

many potential uses in the manufacture of such other products as lubricant additives, waxes, and wetting and emulsifying agents. Markets for these fatty alcohols depend upon the results of application research and product development.

### Acknowledgment

The author wishes to express his gratitude to E. F. Hill and E. C. Steinle for their many contributions in the writing of this paper.

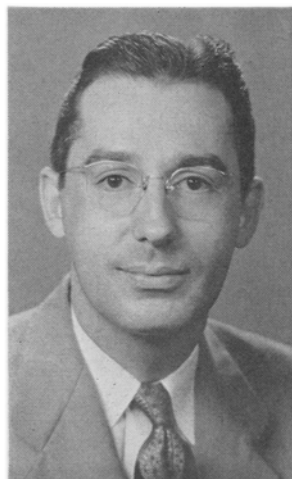
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## Dibasic Acids

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IN CONSIDERING fats and oils as raw material for chemical processing, we find that the production of dibasic acids is an important part of this subject. Sebacic acid, a straight-chain 10-carbon acid, was the first dibasic acid produced from a fat or oil source to become commercially significant. The treatment of castor oil with alkali now accounts for the production of about 20 million lb. of sebacic acid per year. More recently azelaic acid, a straight-chain 9-carbon acid, went into commercial production. Azelaic acid is produced by the oxidative cleavage of oleic acid at its double bond by means of chromic acid or ozone. The third dibasic acid produced commercially from a fat or oil source is dilinoleic acid. This is produced by thermal dimerization, utilizing the linoleic acid content of vegetable fatty acids such as soya and cottonseed acids.



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Numerous other syntheses of dibasic acids from fatty sources have been described in the literature.

This review will emphasize the chemistry of these dibasic acids. Other dibasic acids, particularly the aliphatic ones, will be included also for comparison.

Carboxylic acids are versatile materials, partly by virtue of the variety of chemical reactions of which the carboxyl group is capable. The dibasic acids are unusually versatile because of their two carboxyl groups. This enables many additional types of useful reactions, particularly the building of polymeric structures. The biggest uses today are the simple esters for plasticizers and lubricants, the polyesters for coatings and fibers, and the polyamides for coatings, fibers, and plastics.

The aliphatic dibasic acids vary considerably in their physical properties. The lower members are crystalline solids, very water-soluble and limited in solubility in organic solvents. As the chain length increases through the 6 to 10 carbon range, water-solubility decreases (still soluble in hot water), and solvent solubility increases. Di-linoleic acid represents an extreme in being a viscous oil.

### Occurrence

The lower aliphatic dibasic acids ( $C_2-C_6$ ) occur more abundantly in nature than the higher aliphatic dibasic acids. Oxalic acid occurs as the potassium or calcium salt in several plants. Malonic, glutaric, and adipic acids occur in sugar beet. Succinic acid has been found in amber, turpentine oils, and various

plant resins. Fumaric acid occurs free in many plants and in some fungi and is involved in the respiratory processes of animals. Azelaic acid has been reported present in several fatty materials. This may be as the result of oxidative cleavage since most naturally occurring fatty mixtures contain some fatty acids having a double bond at the 9-position. Thapsic acid was found in the root of *Thapsia garganica*. Even higher molecular weight dibasic acids occur in various plant waxes. The best known source is Japan wax, the coating on sumac berries. "Japanic acid" is the name normally given to  $\text{HOOC}(\text{CH}_2)_{10}\text{COOH}$ , but the dibasic acid component of Japan wax is actually a mixture, containing at least the normal members of the series from  $\text{C}_{19}$  to  $\text{C}_{23}$ .

### Synthesis

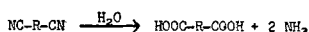
It is convenient to divide the methods of synthesizing dibasic acids into three classes:

- conversion of a difunctional compound by converting each functional group (the same or different) into a carboxyl group;
- conversion of a substituted monobasic acid by operating on the substituent to form a second carboxyl group; and
- methods specifically applicable to dibasic acid formation, such as ring opening.

The first two classes merely involve application of standard monobasic acid syntheses to difunctional compounds.

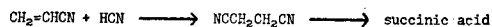
#### CONVERSION OF A DIFUNCTIONAL COMPOUND

##### 1. Hydrolysis of a dinitrile

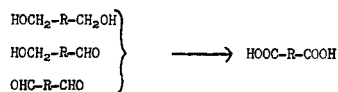


The dinitrile is generally obtained from the corresponding dihalide by reaction with sodium cyanide.

Another route to a dinitrile is:



##### 2. Oxidation of a Glycol or Aldehyde



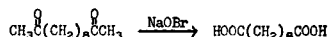
The oxidizing agent may be chromic acid or air in the presence of a catalyst, such as manganese acetate.

3. *Oxidation of Aromatic Hydrocarbons.* The oxidation of *m*-xylene and *p*-xylene to isophthalic acid and terephthalic acid, respectively, is now undergoing commercial development. Closely related is the commercially important oxidation of *o*-xylene or naphthalene to give phthalic anhydride.

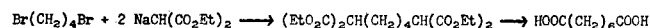
4. *Oxidation of paraffins.* Generally the oxidation of paraffin wax is conducted to yield monobasic acids. Special conditions such as oxidation with air or oxygen in liquid phase at relatively low temperature in the presence of manganese naphthenate catalyst lead to appreciable yields of dibasic acids,  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ . ( $n = 2 - 8$ ) (1).

5. *Oxidation of a Diketone.* Conversion of a dike-

tone of the  $\text{CH}_3\overset{\text{O}}{\parallel}\text{C-R-C}\overset{\text{O}}{\parallel}\text{CH}_3$  type to a dibasic acid can be accomplished by the haloform reaction or by direct oxidation. An example is a synthesis of sebacic acid:



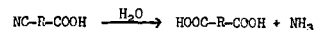
6. *Malonic Ester Synthesis.* An aliphatic dihalide may be used in the conventional malonic ester synthesis. For example:



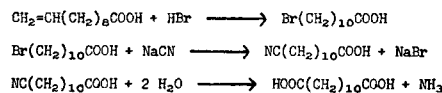
The closely related cyanoacetic ester and acetoacetic ester syntheses may also be used.

#### CONVERSION OF A SUBSTITUTED MONOBASIC ACID

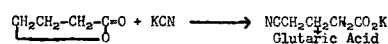
##### 7. Hydrolysis of a Cyano Acid



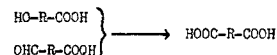
The cyano acid may be obtained from a halo acid as in the synthesis of dodecanedioic acid (2):



Another route to the cyano acid is by opening the lactone ring (3)

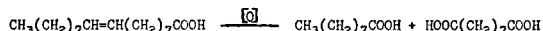


##### 8. Oxidation of an Aldehyde or Hydroxy Acid



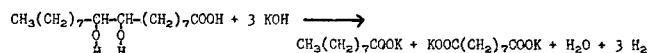
Reaction is conducted as in Synthesis No. 2.

9. *Oxidation of an Unsaturated Fatty Acid.* The oxidative cleavage of oleic acid to azelaic and pelargonic acids is being carried out commercially by two different methods using chromic acid and ozone respectively:

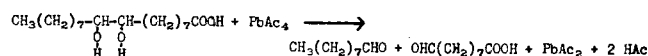


The ozonolysis of oleic acid served to verify its structure which was established about 60 years ago (4). In a similar way brassylic acid,  $\text{HOOC}(\text{CH}_2)_{11}\text{COOH}$ , is obtained from erucic acid and sebacic acid from undecylenic acid  $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{COOH}$ . The undecylenic acid, in turn, is produced by the pyrolysis of castor oil or methyl ricinoleate.

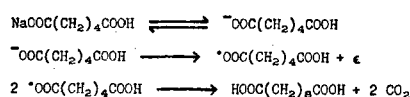
10. *Oxidation of a vic-Dihydroxy Fatty Acid.* The alkaline fusion of 9,10-dihydroxystearic acid produces azelaic and pelargonic acids in good yields (5).



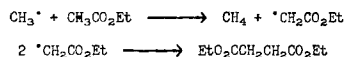
Similar cleavages by alkaline fusion are reported for mono-keto and mono-hydroxy fatty acids but the yields of the desired acid cleavage products are lower. The 9,10-dihydroxystearic acid can be obtained from oleic acid in several ways. One good way is by epoxidation and hydration of the epoxide ring, all carried out in one continuous operation (6). Cleavage of 9,10-dihydroxystearic acid is also accomplished with osmium tetroxide or lead tetra-acetate (7). The products are aldehydes which can then be oxidized to the desired acids.



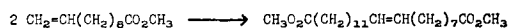
11. *Coupling of Two Saturated Fatty Acid Molecules.* The well known Kolbe electrolysis reaction (8) was used by the Germans during the last war to convert adipic acid into sebacic acid:



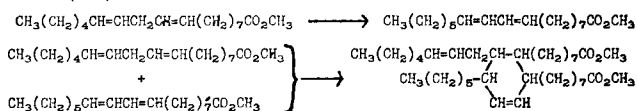
Methyl radicals (from acetyl peroxide) convert ethyl acetate to diethyl succinate (9):



12. *Dimerization of an Unsaturated Fatty Acid.* Heating of methyl undecylenate at 325°C. gives appreciable amounts of the dimethyl ester of 9-docosene-1,22-dicarboxylic acid by "tail-to-tail" dimerization (10).

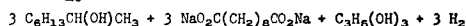
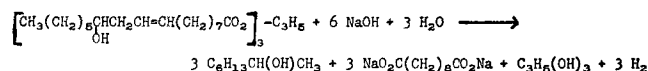


The remaining double bond moves from the 10- to the 9-position. A similar treatment of methyl linoleate converts it to a cyclic dimer. The reaction is generally considered to involve the isomerization of the double bonds of one molecule to conjugated position followed by Diels-Alder addition of a second molecule to the first (11):



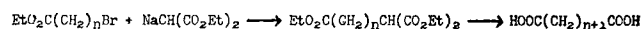
If linoleic acid is used, considerable decarboxylation occurs. However the dimerization is carried out commercially on the free acid. This is done by utilizing the discovery of Goebel (12) that a small amount of water under pressure prevents decarboxylation. A temperature of 360° gives good results (13). The dilinoleic acid consists of a whole family of related isomers since there are numerous ways the above isomerization and addition can take place. There is generally present 15-20% trimer and higher polymers.

13. *Alkali Fusion of a Monohydroxy Acid.* This is a special case of Synthesis No. 8, and one which is commercially important. Fusion of castor oil with alkali at 250°-300° gives sebacic acid and capryl alcohol.



At some stage of the reaction the double bond migrates from the 9-position. Superior results are claimed if the fusion is conducted under pressure (14). Various other improvements have been claimed. For example, heating castor oil with aqueous sodium hydroxide at 275° in the presence of cadmium oxide is reported to give sebacic acid in 84% yield (15).

14. *Malonic Ester Synthesis.* Use of a halo ester as the halide:

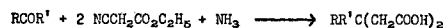


#### SPECIFIC METHODS

15. *Oxidation of Cyclic Ketones or Alcohols.* Glutaric acid, adipic acid, and their substituted derivatives result from the appropriate cyclic ketone or corresponding alcohol by nitric acid oxidation. The commercial production of adipic acid (16) uses cyclohexane, cyclohexanol, or cyclohexanone as raw material. Nitric acid or air may be used as the oxidant. Cyclohexane is derived directly from petroleum or by hydrogenating benzene. The liquid phase oxidation of cyclohexane, using air and a catalyst, gives cyclohexanone and cyclohexanol. Cyclohexanol is also obtained by the hydrogenation of phenol.

16. *Oxidation of a Cyclic Olefin.* Various methods of oxidation will convert a cyclic olefin to the corresponding dibasic acid. Thus the ozonization of cyclopentene gives glutaric acid.

17. *Guareschi Reaction.*  $\beta,\beta$ -Disubstituted glutaric acids are produced from ketones, ethyl cyanoacetate, and ammonia (17):



Here also a cyclic compound is involved, a cyclo di-cyanoimide being an intermediate which is hydrolyzed to the substituted glutaric acid.

18. *Oxidation of Aromatic Hydrocarbons.* The oxidation of benzene and naphthalene by air over vanadium pentoxide catalyst is used commercially to give maleic anhydride and phthalic anhydride respectively (18).

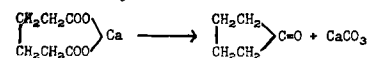
19. *Fermentation.* The action of various microorganisms on carbohydrates produces a variety of carboxylic acids. For example, certain molds lead to fumaric acid, and certain molds and yeasts give malic acid (hydroxysuccinic acid).

#### Reactions

In general, the dibasic acids undergo the typical reactions of monobasic acids. In doing so, two series of derivatives can be formed. Thus esterification can yield a mono-ester or di-ester. In addition, dibasic acids undergo additional reactions specific to them. Only these are considered here. These specific reactions, resulting from the bifunctionality of the dibasic acids, lead to polymer or ring formation or both. Although sometimes a given dibasic acid can form either a polymer or ring, depending on conditions, it is convenient to divide the reactions into these two categories.

#### RING FORMATION OR CYCLIZATION

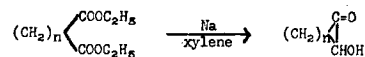
1. *Ketonization.* Pyrolysis of certain dicarboxylic acid salts yields the cyclic ketone with one less carbon atom.



The 5- and 6-membered rings form most easily.

The thorium or cerium salts often work better than the calcium salts, particularly with the larger rings. The dibasic acid also may be heated directly over a metallic catalyst.

2. *Acyloln Condensation.* Refluxing a dibasic acid ester with sodium in xylene gives the cyclic acyloln (19).

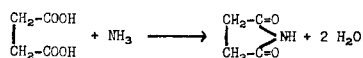


This method is the preferred one for obtaining large rings. Good yields are obtained even in those cases where ketonization works poorly.

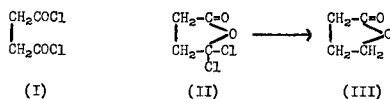
3. *Anhydride Formation.* Heating of dibasic acids forms cyclic anhydrides readily, with loss of water, in cases where a 5- or 6-membered ring is formed. Typical examples are maleic, phthalic, succinic, and glutaric anhydrides. The 7-membered cyclic adipic anhydride can be obtained under special conditions but undergoes spontaneous polymerization (20).

4. *Imides.* The imides are the nitrogen analogs of the cyclic anhydrides, being the cyclic secondary

amides of the dibasic acids. Imides also form readily where the ring is 5- or 6-membered, from ammonia and the acid or anhydride:



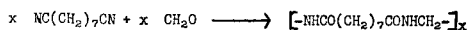
5. *Acid Chlorides*. Both phthalyl chloride and succinyl chloride, prepared by the usual methods from the acids, behave at times as though they had a cyclic lactone structure. Thus succinyl chloride behaves as II instead of I in several reactions such as reduction to butyrolactone (III).



#### POLYMERIZATION

6. *Polyesters*. A dibasic acid is capable of yielding polyesters on reacting with a compound containing 2 or more hydroxyl groups (21). Thus, ethylene glycol and suberic acid yield a linear polymer because each is difunctional. If trifunctional glycerine were used instead of ethylene glycol, a 3-dimensional polyester could be built up. In actual practice the anhydrides, such as phthalic and maleic anhydride, are often used as well as the acids.

7. *Polyamides*. If a diamine is used instead of a glycol, a linear polyamide is produced (22). The best known of the polyamides is ordinary 6-6 nylon. The polyamide from dilinoleic acid and ethylene diamine is produced commercially for use in coatings and adhesives. A polyamide useful for molding can be made from azelaic dinitrile (from azelaic acid) and formaldehyde (23).



Another interesting approach to polyamides is by the use of hydrazine as the diamine (24). The polymers may contain amide units of the type —CONHNH—CO—. By changing the conditions and/or the amount of hydrazine polymers containing the 1,3,4-oxadiazole ring (I) or 4-amino-1,2,4-triazole (II) units may be produced:



8. *Polyanhydrides*. Those dibasic acids which cannot yield cyclic anhydrides as small as 5 or 6 members give, instead, linear polyanhydrides (25). Polyadipic anhydride is a borderline case. It depolymerizes on heating at 200° but the monomeric cyclic anhydride (7-ring) spontaneously re-polymerizes (20).

#### Uses

The versatility of dibasic acids is well illustrated by the many and varied uses to which they have been put. In addition to the uses which have reached commercial reality there is a voluminous patent literature. Simple and polymeric esters and amides have assumed the greatest importance.

#### SIMPLE ESTERS

1. *Plasticizers*. Di-esters of straight chain 6-10 carbon dibasic acids and 4-10 carbon alcohols are valuable plasticizers for vinyl chloride resins, especially where flexibility at low temperature is required (26).

Di-butyl sebacate, di-octyl azelate, and di-decyl adipate are typical examples. These esters are also of value in other resins and in rubbers. They have a high plasticizing efficiency. The half methyl esters have been patented as plasticizers for zein (27).

2. *Lubricants*. Esters similar to the plasticizers just described are also useful as lubricating oils (28). A controlled amount of branching in the molecule is generally preferred as in the i-amyl, 2-ethyl hexyl, and iso-octyl esters of adipic, azelaic, and sebacic acids. Such esters today are finding use in jet engine and other military applications where petroleum-based lubricants are inadequate. These di-ester types have extremely low pour points, high flash and fire points, excellent viscosity-temperature relationships, outstanding resistance to oxidation, and minimum tendency for corrosion of various metals. There is considerable interest in extending the use of these high-performance di-ester lubricants to the civilian automotive field. Di-esters may also serve as bases for outstanding greases when gelled with a lithium soap, such as lithium stearate or lithium 12-hydroxystearate (29). These are also being used by the military, particularly where good performance in extremes of heat and cold is required. Esters of dilinoleic acid are also of interest in greases (30) and oils (31).

3. *Other Functional Fluids*. Di-esters of the type used as plasticizers and lubricants are also of value for other applications where fluids of exacting properties are required. The azelates and sebacates of branched C<sub>8</sub>-C<sub>10</sub> alcohols are useful diffusion-pump oils. A di-ester containing magnesium oxide or aluminum oxide particles is claimed to be a useful dielectric (32). Modification of a di-ester with a little polyacrylic ester gives a useful hydraulic fluid (33).

4. *Miscellaneous*. A variety of other uses for di-esters have been suggested in the patent literature. Typical esters are dibutyl sebacate (cosmetics component, flavor component), dibutyl adipate (tick repellent), diallyl pimelate (plant growth regulator), monovinyl sebacate (vinyl polymer modifier) (34), diallyl phthalate (monomer for thermosetting resin or for increasing hardness and heat and chemical resistance of vinyl resins), adipates (paint and lacquer formulation) and polyglycol ester of dilinoleic acid (emulsifier) (35).

#### POLYESTERS

1. *Plasticizers*. Linear polyesters from a glycol and a dibasic acid are useful plasticizers for vinyl chloride resins (26), rubbers, nitrocellulose, and other resins. Typically, the acid used is adipic, azelaic, or sebacic acid and the molecular weight 1,000-7,000. The lower molecular weight types are generally modified with a monobasic acid or monohydric alcohol as chain-terminating groups. These polymeric plasticizers, as they are known, generally have the superior permanence properties of lower volatility, greater resistance to solvent extraction, and greater resistance to migration. Disadvantages are often higher viscosity and more difficult processing.

2. *Surface Coatings*. Dibasic acids are strongly established as components in alkyd resins (36). The bulk of these resins are based on phthalic anhydride and a polyol such as glycerine or pentaerythritol. The resulting polyester is oil-modified. Flexibility can be

improved by partial or complete replacement of the phthalic anhydride with an aliphatic dibasic acid, such as azelaic or sebacic acid (37). The use of some dilinoleic acid achieves faster bodying of alkyds having greater flexibility, better "through-dry" in Epon varnishes (38). Special alkyds from dilinoleic acid and a dihydric phenol have been patented (39). A drying oil can be modified with azelaic or sebacic acid by interchange before cooking into an alkyd (40).

3. *Lubricants and Other Functional Fluids.* Polyesters have many of the desirable properties of the simple esters when used as lubricants. They contribute higher viscosity when desired, thus having possibilities as blending agents. Greases may also be formulated, based on polyesters. Polyesters of dilinoleic acid have been patented as viscosity index improvers and pour point depressants for petroleum and ester type oils (41). The combination of a polyester (particularly from glutaric or adipic acid) and a solvent has been patented as a hydraulic fluid (42).

4. *Plastics and Rubbers.* A variety of useful plastic compositions are based on polyesters. Polyesters from aliphatic  $C_4$ - $C_{10}$  dibasic acids can be used in the production of linoleum factice (43). Interesting elastomers can be produced by suitable cross-linking or vulcanization of polyesters. The "Norepol" rubber developed during the last war was produced by vulcanization of dilinoleic acid-ethylene glycol polyester (44). The glycol from the hydrogenation of dilinoleic acid can be used in place of ethylene glycol (45). Free radicals can cure polyesters of glutaric and sebacic acids to form rubber-like products (46). The commonly used fiber glass-filled low pressure laminating resins are generally based on styrene solutions of maleic or fumaric acid polyesters. Peroxide curing initiates the formation of numerous styrene cross links with the unsaturated polyester to produce a very strong, rigid structure (47). A recent development involves connecting two different polyesters together by means of a di-isocyanate to give a "block" polymer. The polyester from terephthalic acid and ethylene glycol is produced commercially as film and fiber.

5. *Miscellaneous.* Other uses for polyesters are illustrated by patents covering emulsifiers, emulsion breakers, assistants for viscose rayon preparation (48), and rayon-soaking baths. The last is based on the polyadipate of N-methyl diethanolamine (49). The "Norepol" polyester mentioned above has been modified with rosin and triethanolamine (50) or with cyclized rubber (51) to give an adhesive. A polyester using a liquid acetone-formaldehyde resin as the hydroxy component has been recommended as the bonding agent for abrasive wheels (52).

#### POLYAMIDES

1. *Fibers.* Use of "6-6" nylon (adipic acid-hexamethylene diamine polyamide) in fibers has developed rapidly since Carothers first prepared it in 1935. The first plant to produce nylon hosiery yarns was built in 1939. Nylon's success as a fiber results from its high chemical resistance, tensile strength (much of which is retained when wet), elastic recovery, abrasion resistance, and resistance to micro-organisms along with low water absorption and flammability. In addition to myriad consumer and industrial uses for

woven fabrics, nylon fibers are used in tire cord, insulation, and paint brushes.

2. *Plastics.* The "6-6" nylon is also valuable in extruded or molded shapes. Small electrical components, bearings, and tubing are used. Coarse monofilaments are valuable in window screens, tooth brushes, hair brushes, and many types of industrial brushes. Where high water resistance is required, "6-10" nylon is used in which sebacic acid replaces the adipic acid. Plastic polyamide compositions can also be based on dilinoleic acid (53).

3. *Coatings.* Conventional nylon polymers are used in the coating of paper, electrical wire, and textiles and in industrial finishes. Useful polyamides for hot melt application on paper, metal, etc., are available from dilinoleic acid and a polyamine, such as ethylene diamine (54). Such resins are also available as aqueous dispersions (55). The diamine from dilinoleic acid may also be used (56). An interesting non-drip paint has just been developed based on an alkyd-dilinoleic acid polyamide combination (57).

4. *Adhesives.* Use of conventional nylon in adhesive formulation has been proposed by blending with phenol-formaldehyde resin (58) or as the N-methoxymethyl modification for wood lamination (59). Several patents describe the use of polyamides from dilinoleic acid in adhesives.

5. *Miscellaneous.* Treatment of a polyamide with formaldehyde and application to paper imparts wet strength (60). Application of N-methoxymethyl nylon to wool from solution followed by hydrolysis *in situ* imparts non-felting properties and improved abrasion resistance (61). The use of polyamides from dilinoleic acid as de-emulsifiers and for the sizing of fiber glass has been patented.

#### SALTS AND SOAPS

1. *Lubricants.* The modification of aluminum greases with dibasic acids has received considerable attention recently. Particularly useful are the aluminum greases from stearic and/or oleic acid modified with dilinoleic acid (62). Increased gel strength, storage stability, efficiency, and shear resistance are claimed. Modification with succinic acid has also been described. A variety of azelaic acid derivatives have been described as oil additives (63).

2. *Miscellaneous.* The principle of modifying aluminum soaps with dilinoleic acid has been applied to the "Hydrafrac" process for treating oil wells and to the gelling of hydrocarbon fuels (Napalm) (64). In Napalm the soap is claimed to be dry, free-flowing, and easier to handle as well as to gel more rapidly to a firmer gel. Salts such as triethanolamine adipate are claimed to be good glass-to-glass or glass-to-metal fluxes (65). Copper sebacate is an excellent fungicide (66). The modification of potassium soaps with potassium methyl adipate permits fluid liquid soaps of higher soap content (67).

#### AMIDES

Certain N,N'-dialkyl diamides and N-alkyl half amides of azelaic acid, sebacic acid, etc., are claimed to have advantages over conventional soaps as the gelling agents in lubricating greases (68). Those N,N'-dialkyl diamides from 6-10 carbon diphenolic di-

basic acids, containing 34 carbon atoms or more, are useful foam suppressors (Example: N,N'-di-octadecyl sebacamide) (69). The diester from a dibasic acid and N-hydroxyethylstearamide is a wax (70). Condensation of ethylene oxide with hydroxyalkyl amides of dilinoleic acid yields surface-active agents (71). The bis-imidazolines of dilinoleic acid are useful corrosion-inhibitors for petroleum products (72).

#### MISCELLANEOUS POLYMERS

A great variety of useful polymeric compositions other than polyesters and polyamides have been prepared from dibasic acids. The isocyanate "foamed-in-place" resins are based on a dibasic acid, polyol, and di-isocyanate. The curing reaction is accompanied by carbon dioxide evolution to give light, strong structural bodies. Polymers may be prepared from a di-urethane and a dibasic acid. Adipic acid, glycerine, copal resin, and castor fatty acids give a heat resistant electric-insulating resin. Di-siloxane resins from adipic acid and certain di-siloxanes have been patented.

#### ACIDS THEMSELVES

The dibasic acids themselves can be used as such. The addition of a small amount of dilinoleic acid to asphalt improves its bonding to stone aggregate for road-making (73). Dilinoleic acid is an efficient corrosion-inhibitor for polyoxyalkylene glycol fluids (74), gasoline (75), and petroleum-type lubricating oils (76). The use of dilinoleic acid as a crystallization inhibitor for D.D.T. has been patented (77).

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