

Dr. J. W. Reppe, director of I.G. Farbenindustrie and head of the Hauptlaboratorium at Ludwigshafen, was interviewed with respect to his contribution to the German war effort. He played an important part in the last war (1914-1918) in developing the German process for making mustard gas but has had nothing to do with war gases in this war.

His principal contributions to this war were stated to be:

- a. Synthesis of a substitute for blood plasma called Periston;
- b. An adhesive that makes Buna adhere to fabric and is called Korosin - it formed an essential part of the German synthetic rubber program;
- c. New reactions in the synthesis of butadiene.

Dr. Reppe and his co-workers have developed new processes that involve novel reactions of the acetylenes, olefines and reactions of metallic carbonyls; these developments will probably be of future industrial importance and are discussed below along with other reactions described by Dr. Reppe.

The industrial success of the above acetylene chemistry depended first on the development of safe method and means of handling acetylene ( $C_2H_2$ ) under pressure, and for some of its reactions, and the safe use of large quantities of metallic acetylides - more especially that of copper. Reppe's laboratory has  $C_2H_2$  piped at 30 atm. pressure and plans are made to use it at pressures of 150 atm. Basic

investigations of explosions in compressed acetylene in the absence of oxygen in small bombs showed that the pressures developed to 10 times its initial partial pressure in a mixture and that the large scale application depended (1) on the provision of equipment to withstand such possible pressure increases and (2) restricting possible explosions to rather small volumes. This latter requirement was met in small-scale apparatus by using for a required delivery of acetylene instead of a single pipe a plurality of smaller pipes about one inch in diameter through which more than a given output of acetylene was continuously circulated by looping the lines back to the suction-side of the large capacity compressor and by using one-way bicycle-tire valves at spaced intervals in the lines. In larger installations, the 4-6 inch pipelines were completely filled throughout their length with pipes of small diameter (about 5-10 mm.) to form a sort of honeycomb structure throughout their extent. The latter has worked so well that, in the large plant for manufacturing about 4500 tons per month of butindiol from acetylene and formaldehyde at Ludwigshafen, of the three explosions experienced, only the lines were burnt through in a very small area without further trouble. After these explosions, the tubes were carefully cleaned and reassembled.

Explosions are prevented in large masses of metal-acetylides catalysts by keeping them wet. They are formed in situ by depositing a salt of the required metal, for example the nitrate, on silica-gel pellets and heating the same for conversion of the nitrate to the oxide and thereafter treating them with acetylene under pressure. The only acetylide catalyst in commercial plants is made by reacting copper oxide with acetylene in situ (see butindiol process).

### Acetylene Chemistry.

#### Reactions of Alcohols and Acetylenes.

Dr. Reppe discussed the well-known reaction between acetylene and alcohols and stated that the reaction was quite general for both aliphatic and aromatic alcohols including primary and secondary alcohols, mercaptans and phenols. Potassium hydroxide is employed as the catalyst. Ethers and esters and secondary amines also react with acetylene under pressure. For example, the reaction

between methyl alcohol and acetylene goes very smoothly at about 200°C. to give methyl vinyl ether in the presence of KOH:



Methyl vinyl ether is hydrolyzable at 180°C. with water to give acetaldehyde and methyl alcohol and the latter can be returned to the process.

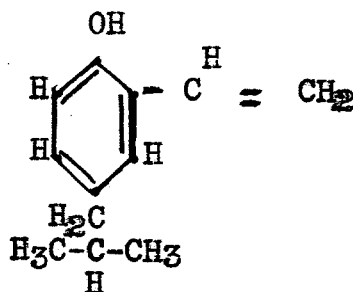
This production of acetaldehyde without a mercury catalyst was considered important for German industry because 2 kgs of mercury are lost in the production of a ton of Buna; however, a plant was never built.

Another important reaction of acetylene and an alcohol is that with phenol, also employing KOH as the catalyst, which gives first phenyl vinyl ether that can convert to vinyl phenol. Depending upon the amount of acetylene substituted on the benzene nucleus, will depend the characteristics of the polymer made from the resultant oxystyrenes wherein the vinyl groups are normally in the ortho and para position to the hydroxy group. To make a resin of the Bakelite type, phenol is reacted with acetylene at a pressure of 10 atm.

Organic zinc salts, for example the naphthenate, are good catalysts for the phenol-acetylene reaction and they can give substituted oxy-styrenes that are solids.

Although the mercaptans, as above mentioned, react with acetylene to give products analogous to those derived from the oxygen alcohols, the products are malodorous and are not of particularly practical value.

Korosin, the adhesive for synthetic rubber, is made by reacting isobutylphenol with acetylene. This was considered an indispensable development in the German synthetic rubber program as this material bound the synthetic rubber to the fabric. It also assists in producing a tire that does not get hot in use. In this case, the acetylene does not form an ether but substitutes for hydrogen on the benzene ring under the influence of zinc naphthenate as the catalyst. The reaction takes place in the liquid phase (Rieselverfahren) forming the hypothetical monomer shown below which, however, polymerizes as formed;



At Ludwigshafen, the I.G. Farbenindustrie has a small plant for the production of vinyl ether especially from methyl alcohol and acetylene. The reaction was carried on in liquid phase at 15 to 20 atm. pressure of acetylene which was delivered to the reaction vessel as a 50-50 mixture with nitrogen; the total pressure in the system was thus about 30-40 atm. The compressors were of the vertically-reciprocating piston type and the connecting rods were enclosed in a transparent case to prevent ingress of dust as a precaution against friction and possible explosion that the presence of dust in the cylinder would cause. The compressors were of the usual type and were capable of delivering 100 and 180 m<sup>3</sup> per hour.

#### Reactions of Aldehydes with Acetylene.

Such aldehydes as formaldehyde, acetaldehyde, propion-aldehyde etc. can be reacted with acetylene under pressure in the presence of metallic acetylides to form unsaturated alcohols. Either one or two molecules of the employed aldehyde can react with the acetylene and the so-formed alcohols have as many carbon atoms as are present in the reacted reagents, for example with acetylene and formaldehyde, there can be prepared both

- (1) Propargyl Alcohol       $\text{HC} \equiv \text{C}-\text{CH}_2\text{OH}$
- (2) Butine 3 diol 1,4  
 $\text{HOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH}$

The reaction is one of the most promising developments of Dr. Reppe and his co-workers. The above alcohols are made by introducing a mixture of reaction products with

sufficient of a 35% aqueous solution of formaldehyde to provide a 10% solution of the latter in concurrent flow into a tower that is packed with copper acetylide (10-12%) deposited on baked silica gel pellets. The catalyst is prepared by depositing  $\text{CuO}$  ( $\text{Cu}(\text{NO}_3)_2$ ) and roasting - it may contain some Bismuth also - and treating with acetylene in situ in the contact vessels in the presence of water at 60-70°C. The reaction may be controlled to make up to 70-80% of the product as propargyl alcohol, but the usual procedure makes 92% of said butinediol and 4% propargyl alcohol. The latter is recycled when only the diol is wanted. The reaction conditions employed are 5 atm. pressure and 100°C. The acetylene is employed in excess and is dry upon entering the process; it therefore evaporates water sufficiently to remove the exothermic heat of reaction. The outlet gaseous mixture from the reactor should be water-vapor and acetylene in the ratio of respectively about 4 to 1.

A plant has been running at Ludwigshafen for two years at a capacity of 4500 metric tons per month of butinediol. In this plant the acetylene is compressed in 2 stages to 5-6 atm. with water-ring centrifugal compressors and the compressed gas (without dilution by  $\text{N}_2$ ) is piped to the honeycomb pipes described above. There are 6 reactors (1.5x 18 m.) designed for 50 atm. pressure which however operate at the above 5 atm. only. They are lined with stainless steel (V<sub>4</sub>A) and have each a volumetric capacity of 20 m<sup>3</sup> of catalyst containing 2000 kg. of copper acetylide. The inlet solution of formaldehyde is dripped (Riesel verfahren) through the tower at the rate of 10 m<sup>3</sup> per hour concurrent to a stream of acetylene of 1 m<sup>3</sup> per hour. The reaction being highly exothermic, the only heating employed is heat exchange in the formaldehyde feed lines. The Leistung is 1 ton of butinediol per cubic meter catalyst per day. The outlet solution from the reactor is distilled to recover 10% unreacted formaldehyde and produced propargyl alcohol which are recycled. Based on formaldehyde, the yield of butinediol is about 98%. There were some difficulties at the beginning of the top of the reactor which were overcome by diluting the formaldehyde solutions, as above described. There have been acetylene explosions in the pipes near the control valve to the reactor, but the only damage was to burn a small hole in the pipe.

The reaction solution contains about 30% butinediol. By evaporation and crystallization from ethyl acetate, the butinediol can be recovered in crystalline form; the butinediol as prepared above in aqueous solution can be hydrogenated while still in such solution to butenediol 1,4 and also to butanediol 1,4 by means of a nickel or copper catalyst at 200-300 atm. by means of circulated hydrogen. The conversion of butinediol 1,4 to butanediol 1,4 by hydrogenation is 96%.

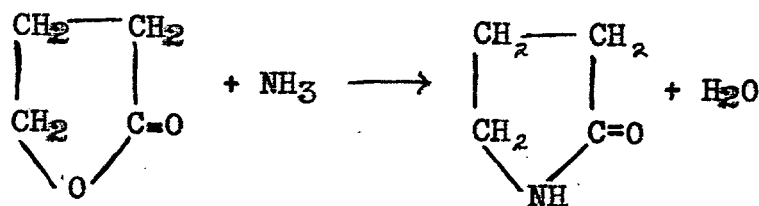
The butanediol 1,4 (n-butylene glycol) can be recovered from the aqueous solution and can be dehydrated in one step to butadiene over a phosphate catalyst as developed by I.G. Farben in 1926. The butanediol is now made at Ludwigshafen for 60 pfg. per kilo and it is expected to reduce this to 40-50 pfg. per kilo.

However, it is preferable because of higher yields and for other reasons according to Dr. Reppe, to dehydrate the butanediol to butadiene in two steps: that is, first to tetrahydrofurane and then the latter to butadiene.

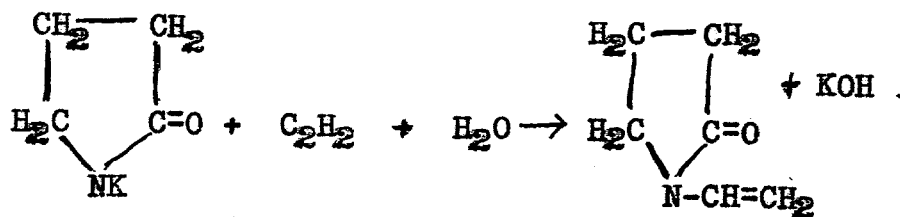
Tetrahydrofurane appears to be an important new building block in synthetic chemistry. It is a good solvent for many types of compounds including also such high polymers as polyvinylchloride, polyvinyl carbazol, natural rubber and Buna. It enters many reactions. Adipic acid can be made therefrom (see below). In the above aqueous solution of 30-35% butanediol 1,4, obtained by hydrogenation of the reaction product of formaldehyde and acetylene, the former can be dehydrated to tetrahydrofurane in said solution by the addition of a small amount of  $H_3PO_4$  and maintaining the pH at at least 2 and distilling the mixture at a temperature of about 260-300°C. and a pressure of 60-100 atm; the THF (tetrahydrofurane) is easily volatilized under these conditions and is quantitatively produced. The Na and Ca ions in the solution added for control of the pH value are substituted by H ions and by ion-exchange media (Wolfatite).

The THF can then be converted at 260-280°C. to butadiene by means of a phosphate catalyst; it can also be treated with metallic carbonyls and converted to adipic acid.

Butanediol 1,4 is also the starting product for the new blood plasma substitute. By oxidation of its hydroxy-groups to aldehydes, by simple spraying over a Cu catalyst at 200°C., by the well-known Cannizzaro reaction, there is produced gamma hydroxybutyric acid and butyrolactone which is the end-product of the reaction, and gamma butyrolactone by reaction with liquid ammonia at 250°C. gives alpha pyrrolidone, as described by Prof. Späth of Vienna, and in accordance with the following equation:



Conversion of pyrrolidone to its potassium salt and the latter's reaction with acetylene, similarly to the known preparation of vinyl carbazole, gives a N-vinyl-pyrrolidone which is the monomer of Periston.

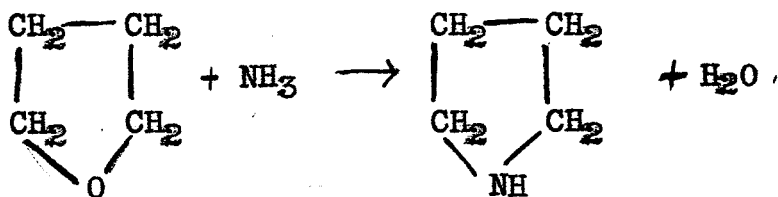


Vinyl Pyrrolidone can be polymerized to Periston by aqueous solution of NaHSO<sub>3</sub> or by oxidation with H<sub>2</sub>O<sub>2</sub> at a temperature of 70-80°C.; the H<sub>2</sub>O<sub>2</sub> is the catalyst and is employed in amounts of 0.05 to 1% plus NH<sub>3</sub> to the extent of 1/4 to 1/2 of the employed H<sub>2</sub>O<sub>2</sub> which determines the degree of polymerization. Periston is neutral, has a high viscosity and is broken down in and eliminated by the human body. It has been used in thousands of German soldiers, but the Allied medical experts have not accepted its use.

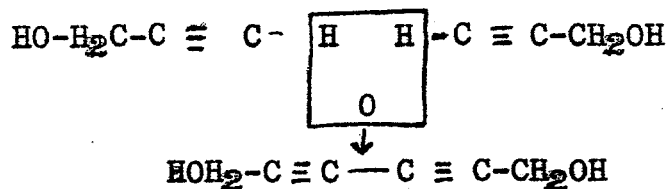
By reaction of NH<sub>3</sub> or amines with THF, it is converted to Pyrrolidine and its N-substituted products; these products are valuable in insecticides and in vulcanization acceleration. The dehydration of pyrrolidine gives pyrrol. The reaction between THF and NH<sub>3</sub> is:

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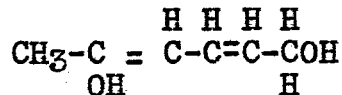
Propargyl alcohol which is made when one mole of formaldehyde adds to acetylene has promising uses. When oxidized with air at 30°C. in the presence of copper chloride, it forms the following:



Hexadiindiol, 2,4 diin, - 1,6 diol.

This latter compound, on incomplete hydrogenation, yields two isomers of hexdienol -

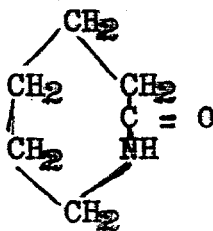
a) Hexadienediol, 2,4 diene, 1,5 diol -



b) Hexadienediol, 2,4 diene, 1,6 diol -



No use is known for the compound (a), but the compound (b) can be converted to either of two Nylon building blocks. It is hydrogenated to hexanediol 1,6 and it then can be oxidized with nitric acid to adipic acid on the one hand, or said diol can be partially oxidized to give epsilon hydroxy caproic acid that easily dehydrates to caprolactone; reaction of the latter with  $\text{NH}_3$  gives epsilon caprolactam which has the following structural formula:



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