Dimer Acids

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Introduction

EARLY RESEARCH on the polymerization of drying oils dealt with the preparation of dimeric and trimeric products but there was never a clear understanding of the products formed. Early patents of De Nordiske Fabriker DE-NO-FA report on the preparation of polymeric fatty acids (16). These patents describe the preparation of alkali soaps of polyunsaturated fatty acids and their polymerization in the presence of excess alkali and, presumably, water under pressure. These conditions are now known to shift nonconjugated 1,4-dienes to conjugated 1,3-dienes and polymerize them. However, the products of DE-NO-FA were apparently not desirable enough for commercial exploitation then. Indeed, the uniqueness of dimer acids were not appreciated in the early 1920's and polyamides were yet to be discovered.

In 1929, Scheiber (35) stated that the conjugation of isolated double bonds was a prerequisite to heat polymerization. Before that time, much investigation had failed to reveal the structure of the products in heat bodied oil, but Scheiber's suggestion has withstood considerable critical investigation. Kappelmeier (26) extended Scheiber's hypothesis to include the Diels-Alder type of reaction between a conjugated and a nonconjugated polyunsaturated fatty acid in a manner similar to 1,4-pentadiene as reported by Farmer (1). Wheeler (42) gave this hypothesis the status of a theory that is now generally accepted, but it may be incomplete. Bradley (7,8) prepared dimer and trimer esters by heat polymerization of the polyunsaturated fatty esters and separated these dimer and trimer esters by molecular distillation. Bradley gave a firm foundation to the development of the technology that followed. Hill and Walker (25) contributed to this early work with a patent describing preparation of partially decarboxylated dimer acids and their use to make bodied oils.

Development Work Leading to Commercial Use. In December 1939, a program of research and development on vegetable oils was initiated at the Northern Regional Research Laboratory in Peoria. W. J. Sparks, a coinventor of butyl rubber (39), was initially in charge and directed the original planning. He returned to industrial research in 1940 before laboratory work was initiated. Later, he found potential uses for dimer acids in a variety of petroleum products (88,89,97,98). Laboratory work at Peoria was initiated soon after Sparks left. The research and development studies led, first, to commercial production of a polyester as a rubber substitute in 1942 and, secondly, to polyamide resins for use in heat-sealing. After commercial development of polyamide resins and dimer acids was clearly assured in the late 1940's, research at Peoria on dimer acids and its derivatives (12,53–60,90,103–105,121,125,135) was discontinued and research along other lines was initiated.

Uniqueness of Dimer Acids. Dimer acids are a unique chemical and have no parallel among other commercial chemicals, i.e., no other commercial chemical has the same or nearly the same properties. First, these acids have good low-temp characteristics and never crystallize. Secondly, they have a comparatively high mol wt—560 for the dimers of linoleic acid. Finally, they contain unsaturated bonds that are difficult to conjugate with either the carboxylic group or with one another. Thus, these double bonds are reactive toward oxygen and sulfur under many conditions, but the reaction can be controlled in a variety of ways. These properties that make dimer acids unique are:

Never crystallize—Mol Wt 560
Distill with difficulty
Cyclic structure—highly flexible
Soluble in hydrocarbons
Unsaturated but not readily conjugated
Reactive but easily controlled

Preparation, Structure, and Mechanism of Formation

Effect of Heat. Dimer acids were first prepared in a relative pure form by heat polymerization of methyl esters of polyunsaturated fatty acids and subsequent molecular distillation (7). In Figure 1 is one of the accepted mechanisms for the formation of dimer acids by heat, I isomerizes to conjugation to give II and II reacts with I by a Diels-Alder mechanism to give III. The reaction rate is first order since the change from I to II is the rate-determining step. Wheeler (42) has depicted these reactions proceeding as in Figure 2 where N is a nonconjugated fatty acid and C is a conjugated fatty acid; subscripts c and t stand for *cis* and *trans,* respectively. The comparative rates of reaction of the different conjugated and nonconjugated fatty acids are shown in Table I, and these rates support Wheeler's view of the formation of dimer acids.

Clingman et al. (11) has reported the preparation of tetramethyl ester of prehnitic acid from dimers derived from a number of polyunsaturated esters. Sutton (27) has recently confirmed this work for methyl linoleate but found evidence for other than the Diels-Alder reaction since conjugation was believed to be present in the dimer and Sutton's conditions were 1 hr at 300C. Sunderland (38) has suggested that hydrogen exchange may occur in dimerization and Sutton's recent work may support this suggestion. Prehnitic acid in the work of Sutton and Clingman is clearly indicated as the expected benzene-1,2,3,4-tetracarboxylic acid. However, there is considerable opportunity for confusion since "Chemical Abstracts" (10), Sonntag in Markley's "Fatty Acids" (37) and some organic text books refer to prehnitic acid as benzene-1,2,3,5-tetracarboxylic acid. Baeyer (2) assigned this correct structure of 1,2,3,5-tetracarboxylic acid to an acid he called prehnitic, and Bamford and Simonsen (3) and Smith and Byrkit (36) confirmed it. However, since prehnitene is 1,2,3,4-tetramethyl benzene, Smith and Byrkit suggested that it was essential to clarity to call the benzene-1,2,3,4-tetracarboxylic acid, prehnitic acid. It is a suggestion that could avoid confusion. Fiesers (18) followed it but others have not. Some argue that the man who first named the compound should have the honor or privilege of having the name retained even though the name may become illogical. "Chemical Abstracts" has indicated that in Volume 56 it will refer to the tetracarboxylic acids by num-

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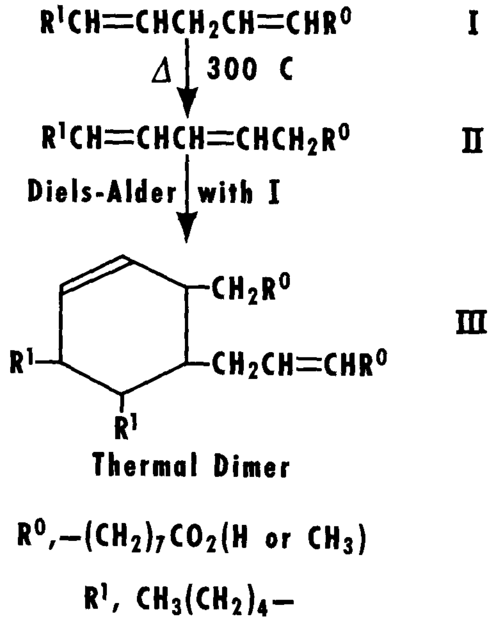


FIG. 1. Formation of dimer acids by thermal polymerization of linoleic ester.

ber and not trivial names. Also, let it be clearly understood that at least 3% of the dimer from linoleate and 9% of the dimer from eleostearate will, on treatment with N-bromosuccinimide (NBS), diethyl aniline (DEA), and potassium permanganate, yield the benzene-1,2,3,4-tetracarboxylic acid, sometimes called prehnitic acid (Fig. 3).

For some years, heat polymerization of methyl esters of polyunsaturated fatty acids in the presence of catalysts was the preferred method of preparation. In addition to the dimer esters, heat gave trimer esters. Although characteristics of the dimeric product closely follow that of the expected product from a Diels-Alder reaction, properties of the trimer acids do not. The dimer acids retain the expected 1 double bond/fatty acid; but the trimer acids react as though they had 3 double bonds for every 3 fatty acid radicals where 2 double bonds are expected. Trimers should have only 2 double bonds for every 3 fatty acids if a second Diels-Alder reaction occurred. Hydrogen exchange and addition of fatty acid through active methylene may occur by Sunderland's mechanism (38).

Goebel (20) found that thermal dimer acids could be prepared by using polyunsaturated fatty acids containing small percentages of water under high pressure. This work is described in the section on commercial production of dimer acids.

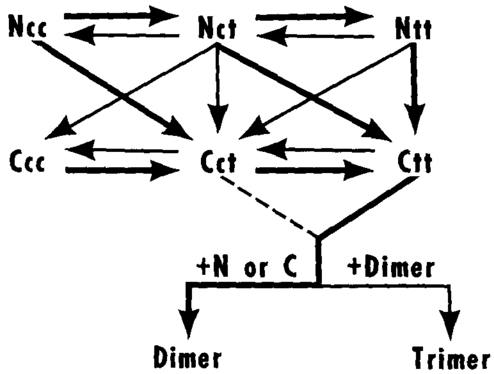


FIG. 2. Equilibria and probable paths followed in formation of dimer and trimer acids.

TABLE I
Comparative Rates of Dimerization of Different Conjugated and Nonconjugated Fatty Esters

Compound			Relative speed
Conjugation	Number of double bonds	*cis, trans* Configuration	
No	2	*cis, trans*	0.74
No	2	*cis, cis*	1.0
No	2	*trans, trans*	1.2
No	3	*cis, cis, cis*	2.4
Yes	2	*cis, trans*	5.8
Yes	2	*trans, trans*	26
Yes	3	*cis, trans, trans*	170
Yes	3	*trans, trans, trans*	340

Heat polymerization of trienoic fatty esters conform to first order kinetics (30) like linoleic esters, but the trienoic gives a somewhat different product than dienoic fatty ester. Monocyclic dimers appear to be formed, which rearrange to bicyclic or tricyclic dimers, but usually a higher percentage of trimeric acids are formed (7,30,42).

Anthraquinones, sulfur dioxide, and other catalysts that give conjugated fatty esters at temp below 300C speed this reaction. Excess alkali can also be used to convert polyunsaturated acids to salts of dimeric fatty acid (31).

Effect of Clay and Lewis Acids. Lewis acids, such as boron trifluoride (15), and clays, such as kaolinite and montmorillonite (4), will also catalyze the polymerization of polyunsaturated fatty acids. Boron trifluoride gives mainly trimeric or higher polymeric fatty acids at 200C in a few min and the clays substantially lower the temp for heat polymerization. Both the Lewis acids (40) and the clays (4) will also polymerize oleic acid to give new and different dimer acids. Dimer acids from oleic acid with boron trifluoride give pelargonaldehyde and pelargonic acid on ozonization. A possible structure and mode of formation are shown in Figure 4. Oleic ester (IV) gives a complex V that reacts with IV to give a new dimer VI (41). Although Russian reports support this mechanism, private communications indicate that even this dimer may be cyclic.

Clay reacts as a dehydrogenating agent but the mechanism of dimer formation has not been reported. Clay is apparently used commercially since it permits preparation of dimer acids from oleic, tall, or other fatty acids at 220C.

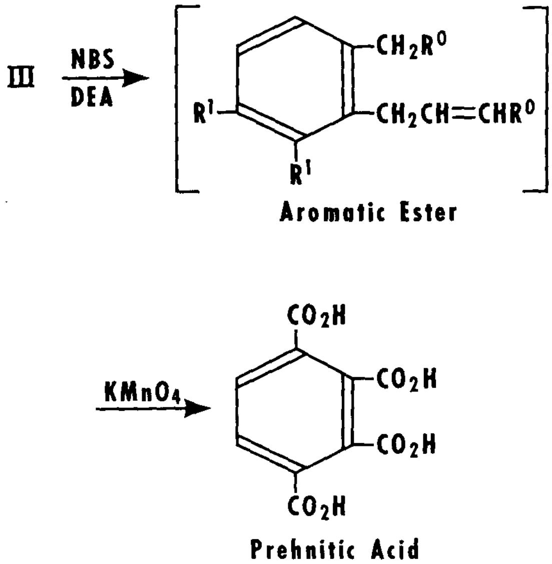


FIG. 3. Conversion of dimer esters to aromatic esters and oxidation to prehnitic acid, benzene-1,2,3,4-tetracarboxylic acid.

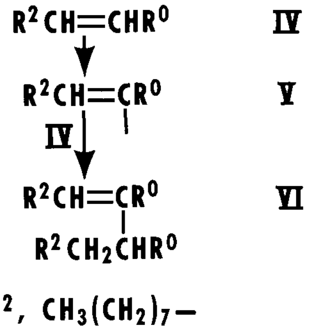


FIG. 4. Suggested formation of dimers from oleic acid or esters.

Free Radical Dimerization. Free radicals can also be used to dimerize and trimerize unsaturated fatty esters. Harrison and Wheeler (24) found that di-t-butyl peroxide gave a dehydro dimer structurally different from the dimers produced with heat alone. Suggested sequences of reactions for monenoic, dienoic, and their mixtures are given in the next several figures. With methyl linoleate, Harrison and Wheeler (24) found that the products contained at least 1 conjugated system and 4 double bonds. They suggested that the oxy free radical (TO·) formed at 130C removed hydrogen from I to give a free radical at the 3-position of the 1,4-pentadiene system (VIIa) i.e., the 11-position of methyl linoleate, ($R^1CH=CH-\dot{C}H-CH=CHR^\circ$, VIIa). They also suggested that this free radical rearranged in part to give VII and VIII, which reacted with VIIa to give the dehydro dimer. The author suggests that VII and VIII are not likely to be reactive enough to catch VIIa to form a dimer before VIIa rearranges to VII and VIII. These two free radicals should react either with themselves or with each other as partially indicated in Figure 5.

The physical properties of the dehydro dimer might better be explained by behavior of IX under the conditions of its formation and isolation. A free radical like VIIa is postulated in autoxidation of methyl linoleate, and the oxygen "free radical" is unable to form a hydroperoxide of VIIa since only 9- and 13-hydroxystearic acids are isolated from the reduction of autoxidation products (5). Thus, the initial dehydro dimer of Harrison and Wheeler (24) probably has a structure similar to IX. On alkali isomerization of dehydro dimer, small additional amounts of conjugation are formed, and this conjugation could result from the presence of 5–10% of methyl linoleate rather than from a dimer of VIIa and VIII. Indeed, on heating at 250C, dehydro dimer gave 10% of monomeric esters, 69% of a new bi- or polycyclic dimer (such as X in Fig. 6), and 21% of trimeric product. It does not appear likely that much cracking could have occurred but that the previous fractionation of the dehydro dimer was probably incomplete.

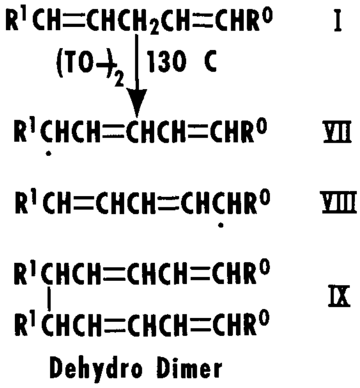
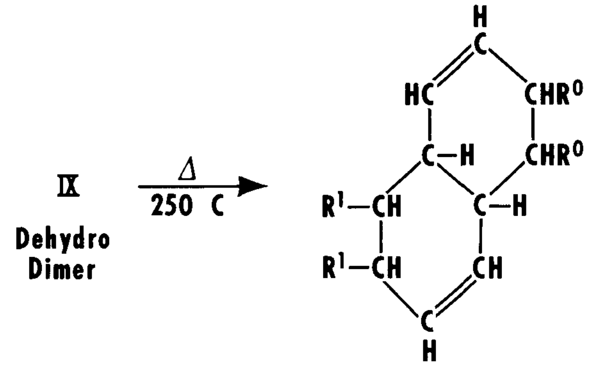


FIG. 5. Free radical reaction to conjugated dimers or dehydro dimers.



Bicyclic Dimer X

FIG. 6. Cyclization of dehydro dimer.

Such a fractionation presents some experimental difficulties even on a micro or analytical scale (28). Unfortunately, these fractions of dehydro dimer were apparently not analyzed by micro techniques; however 10% monomer and 21% trimer in the heat-treated dehydro dimer support the contention that it most likely has structures similar to IX. Further, the fractions of molecularly distilled dimer esters reported by Harrison and Wheeler (24) decreased in isolated *trans* values as the distillation proceeded, suggesting the presence of monomeric esters.

Harrison and McCaleb (23) dimerized methyl oleate IV and oleic acid with d-t-butyl peroxide to a dimer similar to XII and containing 2 double bonds, see Figure 7. Harrison and Wheeler (24) dimerized mixtures of methyl oleate IV and linolate I with this same reagent to give another dehydro dimer containing 3 double bonds and probably similar in structure to XIII in Figure 8. They do not mention presence of conjugation, but unsaturation was determined by hydrogenation—a method suitable for measuring unsaturation in conjugated systems.

An alternate explanation for the formation of dehydro dimers from methyl linoleate was suggested by Harrison and Wheeler (24) based on their experiment with oleate and linoleate. They suggested that a free radical could be formed at either position 10 or 12 with a shift in the double bonds to 8 or 13, respectively. This mechanism may operate, but free radicals would not be expected to form so readily or be as stable as VII and VIII. Some of the data relating to the structure of dehydro dimer and its thermal derivative may be summarized as:

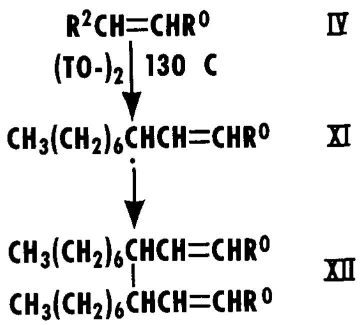


FIG. 7. Free radical dimerization of oleic ester.

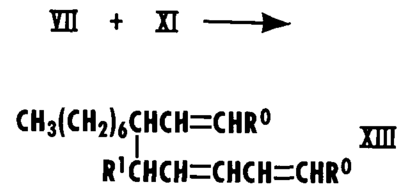


FIG. 8. Free radical dimerization of a mixture of linoleic and oleic esters.

1. Four double bonds/dehydro dimer unit.
2. Conjugation present to the extent of one or more than one conjugated system in dehydro dimer.
3. Heating at 250C gives "thermal" dehydro dimer with 2 double bonds and no conjugation.
4. Monomeric esters present in molecularly distilled dimer and thermally treated dehydro dimer, decreasing *trans* values in molecularly distilled fractions with the amount of or temp of distillation, and the high level of ultraviolet absorption in the diene region support belief that dimeric molecules with one or two sets of conjugated dienes are present.

Commercial Production of Dimer Acids

Although thermal polymerization of methyl esters and sodium salts of polyunsaturated fatty acids has been used commercially, polymerization of fatty acids is now the preferred method of production for dimer acids. Goebel (20,21) found that the addition of small amounts of water and the use of high pressures to retain the water and high temp of 300C gave rapid conversion to dimers and trimers. The addition of water prevented or kept at a minimum the side reactions shown in Figure 9. These dehydration and decarboxylation reactions lower the carboxylic acid content of the oil, and presumably, convert some of the acids to ketones. However considerable doubt remains regarding the decarboxylation to ketones since dehydration or other reactions may account for most if not all of the apparent decarboxylation (32,33).

Later, Goebel and coworkers were able to lower temp required for dimerization by using clay as a catalyst (4), to use commercial oleic acid to give good yields of dimer acids, and to carry out the reaction on a continuous basis (22). Properties of dimer acids made using clay catalysts with soybean, tall, and commercial oleic acids are given in Table II. The properties of dimer acids offered for sale in the U. S. are shown in Table III (17b–e). Dimer acids are now produced in at least four different countries and by more than four companies. Acids available in England are reportedly prepared from dehydrated castor oil (9,34). Also, in the production of sebacic acid from castor oil, some ricinoleic acid is dehydrated and polymerized as the soap in the alkaline reaction mixture. Dimer acids are isolated as an impure mixture from the still residues.

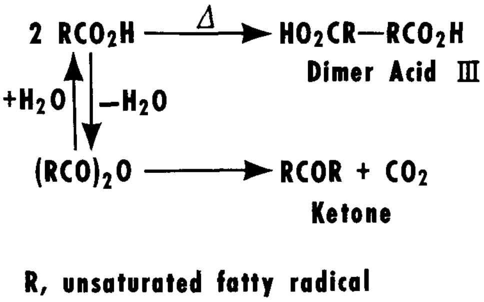


FIG. 9. Probable reactions involved in commercial preparation of dimer acids.

TABLE II

Dimer Acids Formed Using a Clay Catalyst at 220C

Property	Soybean—Dimer		Tall — Dimer		Oleic — Dimer	
I. V.	154	138	130	149	90	114
Neutral equivalent	293	312	292	309	280	300
Saponification equivalent	285	296	291	293	276	280
Color (Gardner)		7	6	10	2	8
Yield—%		56.4		45		45

An examination of Table II shows that clay catalysts may dimerize through a mechanism that dehydrogentaes. However the reaction appears to differ from the free radical reaction by removing additional hydrogen. Since the clays used are acid-activated clays, they may behave as Lewis acids as well as active dehydrogenating agents.

Analysis of Dimer Acids

Determination of acid and saponification values of dimer acid are usually straightforward procedures. Methods used commercially have been published (17f). However, acid and saponification values usually do not agree. Depending on the conditions of formation of the dimer acids, a variety of explanations are possible. Petit and Cazes (33) report the presence of anhydride groups in dimer acids to explain these differences. These authors saponified dimer acids in alcohol, removed the unsaponifiables, and acidified to obtain acid values approx equal to the untreated monomeric fatty acids. Further, they found small amounts of monobasic fatty acids present that had higher mol wt than the original fatty acids (32) and contained as high as 30 or more carbon atoms.

I. V. is, at best, a rough approximation of unsaturation in dimer acids. Apparently the tertiary hydrogens in dimer acid will substitute in different amounts depending on length of exposure, the catalyst used, and excess of reagent (60). Kaufman's bromide number is a superior method, and it is usually unaffected by excess of reagent or prolonged exposure to brominating reagent. Hydrogenation with active catalysts appears to be useful with some acids (24).

Analysis for monomer, dimer, and trimer can be made by alembic distillation (12), molecular distillation (7,24), and micromolecular distillation (28). The best of these methods uses the micro still. Chromatography on silicic acid may eventually be the best method by either column (19) or thin layer chromatography.

Uses for Dimer Acids

New uses for dimer acids have outstripped the first, and continuing, use in a heat-sealing resin based on

TABLE III

Commercially Available Dimer Acids

Property	No. 1	No. 2	No. 3	No. 4	No. 5
Acid value	188–193	188–196	186–194	186–194	......
Sap. value	194–198	192–198	191–199	191–199	198
Neutral equivalent	292–298	287–299	289–301	289–301	300
Color—Gardner[a]	8 max	8 max	9 max	9 max	......
Monobasic acids, wt.%	1.5 max	1 max	2–5 max	1 max	Dark brown
Dimer acid, wt %	95	83	75	75	10
Trimer acid, wt %	4	17	22	25	90
Ratio (mole)	36/1	7/1	5/1	5/1	0.3/1
n_D^{60}	1.4706	1.4704	1.4738	1.4755	1.4830
Viscosity centipoises at 25C	5100	6500	6200	9000	65000

[a] Recent reports give color values considerably lower (lighter) for products similar in dimer-trimer contents to Nos. 1–5.

the dimer acids-ethylene diamine polyamide. A look at the ever increasing patent and technical literature on dimer acids is enough to convince anyone that further increase in uses and technology is likely to follow. When the group at Peoria initiated their research, there were only a relatively few papers on dimer acids. Indeed, the work on the separation of dimer and trimer acids had not been published (7). Today, over 300 patents and other publications have issued and the number is mounting (17a). Any article or book (109) is necessarily out of date before it is published and must omit many references because of space or selected reasons. One manufacturer has indicated that a revision of a bibliography on dimer acids will be available before the end of 1962 (17a).

The derivatives and uses of dimer acid may be divided as follows: The acids, their esters, salts, sulfurized and borated products, and polymeric derivatives as additives to control corrosion, improve lubricating properties, or delay crystallization; as polyesters in rubberlike products, urethane coatings and foams, alkyd resins, epoxy coatings, and other products; and polyamide resins in a wide variety of products and uses based primarily on two types of resins, thermoplastic and reactive. Recently, actual or suggested use of dimer acids, polyamide resins, or their epoxy combinations has been reported for such widely separated items as in racing yachts (113i), milady's shoes (113j), boron derivatives for gasoline (73) and printed circuits (117).

Corrosion Inhibitors. Because of unusual solubility particularly in hydrocarbon systems, low freezing point (never crystallizes), and water insolubility, dimer acids and many of their derivatives have been proposed for a wide variety of corrosion inhibitors. It has been reported that substantial amounts of dimer acid are used for this purpose, but it is difficult to know which of the many patents are actually used. However, a few of the various types of dimer products prepared and their reported advantages can be reviewed.

Dimer acid is useful in inhibiting corrosion and emulsifications in turbine oils (61); in gasoline, kerosene, and heating oils in pipeline and barge shipments (48,87); in oil well digging (67,85,86); to break oil and water emulsions (63); in gasoline to reduce oil free deposits and ash therefrom on the pistons of internal combustion engines; in lubricating oils (76); and in road oils (78).

Illustrative of the protection against rusting given gasoline is the work of Landis and Backensto (76). Their data show that dimer acids are superior to mixtures of monomeric fatty acid when evaluated by a modified ASTM D665-47T test. Scheuman also shows that the addition of dimer acids-lubricating oil compositions to gasoline is advantageous for reducing piston ring wear, piston head deposits, and rusting (87). Table IV gives some of the results he obtained. Dimer acids were 0.2–0.6% of a composition based on light solvent-refined hydrocarbon-lubricating oil (100 S.U.S. at 100F) also containing benzene, isopropyl alcohol, dihexylphenyl amine, and amyl nitrate. For summer, spring and fall, or winter driving, the amounts of isopropyl alcohol were varied, as well as the amounts of this mixture added to gasoline.

Compositions based on derivatives of dimer acid also inhibit corrosion. Gottshall and Peters (71) and others (75) reacted sorbitanoleate with dimer acid and used it as a component of a corrosion-inhibitor system. Thus, the addition of the dimer acid-sorbitan oleate (0.02%) to a lubricating oil with 2,6-ditertiary butyl-4-methyl phenol (1.25%), cocoamine isoamyl octyl orthophosphate (0.01%), and dodecenyl succinic anhydride (0.04%) gave more than a tenfold improvement over the base oil alone (72) as shown by hours required to reach an acid number of 2, see Table V for details.

Dimer acid gives heavier, more suitable corrosion inhibitors for gas, oil, or other wells where corrosive brines shorten life of equipment. When sulfurized with 10% sulfur at 158–165C the alkyl dimerates are reported to give a corrosion inhibitor and an antioxidant for lubricating oils (51). Basic polyamides reduce corrosion of metals (70,121,123); treatment of basic polyamide with boric acid is reported to give improved products for gasoline (73,74) and, in combination with stearic acid, to give improved resistance to corrosion in lubricating oils (84).

Lubricants. Dimer acids and their derivatives not only inhibit corrosion in lubricant applications, they also improve other properties of lubricating compositions (49), such as viscosity, index and stability (88,95,97), wear (92), pour point (83), and stringiness of greases (43).

Dimer acid salts improve the lubricating properties of noninflammable hydraulic fluids containing polymeric alkylene glycols made from epoxides, such as the polyglycol obtained by polymerizing 0.75 mole percent of ethylene oxide with 0.25% propylene glycol to obtain a viscosity of 90,000 S.U.S., at 100F (92). In a composition of water 62.8%, ethylene glycol 11.2%, and polyglycol 25.0%, 1% of sodium dimerates substantially improves lubricating properties. Results from a four-ball wear test are given in Table VI. Amine salts (47,77,136) as well as calcium, barium, and zinc salts (56), have been studied for a variety of uses. Aluminum soaps that are dry and free flowing can be prepared using dimer acid (62).

Dimer acid esters are also useful as bases for special lubricating greases. Thus, Morway, Young, and Cottle (81) were able to prepare greases using a lithium soap mixture of hydrogenated fish fatty acids and crotonic acid with different combinations of

TABLE IV

Comparison of Corrosion Inhibition, Piston Ring Wear, and Piston Head Deposits Using Gasoline Containing No Additive or Less than 1% of a Dimer Acid Composition

Type of Test	Improvement with dimer additive
First motor (Chevrolet)	
Piston ring wear (tracer)	10% less wear
Piston head deposits	
(a) at 0.25% additive, oil-free	6.7% less
(b) at 0.50% additive, oil-free	13.5% less
ash	24.0% less
Second motor (DeSoto)	
Piston head deposits	
(c) at 0.50% additive, oil-free	14% less
ash	30% less
Rusting modified ASTM D665	>54 hr

TABLE V

Corrosion Inhibition of Sodium Dimerate in Lubricating Oil

Method	Test results	
	Base oil	Plus additives
Rust prevention test:		
ASTM-D665-53T		
Procedure A	Rusted	Bright
Procedure B	Rusted	Bright
Oxidation test:		
ASTM D493-53T		
After 1,000 hr—iron coil	Rusted	Bright
Hours to acid number of 2	240	2460

TABLE VI

Lubricating Properties of Sodium Dimerates

Polyglycol fluid plus additive	Wear scar
	Diam. in mm
No additive	1.50
1% Na dimerates	0.54
1% Na "castor" dimerates	0.62
1% Na sebacate	0.71
Typical mineral oil	0.55

TABLE VII

Formulation and Properties of Greases with Dimer Esters

	A	B
Formulation		
Dimerates	50 (methyl)	84 (octyl)
Octyle adipate	34	....
Lithium complex	15	15
Antioxidant	1	1
Properties		
Dropping point	382F	425F
Penetrations 77F,mm/10		
Worked (60 strokes)	210	295
Worked (50,000 strokes)	235	335
Water washing—% loss	None	5

alkyl esters of dimer acids, di-2-ethylhexyl sebacate or octyl adipate, and an oxidation inhibitor. With these compositions, it was necessary to cool the grease rapidly to crystal the soaps properly. One formulation and properties thereof are shown in Table VII.

Dibutyl dimerates can also be used to aid in stabilizing the viscosity of ester lubricants such as di-2-ethylhexyl sebacate and azelate. Table VIII shows that heating dibutyl dimerates increases viscosity, whereas heating the sebacate ester ''oil'' lowers viscosity. By combining the two materials, a more heat-stable oil is achieved (91). Other reports of esters for lubricants include a variety of products and compositions (52,80,83,93).

Dimer polyesters prepared with various glycols can be used to improve the viscosity index and pour point of lubricating oils. The higher the mol wt, the lower the crystallinity, and more linear the polyester, the greater is the apparent improvement. Thus, dimer glycol-dimer acids polyester (60,64) with a melt viscosity of greater than 36.8 poises at 225C and a mol wt greater than 33,200 gave a viscosity index of 241 in PRL 1801, a special petroleum base oil. A comparison of selected polyesters and their effect on Winkler and PRL 1801 are given in Table IX (60).

The effects of increasing mol wt of dimer acids-decamethylene glycol polyester on the viscosities and viscosity index of a lubricating oil derived from Barusa crude are shown in Table X (96). When the polyester was used at low percentages or combined with a pour point depressor, substantial lowering of the pour point but increase in viscosity index were achieved. The polyester in the experimental data reported in Table XI had a mol wt of 9,000 and was prepared by solvent purification of a dimer acids-decamethylene glycol polyester of mol wt 22,000 (95).

Dimer acids reduce the tendency of materials to crystallize, such as DDT in cooled or supersaturated solutions (72) and solid glycerides in the winterization and subsequent refrigeration of cottonseed oil (46). Dimer acids are also useful in the formulation of aluminum greases although lithium soap greases have or are replacing aluminum greases to a considerable extent. The advantage of dimer acids in aluminum soap greases is shown in their stringiness (43). The aluminum soaps are also excellent thickening agents for gasoline (45). Dimer acids are also useful in the preparation of organo-sodium dispersions (82) and in hot-dip tinning of iron for cans (66).

Polyesters

Polyesters derived from dimer acids were among the first dimer products prepared and used commercially. These polyesters are viscous liquids to rubbery solids that resemble natural rubber in some properties. Although soluble in petroleum hydrocarbons, they can be vulcanized with sulfur or crosslinked with oxygen to give insoluble products. Hydrogenated dimer acids would, of course, be slower to oxidize or crosslink with sulfur. Low mol wt polyesters react with isocyanates to give foams; adhesion and flexibility of alkyd resins are improved when dimer acids form a part of the polyester chain, and trimer acids react with epoxy resins to form polyesters that have superior electrical properties.

TABLE VIII

Effect of Heat on Viscosity of Dimer Esters and Blends

Composition	Heating hr at 550F	Change in viscosity (Centistokes)	
		210F	110F
A. Dibutyl dimerates	6	11→26	77→130
B. Blend X[a]	6	470→55	4,700→395
C. Blend X plus 70% dioctyl azelate	6	7.9→7.4	32.9→32.8
D. Blend of 20% A, 10% X, and 70% dioctyl azelate	6	7.2→5.4	31→26
E. Same as D	24	7.2→6.8	31→37

[a] Blend of 40% polybutyl methacrylate and 60% dioctyl sebacate. Octyl groups in these esters were 2-ethylhexyl.

Polyester Rubbers. The reaction of dimer acids with ethylene glycol to give polyesters and their curing to give rubber substitutes was studied extensively by a research team at the Northern Laboratory and their many cooperators (54,60). The Peoria scientists showed that dimer acid could be reacted with ethylene glycol, or an excess of ethylene glycol, to give sticky rubbery polyesters. If this polyester was cured with sulfur and/or rubber accelerators or if the polyesterification was carried to gelation and then cured with sulfur and rubber accelerators, a rubberlike product suitable for jar rings, grommets, and gaskets was obtained (53,54,57,60). Approx 2–3 M lb were used for this purpose in the U. S. in 1942–43.

By use of a technique that is now well-known Cowan and Wheeler (58,59) were able to react pure dimer acids with an excess of ethylene glycol to give superpolyesters. The later part of the reaction is definitely a glycolysis reaction wherein ethylene

TABLE IX

Effect of Dimer Polyesters on Viscosity and Cloud Point of Oils

Polymer from	Mol wt	Base oil	% Additive	Kinematic viscosity centistokes at		Viscosity index	Cloud test
				210F	100F		
Dimer esters and dimer glycols	13,200	Winkler	10	4.02	12.91	223	−65C
Dimer esters and dimer glycols	33,200	PRL 1801	4.5	4.18	12.29	241	−70 Cloudy
Dimer esters and ethylene glycol	8,910	Winkler	6	2.61	7.26	200	+13
Dimer acids and decamethylene glycol (84)	12,000	Winkler	12	17.65	52.29	163	......

TABLE X

Effect of Mol Wt of Dimer Polyester on Viscosity Index

Mol wt of polyester	% Polymer in oil	Viscosity (S.U.S.)		Viscosity index
		100F	210F	
......	0	158	45	116
5350	6	295	59.3	135
8400	6	374	68.3	137
9400	6	434	77.6	141

TABLE XI

Effect of Dimer Polyesters on Viscosity Index and Pour Points of a Mixture of 90% Light Lubricating Oil and 10% Paraffinic Bright Stocks

% of polyesters	Pour point, F	Viscosity index
0	+30	101
1	−20	127
5	0	145
1% + 1% of pour depressor	−30	127

glycol or its derivatives are removed from the reaction under reduced pressure and in the presence of an alcoholysis catalyst such as calcium oxide. The reaction may be visualized as shown in Figure 10 where n equals 1–4. If about 30 mole percent excess of ethylene glycol is used, n might average 2–5 before the acid value drops nearly to zero. By the continued glycolysis of polyester XIV and removal of ethylene glycol, polyesters with mol wt as high as an estimated 25,000 were achieved, i.e., where $x + 7 = 40$ to 43. Vulcanization with sulfur and rubber accelerators gave products comparable in many tests to Buna S at its stage of development in 1942. Wartime secrecy orders prevented publication of the work until later. The glycolysis reaction with ethylene glycol to prepare superpolyesters (mol wt > 10,000) was apparently discovered independently by three different groups; one group worked with terephthalic acid in England (94), another with sebacic and other acids at Bell Telephone Laboratories (68), and the third at Peoria.

The properties of these polyester rubbers are summarized in Table XII. Note that the linear polyester of highest mol wt gave the best rubberlike product. The effect of giving a cure with diisocyanate and subsequent vulcanization (Number 4) is compared with vulcanization of similar polyesters. This example was one of the early polyester-urethane rubbers. Number 3 was prepared in a jacketed mixer under reduced pressure, and Number 5 was cured with sulfur and accelerators before molding to give a millable produce suitable for molding.

Polyurethane Foams. Dimer polyesters proved to be superior or lower in cost to adipic polyesters for many uses, but polyether foams based on polyols from ethylene and propylene oxides are reported to have captured the major part of the market (44). Polyethers are more than 10% lower than dimer acid polyesters in cost of ingredients to make the starting polyols and the polyethers give nearly comparable foam densities and other properties. Dimer foams are reported to be superior in padding for clothing. Dimer polyesters have the following advantages over adipic polyesters: 1) lower loss of water for some mol wt of polyester, 2) less polyol required since dimer contains trimeric functionality and higher mol wt, 3) dimer polyester is compatible with diisocyanates, and 4) dimer acid reacts with polyols without loss of acid or polyol (61a). Characteristics of a typical polyester of low mol wt used to make urethane foams are:

Dimer acids	78.6% by wt (1 mole eq.)
Diethylene glycol	21.4% by wt (1.7 mole eq.)
Final acid value	1.8
Final hydroxyl value	74.0
Viscosity (25C) cp	13,000

A typical one-shot technique is: A mixture of lecithin, catalysts, and water is stirred until a clear solution is obtained. A polyester is added and mixed thoroughly for several min, then tolylene diisocyanate is added, rapidly mixed for several sec, and poured into a waxed mold. After 30 min, the mold is stripped away leaving the foam which can continue to cure at 70–75F overnight. Proportions of the reactants and resultant foam densities are given in Table XIII. The main reactions are shown in Figure 11. Diisocyanate reacts with the hydroxyl groups of the polyester to form a polyurethane XV. In the presence of water, a side reaction occurs to give an amine end to the growing chain and carbon dioxide for foaming XVI. The isocyanate reacts with the amine to give a substituted urea with an isocyanate ending XVII. It can react with water, polyester, or amine.

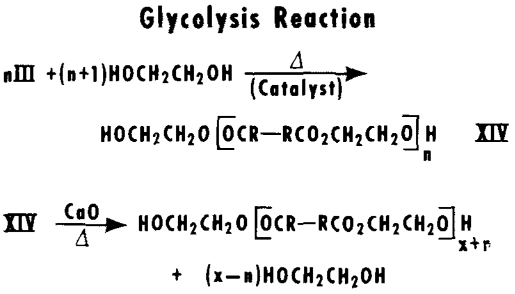


FIG. 10. Preparation of high molecular polyesters by a glycolysis reaction.

Alkyd Resins and Oil-Base Coatings. One of the first attempts to use dimer acid in protective coatings was its incorporation into synthetic oils, long oil alkyds, and into glycerol and pentaerythritol esters of soybean and linseed fatty acids modified with maleic anhydride (22,55). This work showed that dimer acids improved water and alkali resistance and drying rate. The advantages established by Goebel and Moore (69), who extended this earlier work to include a wide variety of alkyd resins and varnishes, may be summarized as:

Increased viscosity
Lengthened set-to-touch time (more uniform coatings)
Improved through-dry
Eliminated wrinkling and resoftening
Improved varnishes (better water and alkali resistance)
Better alkyds (improves flexibility)

TABLE XII

Polyester Rubbers from Dimer Acids and Ethylene Glycol

Polyester number	1	2	3	4	5
Dimer acids	Pure	Pure	35% Trimer	35% Trimer	35% Trimer
Polyester	Linear	Linear	Dry gel	Branched	Sticky gel
Est. mol wt	25,000	14,000	No. 5	4,600 Cured with diisocyanate	3,500 (?)
Tensile strength	2,100	2,200	850	890	320
Elongation	500	375	140	330	180
Tensile product	10,500	8,500	1,200	2,940	570

TABLE XIII
Foam Preparation

Ingredients	Parts by wt	Parts by wt
Polyester	1,000	1,000
Dabco	6.7	0
N-ethylmorpholine	0	67
Water	26.5	16.7
Tolylene diisocyanate	386	267
Lecithin	67 (?)	67
Foam density, lb/cu ft	1.75	4.0

Much other work has also been reported (50) including penetrating seals for wood (79).

Trimer Acids. Trimer acids react with epoxy derivatives to give flexible polyester resins with low dielectric const and with low loss and dissipation factors. Since a tertiary amine is used as a catalyst, it will continue to catalyze the reaction of the epoxy groups to form polyethers when less than the stoichiometric amounts of trimeric acids are used. Thus, a variety of polymeric products can be obtained (65b). Other epoxy products, such as epoxy soybean oil, have also been studied for their potential utility.

Polyamide Resins

The first work on polyamides was carried out by Carothers (101) and led to the commercial production of synthetic fiber, nylon. Carothers also extended his studies to include polyamides from mixtures of di- and tribasic acids. Bradley (100) extended this research to include mixtures of dimer and trimer acids. However, before Bradley's patent issued in 1945, workers at Peoria effected research and development studies that led to the commercial production and use of polyamide resins during and shortly after World War II. Some of the unique properties of polyamides were recognized early in 1941 and led to a series of patents and publications (103–105,108,121, 125,135). Although much of this work has proved valuable and helpful in commercial development of moisture-proof coatings, replacements for shellac, printing inks, and adhesives, the first continuing commercial use was for heat-sealing glassine paper (115). The ethylene diamine polyamide from soybean dimer acids (mixture of dimer and trimer) and ethylene diamine melts at 110–114C and adheres to most surfaces. Its sealing temp is among the lowest available in commercial resins that adhere to and seal glassine paper, and the resin does not easily stick to itself (block) under pressure at 150–160F. Thus, its first use was to heat-seal candy bars, particularly chocolate bars where low temp was important. Since that time, a number of companies have extensively studied the preparation and use of these polyamide resins.

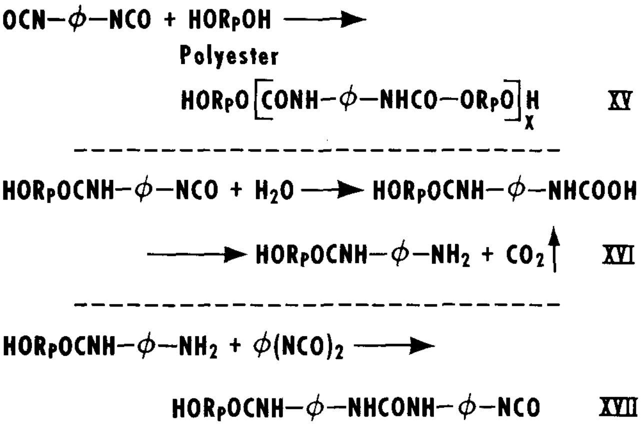


FIG. 11. Reaction of diisocyanates with polyesters and water.

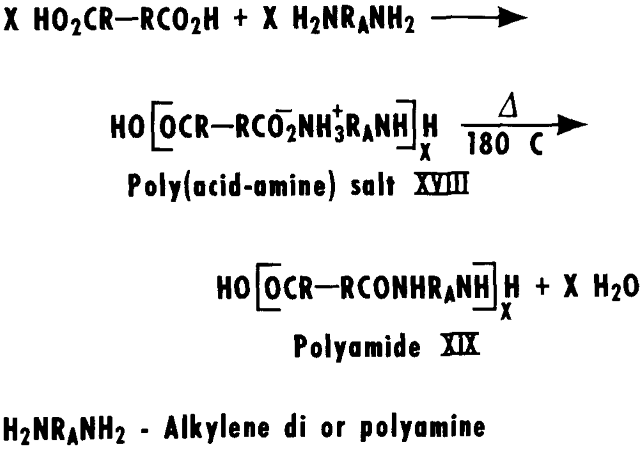


FIG. 12. Polyamide preparation through salt formation and subsequent dehydration.

Preparation. Polyamide resins are readily prepared from either dimer acids or esters. The diamine may be added dropwise to the hot dimer acid or ester in an apparatus for making resins (103,108). This method of addition permits ready removal of the water or alcohol formed. No large amount of volatile amine is added at any one time, and the volatile amine is readily retained. The diamine can be added all at once to the acid if proper equipment is available. The reaction may be written as in Figure 12. The dimer acid reacts with diamine to form a salt XVIII that loses water to give a polyamide XIX. By varying the amounts of dimer, trimer, and other dibasic acids, the composition thereof, and the amount and kind of di- or polyamine, a wide variety of products can be made. A partial list of these polymers and their melting ranges are shown in Table XIV. The properties of some commercially available products are shown in Table XV (113d,e). One other polyamide of low mp can be made from dimer diamine (130,135).

Solubility. Polyamide resins containing dimer acids exhibit somewhat unusual solubility properties. Whereas polyamides are usually only soluble in molten phenol, the dimer acid-ethylene diamine polyamide is soluble in isopropyl, butyl, and higher alcohols and in certain chlorinated hydrocarbons. It is not soluble in most other solvents ordinarily used. Its solubility apparently depends on the ability of the solvent to form hydrogen bonds. Alcoholic solutions permit the addition of hydrocarbon solvent and polyamide up to certain definite limits. When the amount of alcohol becomes lower than that necessary to hydrogen bond with the amide linkages, viscosities of the solution increase and a gel or precipitate forms,

TABLE XIV
Polyamides from Thermal Dimer Acids with Mixtures of Diamines and with Partial Replacement of Dimer Acids with Other Dibasic Acids

Diamine (mole ratio of diamines)	Other dibasic acid or diamine (mole ratio of dimer to other dibasic acid or of diamines)	Melting range C
$H_2N(CH_2CH_2NH)_2H$	$H_2N(CH_2)_6NH_2$ (1/1)	80–87
$H_2N(CH_2CH_2NH)_2H$	$H_2N(CH_2)_2NH_2$ (1/1)	75–81
$H_2N(CH_2CH_2NH)_2H$	$H_2N(CH_2CH_2NH)_3H$ (1/1)	43–48
$H_2NCH_2CH_2NH_2$	Sebacic (1/1)	188–196
$H_2NCH_2CH_2NH_2$	Sebacic (2/1)	164–175
$H_2NCH_2CH_2NH_2$	Sebacic (4/1)	146–155
$H_2NCH_2CH_2NH_2$	Sebacic (8/1)	122–129
$H_2NCH_2CH_2NH_2$	Maleic (4/1)	130–135

TABLE XV
Commercial Polyamide Resins

Type	Amine No.	Softening point, C	Viscosity, poises
Thermoplastic			
A 900	3–8	180–190	3–4 (200C)
B 930	3–8	105–115	30–45 (150C)
C 940	3–8	105–115	15–30
D 950	3–8	90–100	7–15
Reactive			
A 100	88	43–53	10 (150C)
B 115	216	43–53	35 (75C)
C 125	306	43–53	8
D 140	377	43–53	5

see Figure 13. Thus, when the alcoholic content of 35% polyamide solutions in butyl alcohol-toluene is dropped below 10% alcohol (curve 2), gelation will occur.

Let us assume that the alcohol forms a cyclic structure with amide linkages, through hydrogen bonds like XX in Figure 14 (103). Then, for every amide group, one equivalent of alcohol will be necessary for any given linkage to be soluble in the second solvent, such as toluene. The concentration of butyl alcohol necessary to maintain solution of polyamide resin in toluene is approx equivalent to the potential amide groupings. Each polymeric linkage contains two potential amide groups and has a mol wt of 584 (equivalent weight of 292). Each linkage should require 2 equivalents of alcohol for solvation. At a 10% concentration, or 0.09 equivalent of butyl alcohol or 0.11 equivalent of isopropyl alcohol, gelation occurs in 0.12 equivalent solution of polyamide resin.

The viscosities of the isopropyl alcohol-toluene and butyl alcohol-toluene solutions undergo rapid change when the concentration of alcohol drops below 20%. If, as in XX, the alcohol forms a cyclic structure with amide linkages, the nitrogen atom still retains electrons that can bridge with hydrogen. 20% concentration corresponds to 0.22 equivalent of isopropyl alcohol, 0.18 equivalent of butyl alcohol, and 0.24 equivalent of electron donor groups. The shape of the viscosity curve is indicative of an enormous change in solubility behavior, and the suggested hydrogen bonding of alcohols appears to be a satisfactory explanation. With petroleum hydrocarbons, which do not have high dilution rates, the polyamide resin formed gels at approx 20% alcohol content (Fig. 13, curve 1) or 2 equivalents/amide linkage. This gelation is also supporting evidence for the hydrogen bonding of polyamide resin with alcohols.

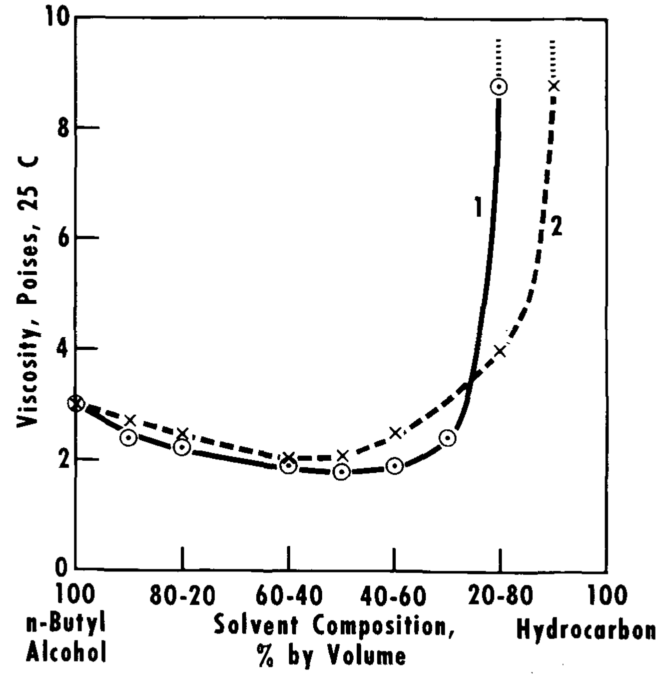
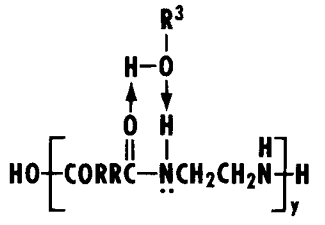


Fig. 13. Viscosity of a 35% polyamide solution at 25C with changes in composition of solvent where hydrocarbon was petroleum ether (Curve 1) or toluene (Curve 2).



XX

Fig. 14. Suggested hydrogen bonding in alcoholic solutions of polyamides.

Although insoluble in water, polyamide resins can be dispersed in water in the form of tiny discrete particles generally called suspensoids (133,138,139, 140). The particles can be given either a positive or negative charge to assist in making a continuous coating when they are spread onto paper, glassine, wood, or other support. The charge is imparted by the ions used in the dispersing agents. Thus, a cationic suspensoid can be changed to an anionic suspensoid by the addition of another dispersing agent. No solvents are necessary to make the suspensoids. Other components can be suspended in combination with the polyamide resin, such as toluene sulfonamides, paraffin wax, and hydrogenated resin esters (133).

Imidazoline Formation. Another facet of polyamide chemistry results when basic polyamides are heated at 285–315C. At these temp the basic amine group will react with the carbonyl of the carboxyl group as shown in Figure 15. At these high temp, a free amine group in an amide will react with the carbonyl of the amide to give an imidazoline. If a five or six numbered ring can form, it does so to give the imidazoline XXI. If the amide has formed at the

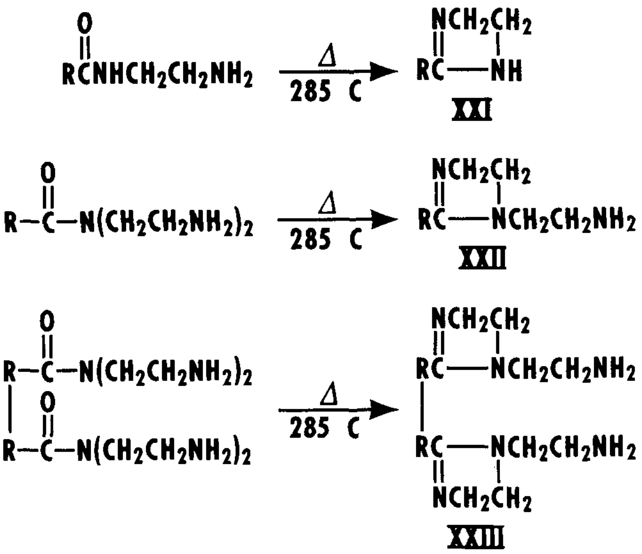


Fig. 15. Imidazoline formation in amides and polyamides.

TABLE XVI

Changes in Epoxy-Polyamide Resin with Increased Imidazoline Content of Polyamide Resins

Imidazoline in polyamide %	Brookfield viscosity Poises	Reaction proportions[a]	Properties	
			Heat distortion temp C	Flexured strength psi
42	675	30–70	59	9,400
61	565	30–70	64	8,900
61	565	40–60	64	10,000
71	285	30–70	72	8,900
71	281	40–60	56	8,000

[a] Reaction with epoxy resin, bisphenol A plus epichlorohydrin having epoxy equivalency of 185.

more basic of the amine groups of diethylenetriamine, an imidazoline ring will form but a free amine will remain, XXII. If the acids are dibasic, a difunctional amine forms XXIII. It can react with dimer acids to give a polyamide and with an epoxy resin to give a crosslinked resin.

If a triamine such as diethylenetriamine is used, a free amino group still remains and is reactive toward epoxy resins and other resins (129). As the imidazoline content increases, the viscosity of the polyamide decreases, the heat distortion temp of the resultant epoxy-cured-resin increases, and the flexural strength is changed as shown in Table XVI. The lower viscosity of the imidazoline derivative permits greater latitude in formulation. Less viscous polyamides can be used to mix with the epoxy resins to give more suitable and more uniform products.

Compatibility. Polyamide resins are compatible with a wide variety of commercially available resins and plasticizers from Acryloid A-10 to Zirex, and Abolyn to zinc stearate. In general, they are compatible with alkyds, bodied oils, phenolics, rosin esters, epoxy resins, phenol modified coumarone-indene, and polystyrene. Of course, any generalization regarding compatibility has to be qualified since under special conditions and with modified products compatibilities will vary. For specile information, you are referred to the manufacturer's bulletin (113b). If your needs go beyond this detailed information, you might wish to consult the supplier or experimentally determine compatibility. The supplier's charts show primarily compatibilities at 10, 50, and 90% polyamide, and, thus, represent limits only. For example, the best composition for shellac of 30% polyamide resins (124) is not shown, but the charts can be very useful to anyone working with these resins.

Uses of Polyamide Resins

Polyamide resins have unusual adhesion, resistance to corrosion, flexibility, chemical resistance, and other properties that can be enhanced by reaction with epoxy compounds and resins. Thus, polyamides can be used alone or in combination with epoxys depending on the specific properties desired. Protective coatings for a variety of materials (102,104,106,107, 110,112,114,119,120,121,124,126,132) is a primary market. Other uses include structural adhesives for autobody repair (111) and other items (107,128), sealers for cans (116), masking tapes (118,122), additives for corrosion resistance (121,135), control of shrinkage of wool (99), and nongelling inks (113c, 141).

Thixotropic Paints. A polyamide resin, such as one of the thermoplastics, can be used to prepare thixotropic paints. By proper heating with a bodied oil, alkyd resin, or other resinous product containing ester groups, a thixotropic additive is obtained (137). The basic groups of the polyamide react with the ester or acid groups in an alkyd resin or varnish to give a gel-forming resin. By varying the proportions of this additive in the paint and the amount of polyamide used in making the additive, "gel" paints of varying thixotrophy can be obtained. The polyamide-ester gel can be used in amounts of 10–50% of the total vehicle. These paints are known as the no drip, no spot, no splatter paints (102). These paints have been marketed in the U.S., Australia, Canada, England, and other countries.

Polyamide-Epoxy Resins. Although polyamide resins have found some utility in surface coatings and adhesives without modification, the reactive resins and their combination with epoxy resins have given versatility and superiority in many uses (106, 107,110,113e–h,116,118–120,122,123,126,127,128,131). In the curing of epoxy resins, a polyamine is used as a catalyst, a crosslinking agent, and an integral part of the final resinous product. The reactive polyamides are condensation products of an excess of polyamine, such as diethylene triamine and dimer acids, and contain variable amounts of amine groups. The epoxy resin (diepoxide) reacts with the amine groups in the polyamide resin in a manner similar to the scheme shown in Figure 16. The resulting product XXIV has both amine and alcohol groups and the remaining epoxy groups can react with either the amine or alcohol group to give a crosslinked polymer XXV depending on the functionality of the polyamide and the proportions of reactants used. Some amine groups are retained and continue to act as catalyst and as a corrosion inhibiting group in the finished resin (70,121). Such combinations are useful in casting and laminating; structural adhesives; patching and sealing compounds; and protective decorative coatings.

For specific applications, reference to the bulletins available from suppliers of polyamide and epoxy resins is suggested. A partial list is found in references 113b–h.

Coatings from Polyamide-Epoxy Resins. Gloss retention of epoxy-polyamide coatings is good and is superior to most amine-cured epoxy resin coatings. Solventless coatings can be obtained by using a liquid polyamide such as reactive polyamide D and a liquid epoxy resin. These combinations of epoxy-polyamide resins are used for a wide variety of coatings such as maintenance coatings for metals wherein the basic polyamides are also corrosion inhibitors (106) primers for metal (110); enamels for metals, plastics and wood; clear varnishes for marine use; and pipe

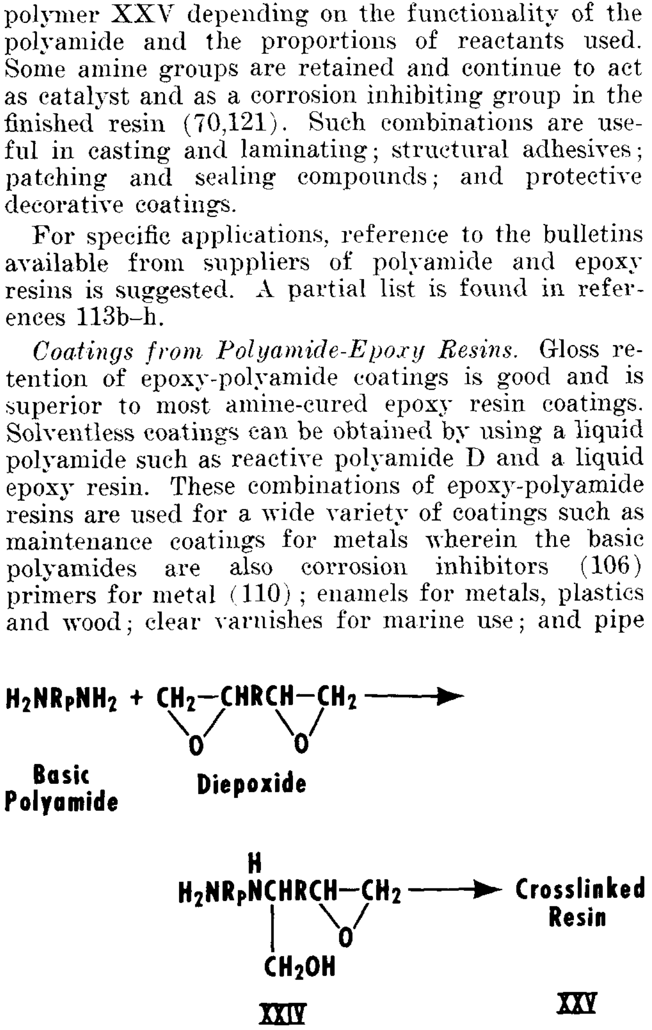


FIG. 16. Basic polyamide reaction with epoxy resins or compounds to give a crosslinked product.

masonry, paper, cellophane, Mylar, and glassine coatings.

Five-year exposure tests and use have shown that these epoxy-polyamide resin coatings have unusual resistance to corrosion to salt spray, to chemical fumes particularly acid, and to tide water exposures where electrolytic action gives alkaline reactions. Even without corrosion inhibiting pigments, the epoxy-polyamide resins give almost as good performances as with them. Thus, the polyamide resins aid as a corrosion inhibitor. Surfaces of several epoxy-polyamide white enamels showed no checking, apparent erosion, or rusting after five years of exposure (114). Genamides are also useful in coatings (112,113h).

Both clear and pigmented coatings can be prepared based on epoxy-polyamide compositions.

Concrete Topping. The patching, repairing, and resurfacing of concrete has always been a troublesome and difficult operation. By use of sand-filled epoxy-polyamide resin blends, such operations can be done readily. Tenacious bonds are formed in layers as thin as $\frac{1}{16}$ in. to $\frac{1}{4}$ in. thick even to uncured or damp concrete (134). Old floors that are not powdered but are cracked can be made like new by adding only $\frac{1}{16}$ in. to $\frac{1}{8}$ in. of polyamide epoxides combined with sand or other filler. Equipment need not be removed. Rapid repair of highways in warm weather (70F or above) is also very effective.

Casting and Laminating Resins. Reactive resins C and D are also useful in casting and laminating for tools, dies, etc. (113f,g,129). By using a proper mold-release agent, such as polyethylene or silicone greases, dies and tools can be readily made. The life of such dies is less than many metallic dies, but they are much cheaper to fabricate if only a limited number of parts are needed. Tools and repairs made with epoxy-polyamide resins have unusual strength and durability. Since the imidazolines are less viscous than most of the reactive polyamides, they may have advantages in laminating as well as other uses. Genamides (113h) have lower viscosities.

Effect of Ingested Products—Toxicity (?)

In the past 20 years, considerable research has been carried out on the nutritional aspects of fats. This work has included studies on the adduct-forming, the nonadduct-forming monomeric, and the polymeric fatty acids present in heat-polymerized soybean, linseed, and safflower oils. Crampton et al. (13,14) showed that nonadduct-forming monomers from the ethyl esters of heat-polymerized linseed oil killed rats when fed at 10 and 20% levels in the diet. Polymeric esters from linseed oil retarded growth. With polymerized soybean esters, the polymeric fraction killed most of the rats fed at 10 and 20% levels. The same fractions from sunflower oil did not prove toxic, but fractions at the 10 and 20% levels adversely affected growth. More recently, Bottino (6) reported that polymeric esters from methyl linoleate were weakly toxic but that their effects could be counteracted by the addition of a good quality vegetable oil. Bottino also studied absorptions showing that the polymeric fatty esters were absorbed to a much lesser extent than the adduct- or nonadduct-forming esters.

The presence of nonadduct-forming esters in heat-polymerized linoleate had been reported by others (29). Undoubtedly, heat polymerization produces toxic products and evidence is convincing that the nonadduct-forming monomers are toxic. However, the failure of these workers to examine their polymeric fractions carefully for nonadduct-forming monomers suggests the polymeric fractions may not be toxic at all. We have seen earlier that dimer acid may contain from 1–10% of monomeric materials (24). Since the nonadduct-forming esters are higher boiling than the adduct-forming esters, it is most likely that Crampton's and Bottino's polymeric fatty acids contained appreciable amounts of the nonadduct-forming fatty acids and gave more adverse reactions than expected. More work is certainly needed to establish the relative toxicity of these two fractions.

According to reports published by one manufacturer of polyamide resins, resins similar to the thermoplastic resins described in Table XVI were nontoxic to rabbits at high levels of dosage (113a). A resin similar to resin C was tested and was relatively nontoxic by the oral or skin route in albino rats and rabbits, respectively. The mean lethal dose was greater than 8.0 g/kg. A mild redness occurred on the skin of the rabbits at the exposure site, but no signs of toxicity appeared.

Summary

Dimer acids are products formed by the combination of two molecules of unsaturated fatty acids, such as oleic or linoleic. They have properties that are unique among commercial and other dibasic acids, and they impart unusual properties to their derivatives. Dimer acids are good corrosion inhibitors for petroleum products and impart this property to some derivatives. Their salts, simple esters, and polyesters improve the lubricating properties of hydraulic fluids, turbine, motor, and others oils and greases. Alkyd resins and varnishes containing dimer acids have better flexibility, more controlled drying, and superior water and alkali resistance. Dimer acid-polyamide resins are widely used as heat-sealing adhesives and as components of special epoxy-resin combinations.

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