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REVIEW

Phthalic Anhydride—A Valuable Petrochemical

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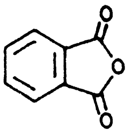
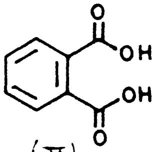
A review on the properties, methods of manufacture and important uses of phthalic anhydride is presented.

Phthalic anhydride (I) is the anhydride obtained by the dehydration of phthalic acid (II). Thelatter is a derivative of benzene having two carboxylic acid groups *ortho* to each other. Theoretically, I may be obtained from II by the loss of a molecule of water. Commercially too, I is manufactured by the *in-situ*, high temperature dehydration of II.



(I)



(II)

The systematic IUPAC name for phthalic anhydride is 1,3-iso-benzofurandione.[1] Its molecular formula is $C_8H_4O_3$ and molecular weight is 148. The elemental analyses correspond to C 64.87%, H 2.72% and O 32.41%. Its density is 1.53, m.p. 130–2°C and b.p. 284–5°C. It exists as white, lustrous needle crystals and sublimes in vacuum. It is soluble in 162 parts water, more in hot water with conversion into phthalic acid, in 125 parts carbon disulphide. It is soluble in alcohol but sparingly in ether, a little more readily in chloroform at room temperature. Titrimetric methods have been described in literature[2,3] for determination of assay of phthalic anhydride.

The systematic IUPAC name for phthalic acid is 1,2-benzenedicarboxylic acid.[1] Its molecular formula is $C_8H_6O_4$ and molecular weight is 166. Its elemental analyses correspond to C 57.83%, H 3.64% and O 38.52%. It is a white crystalline substance with m.p. 230°C. When rapidly heated or when heated to a temperature 10°C above its m.p., it forms phthalic anhydride. 1 g of phthalic acid dissolves in 160 mL water at room temperature, in 10 mL alcohol, in 205 mL ether, in 5.3 mL methanol and is practically insoluble in chloroform at room temperature. In fact, this property (insolubility in chloroform at room temperature) is used occasionally to separate in the laboratory a mixture of phthalic anhydride from

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phthalic acid. This is important since old bottles of phthalic anhydride invariably contain phthalic acid formed by atmospheric moisture-initiated hydrolysis of phthalic anhydride.

Phthalic acid was first prepared[4] by the oxidation of 1,2,3,4-tetrachloronaphthalene with nitric acid. Commercially, it is manufactured by the catalytic oxidation of *o*-toluic acid and by the oxidation of naphthalene. The latter is usually obtained[5] in low temperature carbonisation plants utilising coal which produce coke required for reduction of iron-ore in steel plants (Chart-I). Phthalic anhydride is prepared commercially[6] by catalytic air oxidation of naphthalene or *o*-xylene. The first plant[7] for the manufacture of phthalic anhydride, based on naphthalene, was put up in Europe in 1918 and the one based on *o*-xylene in USA in 1946. *o*-Xylene itself is manufactured[7], as first generation petro-chemical, during the platinum catalysed reforming process (sometimes referred to as platforming) of naphtha fraction obtained in petroleum refining. *o*-Xylene is formed as part of benzene, toluene and xylene mixture (BTX mixture) from which it is obtained on separation (Chart-I). Phthalic anhydride is the principal commercial form of phthalic acid. The world-wide production capacity for the anhydride was 2.5 × 10^6 metric tonnes in 1985.

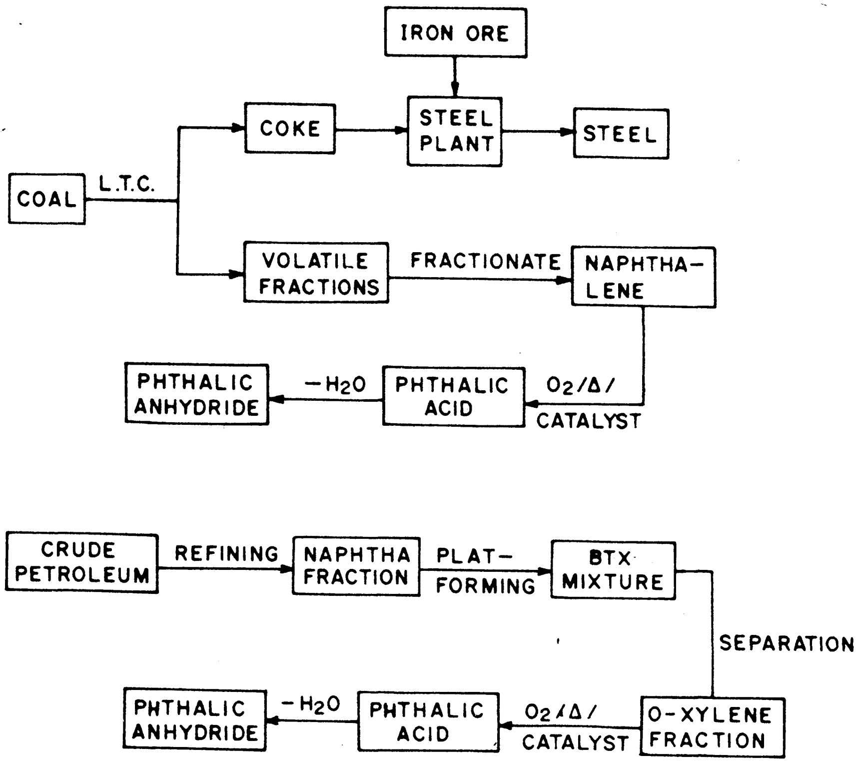
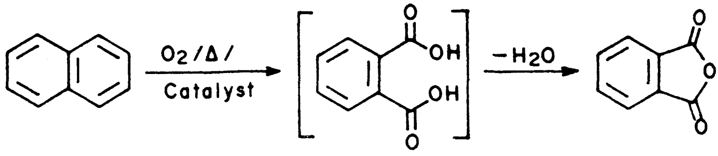
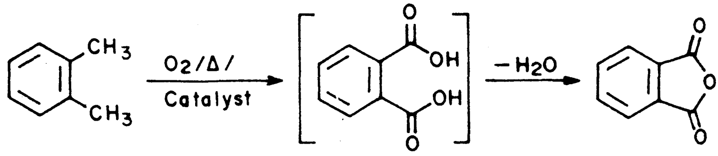
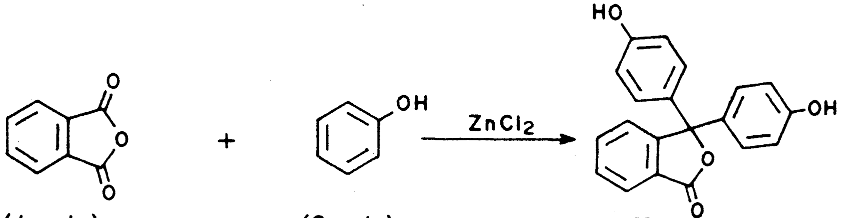


Chart-I



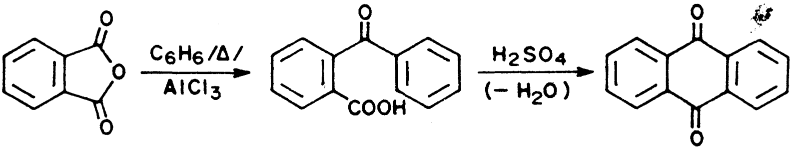


Phthalic anhydride is a second generation petro-chemical and finds use as the principal raw material[4] in the manufacture of a number of commercial products. One of the oldest uses of phthalic anhydride is in the manufacture of phenolphthalein[3] (III) obtained by reaction with phenol in the presence of anhydrous zinc chloride.

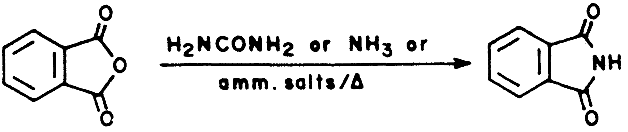


(1 mole) (2 mole) III

Phthalic anhydride reacts with benzene in the presence of anhydrous aluminium chloride followed by dehydration to yield[8] anthraquinones (IV)—the versatile raw materials in dye industry.

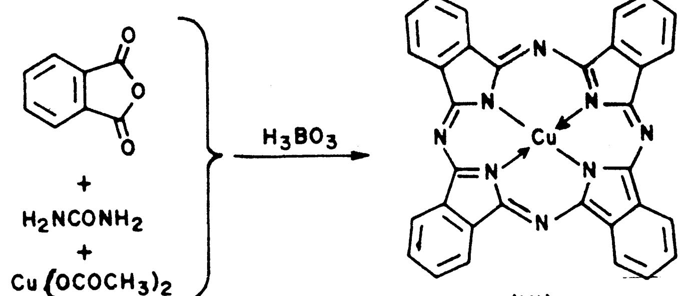


Phthalimide (V) is obtained[9] when phthalic anhydride is heated with urea or ammonia or ammonium carbonate or ammonium acetate.



(I) (V)

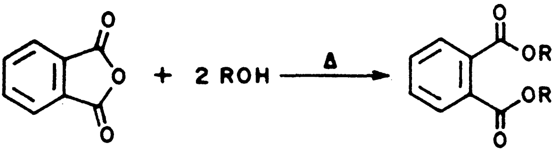
Condensation[4] of phthalic anhydride with urea and metal diacetates leads to the formation of metal phthalocyanines (VI).



(VI)

Phthalocyanine compounds are used in a variety of applications[9]. In addition to their use as pigments in paints, the phthalocyanines have been used in many types of dyestuffs. Phthalocyanine complexes of about 63 metals have been prepared and marketed. Metal-free phthalocyanine, in which the central copper atom is replaced by two hydrogen atoms, is characterised by photosensitive and semiconductor properties.

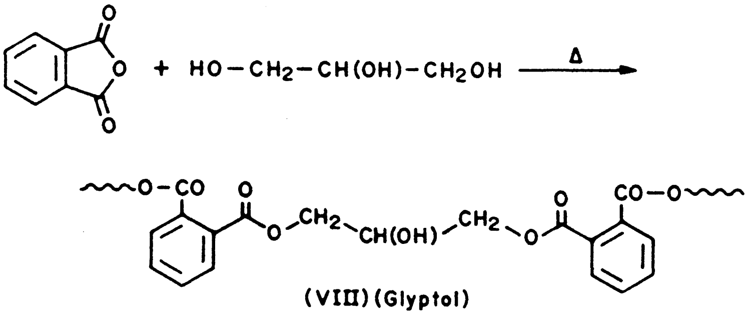
Phthalic anhydride reacts with alochols to form diesters. The diesters (VII) obtained with *n*-butanol and *n*-octanol, namely di-*n*-butylphthalate and di-*n*-octylphthalate, are used commercially as plasticisers[7, 10]



(VII)

The diesters, as plasticisers, are usually added in 3–7% ratio to a polymer such as PVC resin before it is heated-moulded in order to make it more elastic and less brittle. The plasticisers act by reducing the glass-transition temperature (T_g) of the brittle polymer (which is usually above room temperature) substantially to make it elastic (which has T_g much below room temperature).

The manufacture of di-alkyl phthalates is the most important single outlet for phthalic anhydride, accounting for about 50% of consumption in the USA and more than 60% consumption in Western Europe and Japan. Alkyd resins,



(VIII) (Glyptol)

sometimes referred to as glyptollic resins, consume roughly the same proportion of phthalic anhydride production as the diesters. The alkyd resins (VIII) are low molecular weight polyesters with complex, ill defined structures made by reacting phthalic anhydride with glycerol, ethylene glycol, vegetable oils or fatty alcohols.

The alkyd resins are mainly used in surface coatings, like oil-based paints, adhesives and fibre-based plywoods.

It is obvious from the above description that phthalic anhydride is a very valuable industrial raw material. Its principal property which makes it useful for synthesis of commercial products is due to its reactivity with various nucleophiles such as oxygen, nitrogen and carbon nucleophiles.

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