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Sebacic Acid

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Sebacic acid is the highest member of the series of aliphatic dicarboxylic acids for which there is a preparative method suitable for industry. The method comprises the alkaline fission of ricinoleyl compounds, which yield, at the same time, the equivalent amount of octanol-2. The acid provides an intermediate for the manufacture of interesting new products in the realm of synthetic materials such as plasticisers, synthetic resins, polyesters, polyamides, etc. As a component of these materials, it endows them with a reduced sensitivity to temperature of their physical properties (viscosity of fluids, modulus of elasticity of solids), improved water resistance and good chemical stability; compared with shorter chain dicarboxylic acids and those from aromatic sources, sebacic acid plastics usually have a better rubber-like elasticity. The sebacyl group is of low polarity, due to the high ratio of methylene groups ($-CH_2-$) to the polar carbonyl groups ($>C=O$).

The name sebacic, like adipic, means "of, or belonging to fat", and is a reminder that both these materials were originally obtained by the oxidation of certain fatty materials. In the science of chemistry, sebacic acid is a member of the homologous series of dibasic aliphatic acids, represented by the general formula $HOOC(CH_2)_nCOOH$, the members of which are known from $n=0$ (oxalic acid) to $n=20$ (the eicosane acid occurring in Japan wax[1]). In the case of sebacic acid, $n=8$, so that the acid may be regarded as a derivative of either of the hydrocarbons, octane or decane. Hence the names, 1 : 8 octane dicarboxylic acid or decane-di-acid.

Chemistry of the Formation of Sebacic Acid

No simple method for the preparation of sebacic acid is available and certainly no syntbetic method is available to industry. The classical methods applied to the hydrocarbons octane or decane do not easily lend themselves to the usual sequence of reactions (end group oxidation, or chlorination, reaction to form cyanide with subsequent hydrolysis to carboxyl, etc.), on account of the large number of reactions which can occur giving rise to mixtures of different materials and also isomers.

Instead, the starting point for all useful methods is castor oil; essentially is it the *ricinoleyl* residue from which sebacic acid is produced. Usually, the ricinoleyl compound in the form of castor oil (a glyceride which contains approximately 87–88 % of ricinoleyl, about 7 % of oleyl radicals and lesser amounts of linoleic, stearic and dihydroxystearic acid glycerides), or the free acids from castor oil, are treated under conditions of high temperatures with caustic alkalis such as sodium hydroxide. This reaction has been known for about a century, but researches in recent years[2] have led to the clarification of the course of the reaction which clearly proceeds in two stages:

$$CH_3[CH_2]_5CH(OH)\cdot CH_2CH{:}\,CH[CH_2]_7COOH$$
(I)

A. $CH_3[CH_2]_5CO\cdot CH_3 + CH_2(OH)[CH_2]_8COOH$
(II) (III)

B. $CH_3[CH_2]_5CH(OH)\cdot CH_3 + COOH[CH_2]_8COOH + H_2$
(IV) (V)

Reaction A proceeds at temperatures up to 200 °C. and leads to the formation of methylhexyl ketone (compound II) and to ω-hydroxy decanoic acid (compound III). At higher temperatures, interaction of these two compounds leads to the formation of capryl alcohol (octanol-2, compound IV) and to sebacic acid. Evidently the oxidation of the hydroxy acid occurs at the cost of the reduction of the ketone with the liberation of hydrogen.

Other preparative methods of sebacic acid are known, but are not practised commercially. Thus, the dry distillation (pyrolysis) of ricinoleic acid (or its glyceride) is known[3] to proceed as follows:

$$CH_3[CH_2]_5CH(OH)CH_2\cdot CH{:}\,CH[CH_2]_7COOH$$
$$\downarrow$$
$$CH_3[CH_2]_5CHO + CH_2{:}\,CH[CH_2]_8COOH$$
(VI) (VII)

The reaction between compounds (VI) (heptyl aldehyde) and (VII) (undec-10-enoic acid) does not occur in the same manner as the interaction between methylhexyl ketone and ω-hydroxy decanoic acid so that a separate oxidative reaction (nitric, bichromate, etc.) is necessary to convert compound (VII) into sebacic acid. It is known also that the yields of undec-10-enoic acid resulting from

[1] S. SHIINA, J. Soc. Chem. Ind. Japan *43*, 173 B (1940).

[2] G.H. HARGREAVES and L.N. OWEN, J. Chem. Soc. *1947*, 753–6.

[3] BUSSY and LECANU, C. R. Acad. Sci. *21*, 84; J. Pharm. Chim. *8*, 321 (1845); BUIS, Ann. Chim. Phys. *44*, 77 (1855); F. KRAFFT, Ber. dtsch. chem. Ges. *10*, 2034 (1877), *11*, 2218 (1878), and E. NEISON, J. Chem. Soc. *27*, 507, 837 (1874).

the pyrolysis process are low, but the technique is of further interest since by reaction with hydrogen halide (e.g. hydrogen bromide) and subsequently with ammonia, amino-acids may be synthesised which are of great interest in the field of polymer chemistry[4].

The classical method of KOLBE, calling for the electrolysis of e.g. potassium ethyl adipate, has been examined several times in the hope of developing an economic method for the production of sebacic acid; but the several stages for the preparation of the half-ester salt, the large electrical energies required and the further hydrolysis reactions needed, have so far prevented commercial exploitation of this particular synthesis:

$$2C_2H_5OOC[CH_2]_4COO \rightarrow C_2H_5OOC[CH_2]_8COOC_2H_5 + 2CO_2$$

This method was the subject of serious study in Germany where, during the war, castor oil was not easily available as the starting point for the highly desired sebacic acid[5]. Unsuccessful also was the possibility of synthesing sebacic acid through the REPPE technique using acetylene[6].

Manufacture of Sebacic Acid

The original method of the alkaline fission of ricinoleic acid or its derivatives (ester, salts, glycerides, etc.) has been the subject of many technical investigations in recent times. Always, the main object has been the development of industrial processes with good yields and researches have been on the lines of improving the reaction conditions since, from the point of view of plant design and good chemical engineering principles, it is not easy to heat castor oil, or ricinoleic acid soaps, at very high temperatures and to keep the mass in a homogeneous form. Also, capacious fusion pots are required since severe foaming of the highly viscous reaction mass occurs; rapid and even heating is required, since overheating as well as slow heating is detrimental. The provision of adequate stirring for rapid movement and turnover of the thick soap mass is important. The design and choice of constructional material for the plant is clearly of the highest importance; attention must be paid to the corrosive effects of alkalis at high temperatures.

Many methods are discussed in the literature for the improvement of the reaction conditions, but chiefly the improvements depend upon one or more of the following:

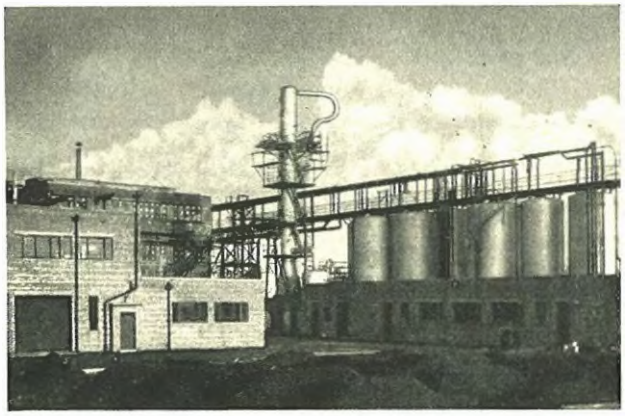
(a) The use of concentrated aqueous solutions under high pressures and high temperatures[7].
(b) The use of ricinoleyl alcohol as starting material[8].
(c) Slow controlled addition of alkali in order to minimise foaming[9].
(d) Carrying out of the process in two stages:
    1. to give ω-hydroxy decanoic acid[10],
    2. oxidation of the latter to sebacic acid.
(e) Introduction of inert liquid diluents to minimise foaming and to facilitate stirring and homogeneity of the reaction mass, e.g. mineral oil[9].

At the present time, sebacic acid is made on an industrial scale by two companies in the U.S.A. and by one in the United Kingdom. The latter company arises by the collaboration of one of the American manufacturers, The Hardesty Chemical Company Inc., with the Geigy Company Limited, of Manchester, England. This is the so-called Geigy-Hardesty Company Limited, whose manufacture of sebacic acid and octanol-2 has just commenced in England. The process which is used is based upon that employed by the Hardesty Company in the U.S.A., but embodies certain refinements.

Essentially, the process employed satisfies most of the chemical requirements already discussed, but above all, it can be stated that successful economic industrial production is reached by the application of good chemical engineering principles. By these means, a plant is now in being which is the most modern in the world and is now providing, for the first time in Europe, these important new chemicals on a large industrial scale.

The style of the plant is shown by the illustrations (Figure 1).

After the reaction between the alkali and the ricinoleyl compound has been effected, and the octanol-2 has been steamed out of the mass, the aqueous solution of the so-called "sebacic salt" is treated with acid, firstly to precipitate the remaining or unchanged monobasic acids and secondly, to precipitate the sebacic acid itself. According to the degree of purity required, further



(a) (b) (c)

Figure 1. General view of sebacic acid plant showing: (a) Reactor House, (b) Capryl Alcohol distillation column, (c) Pump Houses and bulk storage vessels

[4] F.P. 958,178.
[5] C.I.O.S, File No. XXXIII—50, *Synthetic Fibre Developments in Germany*, Part II., p. 743–5.
[6] B.I.O.S. Report No. 266, *New Technical Applications of Acetylene*, and F.I.A.T. Technical Bulletin, T-1, *Manufacture of Sebacic Acid in Germany*.
[7] U.S.P. 2,182,056 and 2,217,516.
[8] U.S.P. 2,304,602.
[9] U.S.P. 2,217,516 and B.P. 534,322.
[10] U.S.P. 2,217,515.

solution in alkali, carbon/earth decolorisation and precipitation are necessary. For the highest qualities, recrystallisation from solvents, e.g. o-dichlorobenzene[11], becomes desirable. The quality of the sebacic acid which arises varies from 98 % to almost 100 % purity according to the method of refinement employed. For most technical processes in industry a grade of 98 % minimum is satisfactory. A description of this grade is as follows:

Purity (calculated as sebacic acid) . . .	98 % min.
Colour (of 20 % w/w solution in 7 % ammonia)	200 Hazen max.
Crystallising point	131 °C. min.

Sebacic acid comes into use as a white, free flowing powder having a mild fatty acid odour (Figure 2). It is very lowly water soluble (below 0.1 % at 20 °C.) but is soluble in alcohols, esters and ketones. In hydrocarbons, chlorinated hydrocarbons and ether, it is very lowly soluble.

The highest recorded melting point is 134.5 °C.[12], whilst the degree of acidity is shown by its neutral reaction to helianthin and the values of its dissociation constants:

$$K_1 = 2.6 \times 10^{-5} \quad \text{and} \quad K_2 = 2.6 \times 10^{-6}.$$ [13]

Its boiling point at 100 mm. is 294.5 °C.[14]

The aqueous distillate of capryl alcohol (octanol-2) is separately refined by modern distillation methods (multiplate and high-reflux ratios) and leads to a high grade of alcohol used, inter alia, for the production of plasticisers (phthalate, adipate, sebacate, etc.) as anti-foam agent, in lacquers, in solvent processes and for synthetical processes calling for the introduction of C_8-groups. The purpose of the distillation is firstly to remove the water and secondly to eliminate the small quantities of methylhexyl ketone which arise to an extent proportional to the degree of reaction between methylhexyl ketone and ω-hydroxy decanoic acid, which in practice is never, of course, 100 % complete. The boiling range of technical quality capryl alcohol is 173–180 °C., whilst with good refining the content of methylhexyl ketone falls below 1 %.

Chemical Applications of Sebacic Acid

The properties of sebacic acid are the conventional ones expected of carboxylic acids generally. Thus, the formation of salts, esters, amides, anilides and the like, proceeds normally in two stages according to whether one or two carboxyl groups are concerned in the reaction.

[11] F.D. Report No. 2136, 46, *Über die Herstellung von Sebacinsäure.*
[12] Beilstein, *Handbuch der Organischen Chemie*, 4th Edition, II, 718; Voerman, Recu. Trav. Chim. *23*, 272.
[13] Beilstein, *Handbuch der Organischen Chemie*, 4th Edition, II, 718; Beilstein, *Handbuch der Organischen Chemie*, 4th Edition, II, First Supplement, 293.
[14] Beilstein, *Handbuch der Organischen Chemie*, 4th Edition, II, 718; Krafft et al., Ber. dtsch. chem. Ges. *22*, 818.

Outstanding, however, are the reactions which arise from the presence of *two* carboxyl groups, situated at the ends of a long alkyl chain, in the sense of the polyfunctionality, the concept of which is due to Kienle, Carothers, et. al. The molecule can thus be combined with other reactants, on the one hand to form diesters, etc.,

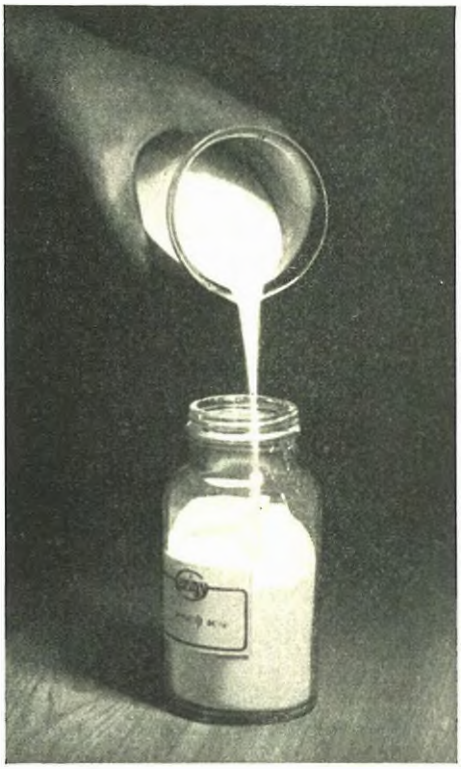


Figure 2. Sebacic Acid produced as fine, free flowing granules

by reaction with two molecules of a mono-hydric alcohol and, on the other hand, to form "polymeric" materials by reaction with di-, tri-, or higher functional materials such as glycols and other polyhydric alcohols, diamines and so on.

(a) *Di-ester Plasticisers*

In the first case, reaction with monohydric alcohols gives rise to extremely useful esters. These are well established as high efficiency plasticisers, since they combine the essentials of plasticiser activity:

(1) The presence of two polar carbonyl groups in the ester structure which are conducive to good mixing or solvent power for synthetic resins and,
(2) The presence of a long normal hydrocarbon chain ($-[CH_2]_8-$) which is conducive to a low temperature coefficient of viscosity, a property which is much sought after in the fields of plasticisers and polymer chemistry generally, since the plastic materials made therewith show a minimum change of physical properties with change of temperature.

Often these factors work in opposition, since the two carbonyl groups of sebacic diesters give the necessary

polarity for the mixing with polymers, whilst the long hydrocarbon chain between them gives the opposite effect. Fortunately, however, the choice of alkyl groups (from the monohydric alcohol employed) is a means of controlling the overall behaviour of the sebacic acid ester plasticiser. Thus, dimethylglycol sebacate mixes with polymers of medium to high polarity (cellulose nitrate, cellulose acetate, etc.) whilst the dibutyl ester mixes with polyvinyl chloride and its copolymers. Dioctyl sebacate is immiscible with cellulose acetate, it is lowly miscible with cellulose nitrate and of good miscibility with polyvinyl chloride; with purely hydrocarbon polymers it is highly miscible.

On account of the higher molecular weight of the sebacate esters in the normal series of esters used as plasticisers, they show a lower vapour pressure and consequently give better ageing compositions (Table 1).

Table 1. Molecular Weight of Diesters of 2-ethylhexanol and the Weight Ageing Losses from Polyvinyl Chloride Compounds made with the same esters

	Adipate (D.O.A.)	Phthalate (D.O.P.)	Sebacate (D.O.S.)
Molecular weight of ester .	370	390	426
% loss on ageing of polyvinylchloride compounds .	9.6	2.0	1.1

The polyvinyl chloride compounds consisted of 65 parts of polymer and 35 parts of diester used as plasticiser; the ageing was carried out for 100 hours at 82.5 °C.

Table 2. Effect of temperature on the Modulus of Torsional Rigidity of the plasticised Polyvinyl Chloride Compounds described in Table 1

Plasticisers used in P.V.C. Compounds	Modulus of Torsional Rigidity kgs/cm², at						Ratio of Values at −40 °C. and +60 °C.
	−40 °C.	−20 °C.	0 °C.	20 °C.	40 °C.	60 °C.	
Di-2-ethylhexyl Adipate (D.O.A.) ...	955	240	74.1	26.9	13.2	6.61	145
Di-2-ethylhexyl Phthalate (D.O.P.) ...	5890	1700	188	38.9	15.9	10.0	589
Di-2-ethylhexyl Sebacate (D.O.S.) ...	1410	183	151	61.7	26.3	15.9	89

The viscosity-temperature properties of plasticisers based on sebacic acid are of considerable interest in plasticiser technology. The customary portrayal of these properties is on either the UBBELOHDE or A.S.T.M. viscosity charts, which plot the double logarithm of the viscosity against T°A. Figure 3 shows the effect of the sebacic acid residue in a series of octyl esters commonly used as plasticisers.

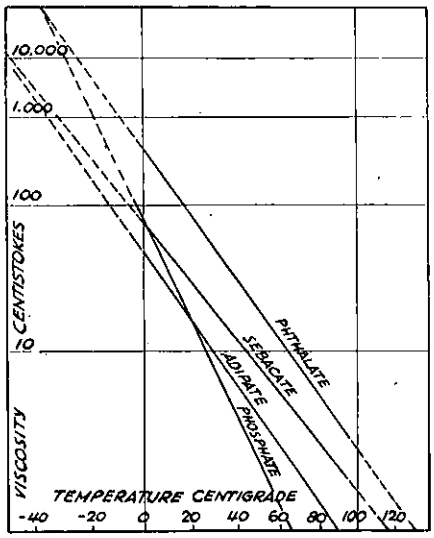


Figure 3. Viscosity characteristics of 2-ethylhexanol esters

Plastics made from esters of sebacic acid in combination with P.V.C. and synthetic rubbers show a smaller change of physical properties with change of temperature than is the case with esters from other acids.

For these reasons of attractive viscosity properties, synthetic diesters of the type of D.O.S. are finding favour in other fields, e.g. as hydrocarbon replacements in the production of low temperature greases[15].

(b) *Polymeric Applications of Sebacic Acid*

The polyfunctionality of sebacic acid is best applied in the production of the following materials for industry:

(1) Synthetic resins of the alkyd or polyester type, produced by reaction with glycerol, pentaerythritol, trimethylolpropane, etc. These are used as such, or modified with long chain fatty acids (lauric, palmitic, ricinoleic, etc.) in surface coatings and in the floor covering industry.

(2) Synthetic materials, also of the alkyd type, made by reaction with dihydric alcohols such as 1 : 2 propylene glycol which give rise to highly viscous liquids, so-called "polymeric plasticisers", which are the most recent innovations in the plasticiser fields since, on account of their high molecular weight (10–50,000), they are non-volatile and do not diffuse from the polymers with which they are used as plasticisers. These materials constitute the group of so-called "nonmigrating" plasticisers.

(3) Synthetic rubbers made by the reaction of sebacic acid with selected glycols, the products being capable of cross linking either by poly-iso-cyanates (the Desmodurs and Vulkollan of the I.G.) or with organic

[15] E.M. BRIED, H.F. KIDDER, C.M. MURPHY, and W.A. ZISMAN, Ind. Eng. Chem. *39*, 484–91 (1947); D.C. ATKINS, Jr. H.R. BAKER, C.M. MURPHY, and W.A. ZISMAN, *ibid.* *39*, 491–7 (1947); G.M. HAIN, D.T. JONES, R.L. MERKER, and W.A. ZISMAN, *ibid.* *39*, 500–6 (1947); A.S.T.M. *Symposium on Synthetic Lubricants*, Special Tech. Publication No. 77, etc.

peroxides ("polyester rubber" of the Bell Telephone Labs).

(4) Synthetic fibres of the polyamide type; whilst adipic acid used with hexamethylene diamine, gives rise to the now well known Nylon of the American du Pont concern, interesting variations are being produced on an industrial scale using sebacic acid in place of adipic acid. The effect is to give products of a slightly more rubbery character and, on account of the reduced incidence of amide groups, to give products of better resistance to hydrolysis. By the choice of diamine, suitable combinations arise for use in rayon manufacture, whilst partial admixture with terephthalic acid in the Terylene series also gives interesting new polymers applicable as plastic materials, as distinct from textiles for which the ethylene-glycol terephthalic acid ester is itself most suitable after drawing and crystallisation.

Conclusion

It will thus be seen that the commercial availability of sebacic acid has given a great assistance to synthetic materials to which the acid itself or its derivatives contribute properties not hitherto obtainable.

Sebacic acid is so far unique, since it is probably the highest molecular weight polyfunctional chemical which is commercially available between the α- and ω-reaction points of which there is a long normal alkyl chain $-[CH_2]_8-$. It is unique also because it is not so far seen as derivable from either synthetic means or from petroleum sources. Since it derives from an agricultural product (castor oil beans), it is based on a raw material which arises each year and is not dependent upon rapidly diminishing resources in the earth. It is a brilliant example of the use of chemurgical methods (chemicals from agriculture) assisting the modern synthetic industries.