as well as to differences in electron density. The distribution of *cis* and *trans* bonds in the conjugated system not only influences the isomers obtained in the Diels-Alder reaction but also the rate of reaction (Fig. 13).

Diels-Alder reactions of conjugated octadecadienoic acids from other sources have been described with ethylene, isoprene and other dienes, nitroethylene and β-nitrostyrene, α, β-unsaturated acids and maleic anhydride.

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The Chemistry of Dibasic and Polybasic Fatty Acids

R.W. JOHNSON, Union Camp Corporation, Chemical Products Division, PO Box 2668,
Savannah, GA 31402

ABSTRACT

Current processes to produce dibasic and polybasic fatty acids including azelaic, sebacic, dodecanedioic, C_{21} diacid, fatty dimer and trimer acids are discussed. A number of alternative routes to produce azelaic, sebacic and fatty dimers are also discussed, including the preparation of azelaic and sebacic acids from butadiene and sebacic acid from adipic acid. Physical properties of the various dibasic acids are compared. Preparation of important derivatives and their applications is discussed, including: (a) esters and polyesters as vinyl plasticizers and as base stocks for synthetic lubricants; (b) polyamide resins in coatings, fibers, inks and adhesives; (c) salts as surfactants; and (d) amido amines and imidazolines as corrosion inhibitors. Dimer acids have found application in the petroleum industry as drilling mud thickeners in oil recovery.

INTRODUCTION

State-of-the art technology is presented on dibasic and polybasic fatty acids including azelaic acid, sebacic acid, dodecanedioic acid, C_{21} dicarboxylic acid and dimer acids. These higher molecular weight dibasic acids are well established and are important in many commercial applications today. Each of these five dibasic acids are produced in multimillion pound quantities. Only one of the five, dodecanedioic acid, is produced from nonrenewable resources.

Azelaic acid is produced commercially by Emery in Cincinnati, Ohio, and by Unichema in Gouda, The Netherlands. The process used is based on ozonolysis of oleic acid followed by the decomposition of the ozonide with oxygen. Oleic acid is mixed with pelargonic acid which functions as a solvent. This mixture is fed into an ozone absorber countercurrently in relation to a continuous flow of oxygen gas containing ca. 2% ozone. A reaction temperature of 25-45 C is maintained through external cooling. The ozonized oleic acid is then fed continuously into reactors at ca. 100 C where it is decomposed and oxidized as rapidly as possible.

The mixed oxidation products are then fed to a still where the pelargonic and other low boiling acids are removed as overhead while the heavy material is removed as residue. The sidestream contains azelaic acid and other acids which boil in the same temperature range. This sidestream product is treated with hot water to dissolve the azelaic acid and remove it from the water-insoluble acids such as palmitic and stearic acids. The azelaic acid is recovered by removing the water in an evaporator or through crystallization (1,2).

A generalized scheme showing reactions believed to occur during ozonolysis is shown in Figure 1. The first step in ozonolysis is thought to be the formation of a complex which rearranges to the 1,2,3-trioxolane or the initial ozonide. This ozonide is unstable and rearranges to a carbonyl fragment and a zwitterion. Recombination of these cleavage intermediates leads to the final ozonolysis product, 1,2,4-trioxolane. Oxidation of this final ozonide with molecular oxygen gives two carboxylic acids, azelaic and pelargonic acids (3-5).

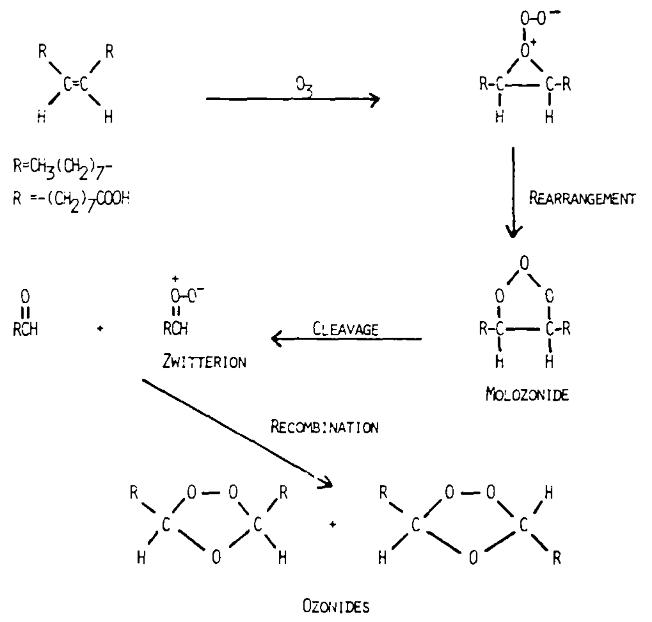

FIG. 1. Generalized ozonolysis mechanism.

Properties of Emerox commercial azelaic acids are shown in Table I. Emerox 1110 is the lowest purity grade produced and finds application where high purity is not essential, such as in plasticizers. Emerox 1144 is the highest purity grade offered and is used in making high molecular weight polymers. Further applications will be given later in the paper.

Alternative routes to cleavage with ozone have been reported in the literature and include: chromic acid (6), potassium permanganate (7), nitric acid (8), ruthenium tetroxide (9), dihydroxylation followed by caustic fusion (10), or cobalt catalyzed air oxidation (11), or nitric acid oxidation (12). None of these methods are commercial because of either economics or the lower purity azelaic acid that is obtained.

Another alternative route, shown in Figure 2, is based on the dimerization of butadiene to 1,5-cyclooctadiene followed by carbonylation to a monoester in the presence of an alcohol. Simple hydrolysis of the ester followed by a caustic cleavage step reportedly produced azelaic acid in high yield and purity (13).

Sebacic acid is produced commercially by Union Camp in Dover, Ohio, and by Hokoku Oil Company in Japan. It has been reported that sebacic acid is also being made commercially in China. The process currently used is based on caustic oxidation of castor oil or ricinoleic acid in either a batch or continuous process. The castor oil or ricinoleic acid and caustic are fed to a reactor at a temperature of 180-270 C (14) where the ricinoleic acid undergoes a series of reactions to give disodium sebacate and capryl alcohol. After reaction is complete, the soaps are then put into solution and acidified to a pH of ca. 6. At this pH, all the soaps of monobasic acids are converted to free acids which are insoluble in water. The disodium sebacate is converted to the half acid salt which is water-soluble. The layers are separated and the pH is lowered to ca. 2, resulting in the sebacic acid precipitating out of solution. It is then filtered, washed and dried.

Weedon has proposed a mechanism shown in Figure 3 for the conversion of ricinoleic acid to sebacic acid (15). The first step in the proposed mechanism is dehydrogenation to give a keto acid. In alkaline media, β,γ-unsaturated carbonyl compounds readily undergo isomerization to α,β-unsaturated carbonyl compounds. Fission by a reaction of the "retro-aldol" type then should give a saturated ketone and an ω-aldehydo acid. The ω-aldehydo acid, in the presence of strong alkali at elevated temperature, would undergo an irreversible oxidation to the carboxylic acid. Properties of commercial sebacic acid are shown in Table I.

Some process improvements have been described in the patent literature and include the use of white mineral oil having a boiling range of 300-400 C (16) or the use of a mixture of cresols (17). Both of these materials act to reduce the reaction mixture's viscosity. A number of catalysts have been described which claim to give higher sebacic acid yields: cadmium salts (18), barium salts (19), lead oxide or salts (20), sodium nitrate (21) and zinc oxide (22).

Alternative methods to prepare sebacic acid from petrochemical-based feeds have been described. An electrooxidation process was developed by Asahi Chemical Industry in Japan and produces high purity sebacic acid from readily available adipic acid. The process consists of 3 steps, beginning with partial esterification of adipic acid to monomethyl adipate, followed by electrolysis of the potassium salt in a mixture of methanol and water. The last step is hydrolysis of the dimethyl sebacate to sebacic acid. Overall yields are reported to be ca. 85% (23).

Dodecanedioic acid (DDDA) is produced commercially by Du Pont in Victoria, Texas, and by Chemische Werk Huls in Germany. It is the only dibasic acid described in

TABLE I

Properties of Commercial Dibasic Acids C_9, C_{10} and C_{12}

Acid	Azelaic (Emerox)			Sebacic	Dodecanedioic
Grade	1110	1133	1144	Union Camp purified	Du Pont
Melting Point (C)	96-103	96-101	101-102	132-134	129-131
Composition (%)					
C_9 Dibasic	79.0	82.0	90.0	–	–
C_{10} Dibasic	–	–	–	94.0	–
C_{11} Dibasic	–	–	–	3.5	–
C_{12} Dibasic	–	–	–	2.5	99.0
$<C_9$ Dibasic	11.0	9.5	1.0	–	–
$>C_9$ Dibasic	9.0	8.0	9.0	100.0	–
Other dibasics	–	–	–	–	1.0
Monobasic	1.0	0.5	nil	nil	0.1
Decarboxylation temperature (C)	–	–	330	360	–
Solubility in H_2O					
@ 20 C (wt %)	–	–	0.2	0.1	0.003
@ 60 C	–	–	2.7	0.36	0.04

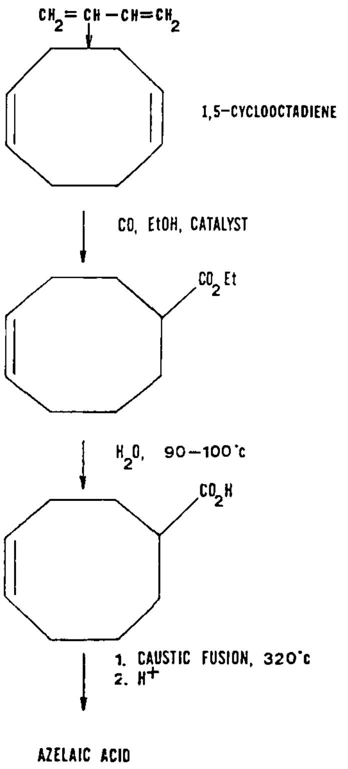

FIG. 2. Azelaic acid from butadiene.

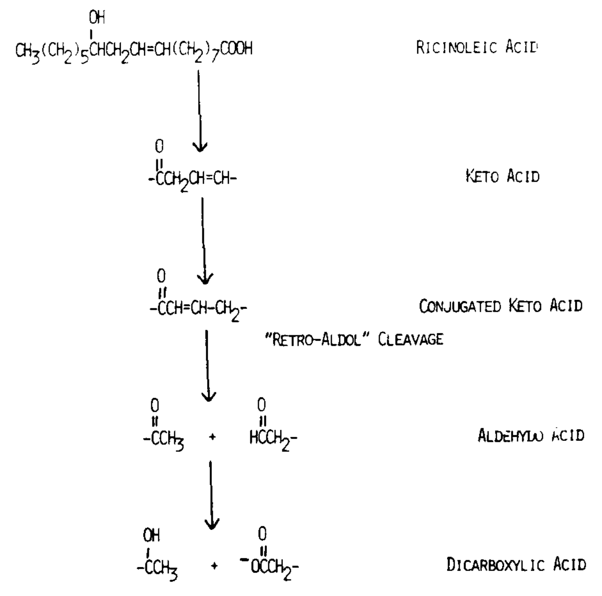

FIG. 3. Proposed mechanism for conversion of ricinoleic acid to sebacic acid.

TABLE II

Properties of C_{21} Dibasic Acid

	Westvaco diacid 1550
Acid value	272-278
Saponification value	300-308
Color, Gardner	8
Monobasic acid (%)	10-12
Viscosity (cps @ 100 F)	5000
C_{21} Dibasic acids (%)	88-90

this paper that is based on a nonrenewable resource. The feed is butadiene which is converted to cyclododecatriene using a nickel catalyst. The triene is hydrogenated to cyclododecane which is then oxidized with air to a mixture of cyclododecanone and cyclododecanol. This mixture is further oxidized with nitric acid to give dodecanedioic acid (24). This sequence is similar to the well known method of producing adipic acid from cyclohexane and will not be further elaborated here. Properties of commercial dodecanedioic acid are shown in Table I and can be compared to the other straight chain dicarboxylic acids.

C_{21} Dicarboxylic acid is produced by Westvaco in Charleston, South Carolina. The process involves treating tall oil fatty acids (TOFA) (containing ca. 50% oleic acid and 50% linoleic) with acrylic acid and iodine at 220-250 C for ca. 2 hr. The function of the iodine apparently is to conjugate the double bond in linoleic acid, after which the acrylic acid adds via Diels-Alder type reaction to form the cyclic reaction product. After the reaction is complete, the unreacted oleic acid is removed by distillation and the crude C_{21} diacid can be further purified by thin film distillation or molecular distillation (25). Properties of C_{21} diacid are shown in Table II.

Dimer acids are made by seven producers in the United States: A-Z Corp., Chemtall (formerly Riceboro Chemical Co.), Emery Industries (National Distillers), Henkel (formerly General Mills), Humko Sheffield (Witco), Sylvachem (formerly Crosby Chemical Co.), and Union Camp Corp. Most of the dimer acids made today are produced from tall oil fatty acids; however, a small amount is produced from oleic acid and from dehydrated castor oil. The process involves heating a mixture of fatty acids, a clay catalyst and water at a temperature of ca. 220-280 C, under pressure, for several hours. The reaction mixture is then cooled to ca. 125 C, phosphoric acid added to complex the metal ions leached from the clay, and then filtered. The crude dimer contains ca. 40% "monomer" acids which are removed by distillation using a simple type still or a wiped film evaporator (26).

The dimerization reaction can best be explained through a carbonium ion mechanism: double bond isomerization, acid-catalyzed dimerization and chain branching, Diels-Alder cyclization, and hydrogen transfer. Oleic and elaidic acids give significant amounts of acyclic dimer, whereas linoleic acid gives primarily monocyclic and polycyclic dimers with only small amounts of acyclic dimer (27).

Other methods to produce dimer and trimer acids involve thermal polymerization (28), strong acids (29) and free radical catalysts (30). Tetracarboxylic acids and higher have been prepared from dimer acids using a peroxide catalyst (31). Properties of commercial dimer acids are shown in Table III.

APPLICATIONS

The C_9, C_{10} and C_{12} dibasic acids have similar uses, among which are: (a) monomeric and polymeric plasticizers for polyvinyl chloride; (b) diesters for engine lubricants; and (c) polymer intermediates for polyamides, polyester and polyurethane adhesives, coatings, fibers, inks and resins.

The monomeric plasticizers of commercial importance are usually made from butyl, hexyl, 2-ethylhexyl or octyl alcohol and are very efficient, low-temperature plasticizers.

The esters of C_9, C_{10} and C_{12} dibasic acids can be interchanged in many applications and depending on processing and environmental conditions, one might be preferred over another. All are considerably less water-sensitive than the adipates, in addition to being less volatile. As the alkyl group becomes larger, e.g., in going from butyl to octyl, the

TABLE III

Properties of Commercial Dimer Acids

	Standard dimer	Low monomer	Distilled dimer	Trimer
Emery	E 1022	E 1018	E 1014	E 1040
Humko	H 3675	H 3680	H 3695	H 5460
Union Camp	U 22	U 18	U 14	U 60
Property				
Acid value	190-196	190-196	192-198	175-192
Saponification value	191-199	192-198	197-201	192-200
Color, Gardner 1963 (max)	8-9	8	5	–
Monobasic acid (%)	3	<1	0.2-1.5	trace
Dimer acid (%)	75	83	93.5-97	40
Trimer acid (%)	22	17	3-5	60

TABLE IV

Comparison of *bis*-(2-Ethylhexyl) Dibasic Acid Performance in 1-mm Thick PVC Sheet

Dibasic acid	Volatility, plasticizer loss[a] (wt %)	Low temperature flex (T_F, C)	Water extraction loss[b] (wt %)	Kerosene extraction loss[c] (wt %)
Adipic	13.9	−66	0.1	>70
Azelaic	5.7	−67	0.06	73
Sebacic	4.2	−69	0.02	70

[a] 24 hr @ 87 C.
[b] 24 hr @ 50 C.
[c] 24 hr @ 23 C.

plasticizing efficiency decreases slightly while the low-temperature properties improve somewhat. A comparison of the 2-ethylhexyl esters of adipic, azelaic and sebacic acids are shown in Table IV. The volatility and the water extraction loss of the plasticizer decreases as the chain length of the dibasic acid increases. The low temperature flexes on all three plasticizers are outstanding, ca. −68 C. The kerosene extraction loss, however, is very high and for this reason, monomeric plasticizers are generally not used in nonaqueous solvent systems. Since the monomeric plasticizers have good low water extraction and exhibit excellent low-temperature properties, they are used as plasticizers for PVC in items such as raincoats and shoes and in garden hoses.

Dibutyl sebacate and di-*n*-hexyl azelate have been approved for use in plastics directly in contact with food, e.g., in polyvinyl chloride food wraps. Dibenzyl sebacate, because of its aromatic characteristics, is superior in oil and solvent resistance but inferior to the alkyl sebacates in low-temperature properties. It has found application in buna-N-type printing roll rubbers because of its resistance to printing ink solvents (32).

Because of cost and compatibility limits of the monomerics from C_9, C_{10} and C_{12}, they are usually used with other plasticizers such as dioctyl phthalate for best overall results.

Polymeric plasticizers have molecular weights from ca. 500 to over 3000 and are usually highly viscous materials in comparison to the monomerics. The polymeric plasticizers are less efficient and have poorer low-temperature characteristics than the monomerics. However, the polymerics have better resistance to oils and solvents, lower volatility and generally less migration. Polymeric plasticizers are prepared from the C_9, C_{10} or C_{12} dibasic acids and glycols, usually 1,2-propylene or 1,3-butylene, and a monofunctional alcohol or acid. Adipic acid is used in some formulations to lower costs. A small excess of glycol is normally used in preparing the polymerics, resulting in terminal hydroxyl groups. This improves the compatibility of the polymeric plasticizer. Termination with fatty acids or monohydric alcohols allow one to achieve the properties desired in these polymeric plasticizers (32).

Ester-based synthetic lubricants based on C_9, C_{10} and C_{12} dibasic acids show a number of advantages when compared with conventional petroleum lubricants. They exhibit extremely good viscosity/temperature relationships, have higher flash points, low viscosity rise during oxidation, excellent lubricity, low coking, low peroxide values and good additive response. The dioctyl, didecyl and ditridecyl esters of C_9, C_{10} and C_{12} dibasic acids are good examples of ester-based lubricants and are used primarily in aircraft turbine engines (33).

The other major use area for C_9, C_{10} and C_{12} dibasic acids is in polymer intermediates. They are used in making 6/9, 6/10 and 6/12 nylons. Some of their physical properties are shown in Table V. Nylons are used in fibers, monofilaments, wire coatings, and extruded and molded articles where a better moisture resistance over conventional 6/6 nylon is required. Quiana, a Du Pont synthetic fiber, is reportedly made from C_{12} dibasic acid and *bis*(4-aminocyclohexyl) methane (34). Azelaic and sebacic acids are used as modifiers in dimer-based polyamides where higher melting resins with high tensile strengths are required. These dibasic acids are also used as modifiers in polyethylene terephthalate systems (Mylar) to obtain specific polymer properties such as melting point, flexibility and improved dye receptivity for end uses in adhesives, films and fibers.

Hydroxyl terminated polyesters based on C_9, C_{10} and C_{12} dibasic acids and glycols can be used for the preparation of polyurethane elastomers. Applications for such materials include fabric coatings, spandex fibers and specialty films (33).

TABLE V

Properties of Nylons

	6/6	6/9	6/10	6/12
Specific gravity	1.14	1.09	1.09	1.07
Water absorption (%)				
24 hr	1.5	0.5	0.4	0.5
Saturation	9.5	4.5	3.5	3.0
Melting point (C)	265	205	222	217
Tensile strength (k Pa*)	8.3 X 10^4	5.5 X 10^4	5.9 X 10^4	5.5 X10^4
Elongation at break (%)	40-80	125	50-200	150

C_{21} Dibasic Acids

The C_{21} dibasic acids are used primarily in surfactants but they also have uses as modifiers in polyamide resins.

The reactivity of one of the carboxyl groups in C_{21} dibasic acid is different from the other as one is a primary carboxyl, whereas the other is a secondary carboxyl. This difference in reactivity can be demonstrated in a titration curve in the reaction of C_{21} dibasic acid with potassium hydroxide as shown in Figure 4. The more acidic primary carboxyl group has a pKa of 6.4 and the secondary carboxyl group, complete solubility of C_{21} dibasic acid takes place, thus allowing for preparation of nearly neutral salts.

The water solubilities of C_{21} dibasic acid salts are unique. A comparison of the viscosity/concentration characteristics of C_{21} dibasic acid salts with oleic and coconut acid soaps are shown in Figure 5. Note that the salts of C_{21} dibasic acid are lower in viscosity at higher solids content than those of the monobasic acids. It is also to be noted that the potassium salt of C_{21} dibasic acid can be prepared as aqueous solutions and easily handled up to 92% solids and the sodium salt up to 80% solids (35).

Salts of C_{21} dibasic acid are excellent hydrotropes and assist in solubilizing other substances into aqueous systems where these substances are usually insoluble or in solubilizing nonionics and anionic surfactants in high electrolyte systems. They are insensitive to ions in hard water and often provide stability without the cost of adding sequestering agents. Salts of C_{21} dibasic acids also have the ability to improve both the rate of foaming and volume of foam produced when used with potassium oleate in emulsified styrene-butadiene latex for making foam rubber. It has been shown that C_{21} dibasic acid salts in nonionic systems always give faster wetting speeds than SXS/nonionic systems at any level of total surfactant activity. This is significant because it shows that soil removal actually begins at lower levels of surfactant concentrations in the C_{21} dibasic acid system (36). Finally, polyamides prepared from C_{21} dibasic acid have found limited use in areas where dimer-based polyamides are currently used. Polyamide ink resins made from C_{21} dibasic acid are reported to be nearly identical to those produced from dimer acids except in gellation tendencies where the C_{21} dibasic acid based material is superior (37).

Dimer Acids

The most important use of dimer acids is in the production of polyamide resins. These resins are prepared from dimer and trimer acids by condensation with a large variety of diamines, including aliphatic and aromatic diamines, heterocyclic diamines and polyamines. Dimer acid and ethylenediamine give a polyamide having a melting range of 90-110 C. Higher melting points are obtained by using shorter chain dibasic acids, e.g., adipic, azelaic or sebacic acids, in the polyamide formulation. Monofunctional reactants are used to modify the properties of the polyamide resin and include fatty acids, amines and alcohols. These materials are useful in modifying certain physical properties such as viscosity, solubility characteristics and gel tendencies.

Polyamides based on dimer acids fall into two basic categories, nonreactive or "neutral" polyamides and reactive polyamides. The "neutral" polyamides are prepared from diamines and usually have relatively sharp melting points.

Their major applications are in printing inks, hot-melt adhesives and in coatings. Reactive polyamides are prepared from polyamines and are usually viscous liquids. Their

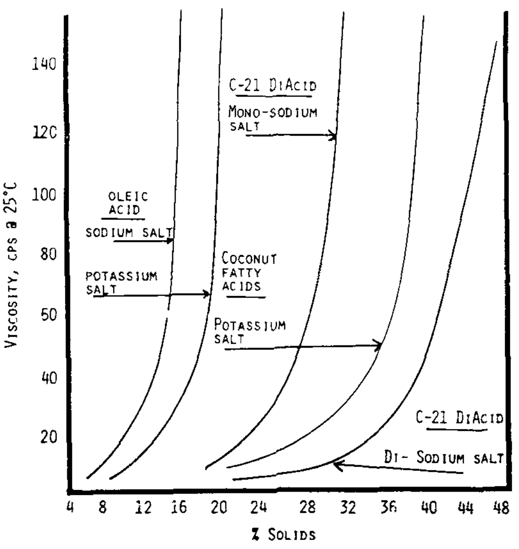

FIG. 4. Titration curve of C_{21} dibasic acid.

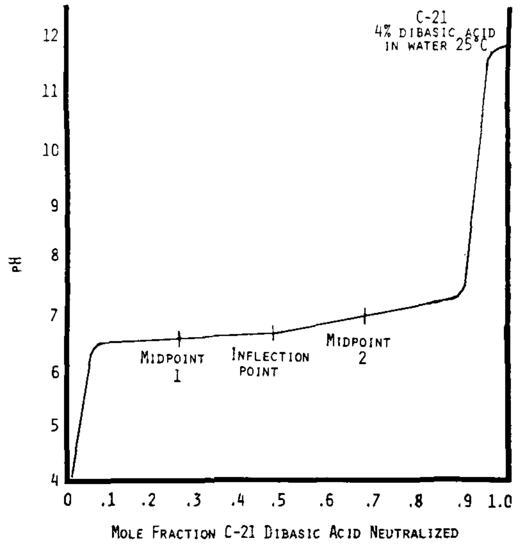

FIG. 5. Viscosity/concentration relationships of fatty acid salts.

applications are as curing agents for epoxy resins which are used as thermosetting surface coatings, adhesives and potting and casting resins.

"Neutral" polyamide resins are used in flexographic printing inks. Flexographic printing is a rotary, letterpress printing process employing fast drying inks and flexible rubber printing plates or rollers. Dimer-based polyamide resins are especially suited for printing on plastic films and metallic foil laminates because the resins adhere well to the substrate. These resins can be formulated to give an ink with a high gloss, excellent adhesion, good alcohol dilution, low gelation, good drying and low odor properties. Preferred solvents for flexographic printing inks are low molecular weight alcohols since these alcohols do not attack the rubber plates and they evaporate rapidly, allowing high speed printing. A number of patents have issued describing formulations to prepare polyamide resins having the necessary alcohol solubility as well as other desired properties mentioned above. Recently, patents have issued describing water-reducible polyamide resins systems. Advantages of using water in such systems are: water is less expensive than an organic solvent, does not pollute the atmosphere, is nonflammable, is readily available, and is nontoxic (38).

Another large use for neutral polyamide resins is in hot-melt adhesives. These dimer-based adhesives are used in the shoe industry because their excellent adhesion bonds the shoe soles to the upper parts without having to stitch with thread. The resin is applied in liquid form and adhesion occurs almost immediately on application, and on cooling, a strong adhesive bond is formed. Other uses are as side-seam sealants in the formation of cans, thus eliminating the need for soldering. Polyamide based hot-melts are also used in laminating metal films and various plastics.

Other uses for "neutral" polyamide resins include the preparation of thixotropic coatings, water-based glues for household use, antistatic agents for textiles, detergents and in making transparent candles (39-43).

Reactive polyamide resins are made from dimer and polyamines such as diethylenetriamine (DETA), triethylenetetramine (TETA) and pentaethylenehexamine (PEHA). The resins thus formed are capable of undergoing further reaction and are used as curing agents for epoxy resins. The use of dimer-based polyamide curing agents imparts adhesion, flexibility, chemical resistance, toughness, moisture resistance and surface gloss to epoxy resins.

Dimer acids are also used to prepare polyesters which have found application in fibers (44), synthetic lubricants (45), coatings (46), and in alkyd resins (47).

Esters prepared from dimer acids and monofunctional alcohols have found use as lubricants and lubricant additives (48), textile-dyeing assistants in fibers (49) and PVC plasticizers (50).

Finally, dimer acids, per se, have found application as corrosion inhibitors in the petroleum industry. In addition, a potential multimillion pound use for dimer acid is described in a patent in which dimer is used in a gasoline antiknock package (51).

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