the addition of 95% ethanol. The mixture was poured cautiously into ice water, and the product separated by ether extraction. Distillation afforded two fractions. The first fraction had a bp 100–120C/0.25 mm, 67.7 g,  $n_D^{20}$  1.4714, and about 12% amine. The second fraction had a bp 120–150C/0.25 mm, 57.8 g,  $n_D^{20}$  1.4840, and about 71% amine.

Systematic distillation through 2 ft concentric tube column provided 40.9 g of about 97% pure amine. This material had bp 130–148C/0.2 mm,  $n_D^{20}$  1.4840, sp gr 30/30 0.8941, equivalent wt 274, and approximate fp  $-34$ C.

**Hydrogenated Cyclic N,N-Dimethyl Amine.** In a 500-ml flask equipped with stirrer, thermometer, and reflux condenser, 40 g (0.15 mole) hydrogenated cyclic amine, 18 ml water, and 200 ml 95% ethanol were placed. To this solution, 25 ml (0.46 mole) 100% formic acid was added with cooling to maintain temp below 30C. Thirty ml (0.4 mole) formaldehyde solution were added, and the mixture was warmed to 60–80C for 2 hr until the evolution of carbon dioxide ceased. The mixture was made basic and diluted with water. The product was isolated by ether extraction and distillation. It had bp 128–140C/0.3 mm,  $n_D^{20}$  1.4762, sp gr 30/30 0.8656, equivalent wt 304, and fp  $-54$ C. It weighed 29.5 g.

**Trimethyl Hydrogenated-Cyclic-Alkyl Ammonium Iodide.** In a 125-ml glass-stoppered flask were placed 10 g (0.033 mole) hydrogenated cyclic N,N-dimethyl amine, 40 ml pentane-hexane, and 7.2 g (0.05 mole) methyl iodide. A solid cake formed in 15 min. The solid was removed by filtration and dried *in vacuo*. It weighed 8.8 g and contained about 5% basic amine. Recrystallization from chloroform hexane gave a colorless, waxy solid free of basic amine and having mp 204–209C. Surface properties of this quaternary are shown in Table III.

Calculated for Iodine on basis of the equivalent wt of the tertiary amine 28.4%; found 28.8%.

Approximate solubilities were as follows in g per 100 ml. of solvent: water, 0.4; methanol, 40.3; acetone, 48.0; ethyl acetate, 1.1; and benzene, 0.05.

### Discussion

The amides of the hydrogenated cyclic and monomer acid mixtures had low mp of 33 and 43C, respectively. Since these are mixtures, different preparations of amides, as well as the other products reported here, would have slight differences in properties depending upon the method of preparation and the

degree of fractionation of the product upon isolation. Even so, these amide mixtures do have remarkably low mp in comparison with commercially available amides made from fatty acid mixtures of similar molecular size.

Because the two amide mixtures have low mp, one might anticipate good solubility in organic solvents. This expectation is borne out by the data in Table I 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 methanol; however the two amides of the cyclic acids show much higher solubility in benzene and carbon tetrachloride than in alcohols. It appears that 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.

Data in Table II show that the 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.

The nitrile mixtures prepared from the monomer acids and hydrogenated cyclic acids also have low mp,  $-21$  and  $-25$ C, 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 V. These data show the superiority of the nitriles with respect to Clash-Berg temp as compared to the control; 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 weaknesses 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 while the control had not failed after 600 hr. Similarly, the cyclic acid derivatives showed very rapid drop in light transmission at 600  $\mu$  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 exhibits a low freezing point ( $-34$ C) as does its N,N-dimethyl derivative ( $-54$ C). It is noteworthy that the amines derived from soybean, coconut, tallow, and hydrogenated tallow acids have mp greater than 20C (8). Even commercial octyl amine has a mp of  $-13$ C.

The surface-active properties of the diethanolamides prepared from the two acid mixtures, the ethenoxyated hydrogenated cyclic-acid amine and

TABLE V  
Properties of the Nitriles and Morpholides as Plasticizers<sup>a</sup>

Name	Tensile strength (psi)	Modulus at 100% elong. (psi)	Elongation %	Clash-Berg		Migration after 14 days % loss	Volatility at 70C % loss
				T <sub>135,000</sub> C	T <sub>10,000</sub> 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

<sup>a</sup> Plasticization was at the 33% level of a commercial polyvinyl chloride resin (Geon 101).

the trimethyl hydrogenated-cyclic-alkyl ammonium iodide, are shown in Table III. Solubility data on these materials are found in Table IV. The high solubility of the simple amides disappears with the substitution of the ethanol groups for hydrogen on the amide nitrogen in the diethanolamides. The diethanolamides of coconut acid exhibit superior solubility, probably reflecting their lower average mol wt.

### Conclusions

Amides prepared from hydrogenated cyclic acids possess unusually low mp, high solubility, and good compatibility with synthetic resins, which suggest their utility as mutual solvents for waxes and resins. Nitriles of hydrogenated cyclic acids and monomer acids, as well as the morpholides of the two acid mixtures, are compatible with polyvinyl chloride-vinyl acetate copolymer and may have potential as plasticizers.

The amine of hydrogenated cyclic acids and its *N,N*-dimethyl derivative provide amines of high mol wt and of extremely low fp.

The surface-active materials appear on the whole to be similar to other fat-derived substances.

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## Reactions Between Zinc Chloride and Surfactant Solutions<sup>1</sup>

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### Abstract

Formation of precipitates or soluble complexes between solutions of zinc chloride and surfactants was investigated by means of pH and conductivity titrations. Precipitates were characterized by chemical analysis and X-ray diffraction.

Triton X-102 and zinc chloride appear not to react. Sodium dodecyl sulfate likewise appears non-reactive, but on addition of alkali a basic salt is formed at a pH between 7.9 and 8.5 which, however, does not precipitate if the concentration of sodium dodecyl sulfate is above the critical micelle concentration. The precipitate has a marked destabilizing action on oil-in-water emulsions. With the sodium salt of Empol 1022 the normal zinc salt precipitates on addition of the stoichiometric amount of zinc chloride.

Tamol 731 is neutralized in two steps by hydrochloric acid, the pH at the two endpoints being 7.0 and 3.3. It apparently forms a soluble complex with zinc ion which is not precipitated even in alkaline solutions.

### Introduction

THE MAJOR PRACTICAL PROBLEM to which the present work should have application is that addition of zinc oxide to bodied linseed oil emulsions raises serious stability problems. In order to provide background information for the solution of this problem it was considered important to study the types of interaction which might occur between zinc oxide or zinc ion and a variety of surfactants of types found in emulsion paints.

Reaction between residual fatty acids and zinc oxide can lead to formation of zinc soaps which are stabilizers for W-O emulsions and would consequently have an adverse effect on the original O-W dispersion.

Zinc oxide itself, depending on its method of preparation and incorporation, may stabilize either O-W or W-O emulsions (1). Loss of stabilizer by adsorption on the metal oxide may reduce the concentration in solution to so low a value that instability results. The same effect could also result if the surfactant reacted chemically with the metal oxide, or if zinc ion furnished by solubility of zinc oxide either precipitates the stabilizer or reduces its concentration by formation of a soluble complex. Any or all of these processes may be the explanation for the common observation that larger quantities of surfactants are required to form stable linseed oil emulsions when driers or pigments are present than in their absence. Consequently this work was undertaken to explore the possible effects of zinc ion in O-W emulsions containing a number of common stabilizing agents.

### Materials and Apparatus

All inorganic chemicals used were Baker and Adanson, reagent grade. Standard solutions of zinc chloride were prepared by adding a very slight excess of the acid to a known wt of zinc oxide dried at 110C.

Pure sodium dodecyl sulfate (SDS) was used as a stabilizing agent, either the same sample prepared by Phansalkar (2) or a slightly less pure preparation by H. M. Princen from combined lauryl alcohol fractions of mp 23.40 and 23.71C. The two preparations of SDS gave identical X-ray diffraction patterns, and were freshly extracted with ether before use.

Other surfactants were used directly as received without further purification. Triton X-102<sup>3</sup> and Tamol 731-25%<sup>4</sup> were supplied by the Rohm and Haas Co.

<sup>3</sup> Triton X-102 is an alkyl aryl polyether in which the polyoxyethylene chain has a length of twelve to thirteen carbon atoms.

<sup>4</sup> In this paper per cent Tamol is in terms of a 100% product and not in terms of the 25% solution as which it is supplied. Tamol is described as being the sodium salt of a carboxylated polyelectrolyte.

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