

An Organic Process for the Manufacture of Hydrogen Peroxide

A new plant costing some £2½ million—the largest of its kind in the world—has recently been opened by Laporte Chemicals Ltd to produce hydrogen peroxide by the autoxidation of an anthraquinol. After separation of the hydrogen peroxide the anthraquinone formed is hydrogenated back to the quinol over a palladium catalyst and the solution recycled.

During the last four or five years the increasing use of hydrogen peroxide, not only in bleaching and the manufacture of other per-compounds, but also as a propellant and as a reagent in organic synthesis, has resulted in a great deal of work being carried out on alternative methods of manufacture to the electrolytic processes developed over the last fifty years. Of these alternatives, that which has received the most attention has been the use of organic intermediates, particularly substituted anthraquinols, which autoxidise to form hydrogen peroxide.

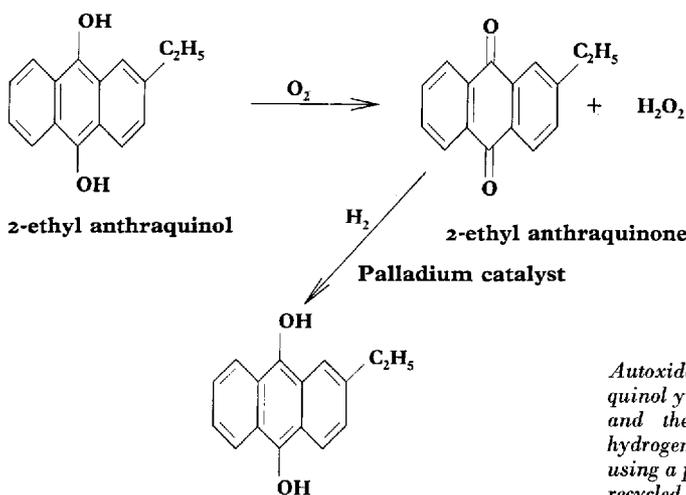
The early work on such a process was carried out by I. G. Farbenindustrie in Germany, and it was taken to the pilot plant scale during the war years. The intermediate used was 2-ethyl anthraquinol, which in solution was autoxidised yielding hydrogen

peroxide and the quinone. After separation of the hydrogen peroxide by aqueous extraction, the quinone was catalytically hydrogenated to the quinol and the solution recycled.

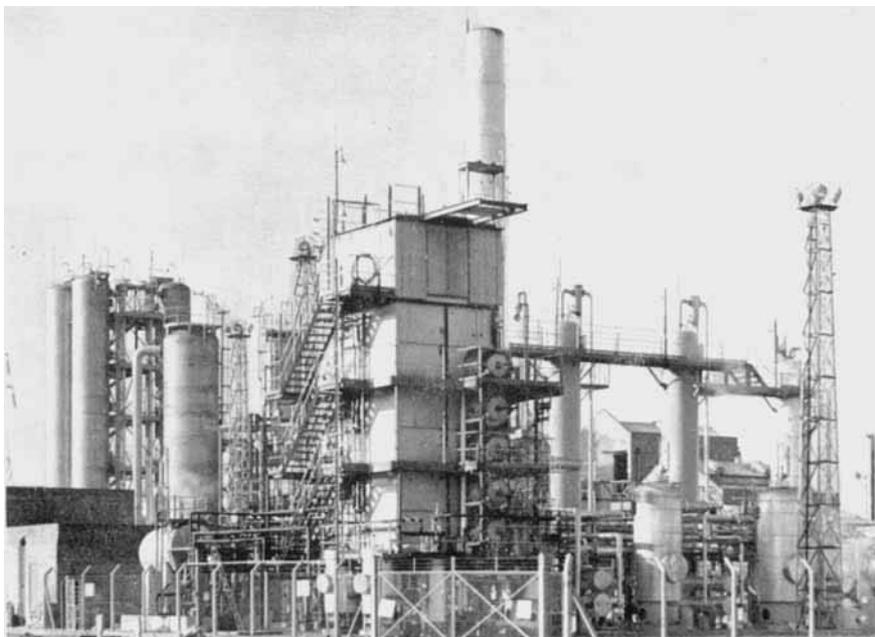
The original German process has been further developed since 1945 in a number of other countries, and several processes are now in use. Laporte Chemicals Limited has been particularly active in this field, and is now operating the only plant of its kind in Britain and the largest in the world to provide high test peroxide fuel for rocket motors and guided weapons.

Selection of Catalyst

Raney nickel was used as the hydrogenation catalyst in the German process, but this suffers from the disadvantages that it is easily deactivated by dissolved oxygen or hydrogen



Autoxidation of 2-ethyl anthraquinol yields hydrogen peroxide and the quinone, which is hydrogenated back to the quinol using a palladium catalyst and recycled



The new autoxidation hydrogen peroxide plant erected by Laporte Chemicals Ltd. at their Baronet Works, Warrington

peroxide, and is pyrophoric. A number of patents have described the use of palladium on an inert support as the hydrogenation catalyst, these supports including alumina, silica gel and certain silicates, and calcium phosphate. A major advantage of these catalysts is that any palladium oxides formed are reduced to the metal by hydrogen at ambient temperature.

The Laporte Process

The process developed by Laporte Chemicals Limited and now in operation at their Baronet Works is based on the use of 2-ethyl anthraquinone.

Hydrogen is made by cracking butane, supplied from Stanlow Oil Refinery. The autoxidation process organic cycle consists of two identical units which operate in parallel up to the extraction stage where solution from both streams mixes. Hydrogenation is carried out in vertical vessels, using palladium on an inert support in free suspension as the catalyst, which is manufactured on the site. The catalyst is suspended in a stream of

hydrogen which is passed through the reactor in excess of the theoretical requirement, the excess being recirculated together with fresh hydrogen. Catalyst is added to the reactor at the rate necessary to maintain the required rate of reaction. Hydrogenated solution passes through filters which retain the catalyst in the hydrogenator.

Hydrogen peroxide is extracted from the organic solution using counter-current flow in columns fitted with perforated plates. As the organic solution is less dense than water it is fed to the base of the columns. The aqueous product, which is withdrawn at a constant rate, contains approximately 20 per cent hydrogen peroxide. The extracted organic solution passes to a storage tank before being returned to the hydrogenator. The process is thus continuous and cyclic, and it will be seen that the major raw materials are hydrogen, atmospheric oxygen and water.

The new process shows a considerable saving in cost by comparison with the electrolytic method.