

## Reppe Chemistry

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A class of chemicals that have become increasingly important are derived from acetylene and originated with Dr. W. Reppe. The family of reactions, which are collectively called *Reppe Chemistry*, result in a class of materials found commonly in personal care applications including denture adhesive, toothpaste, conditioners, fixatives and many others. This article will discuss some of the salient chemistry and applications. During his career, Reppe was issued some 97 U.S. patents on some basic chemistry, these patents are referenced throughout this work and are available on [www.uspto.gov](http://www.uspto.gov)

Walter Julius Reppe, (1892-1969)

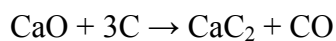


After studying in Jena and München in 1921 Reppe joined the main laboratory of the chemical company BASF. In 1928 he started research on acetylene reactions under high pressure ('Reppe chemistry'). He studied the vinylisation of alcohols, carboxylic acids and nitrogen compounds and developed the technical means for all these processes. He also found a process for the catalytic hydration of acetaldehyde.<sup>1</sup>

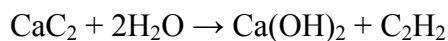
1. <http://www.euchems.org/Distinguished/20thCentury/reppe.as>

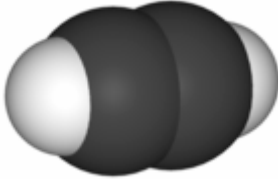
## 1. Acetylene Chemistry<sup>2</sup>.

Acetylene (IUPAC name: ethyne) is the simplest alkyne hydrocarbon, consisting of two hydrogen atoms and two carbon atoms connected by a triple bond. The principal raw materials for acetylene manufacture are calcium carbonate (limestone) and coal. The calcium carbonate is first converted into calcium oxide and the coal into coke, then the two are reacted with each other to form calcium carbide and carbon monoxide:



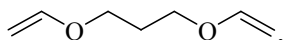
Calcium carbide (or calcium acetylide) and water are then reacted by any of several methods to produce acetylene and calcium hydroxide. This reaction was discovered by Friedrich Wohler in 1862.



Acetylene	
$\text{H}-\text{C}\equiv\text{C}-\text{H}$ 	
<a href="#">Chemical name</a>	Acetylene
<a href="#">Chemical formula</a>	C <sub>2</sub> H <sub>2</sub>
<a href="#">Molecular mass</a>	26.0373 g/mol
<a href="#">CAS number</a>	74-86-2
<a href="#">Density</a>	1.09670E-03 g/cm <sup>3</sup>
<a href="#">Melting point</a>	-84 °C
<a href="#">Boiling point</a>	-80.8 °C
<a href="#">EINECS</a>	<a href="#">200-816-9</a>
	2. <a href="http://en.wikipedia.org">http://en.wikipedia.org</a>

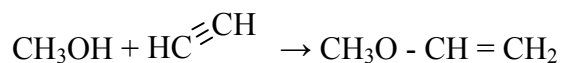
Since acetylene in mixtures with air containing between 3% and 82% acetylene are explosive on ignition. The ability to make derivatives of acetylene under high pressure is no small accomplishment. Reppe's laboratory had acetylene piped in at 30 atmospheres of pressure. First and foremost the process requires the development of safe method and means of handling acetylene under pressure.

Faced with a lack of availability of  $\text{H}_2\text{C}=\text{CH}=\text{CH}_2$  to make rubber, and an availability of acetylene  $\text{HC}\equiv\text{CH}$  the problem became how can one make an alpha omega double bond for polymerization? Reppe Chemistry provided a potential answer and with it a series of new products for the [resonol care market. The material was



#### 4. Reactions of Alcohols and Acetylene – Vinyl Ethers

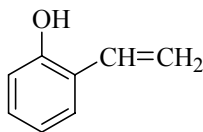
Dr. Reppe and his associates pioneered the now well-known reaction between acetylene and alcohols. The reaction is applicable to both aliphatic and aromatic alcohols, primary and secondary alcohols, and phenols. Potassium hydroxide is employed as the catalyst. Ethers and esters and secondary amines also 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:



The importance of this reaction is the introduction of a vinyl group which is used in subsequent polymerization.

## 5. Phenol – Acetylene Reactions

The reaction of acetylene with phenol, employing KOH as the catalyst, which gives first phenyl vinyl ether that can convert to vinyl phenol.



Commercially, Korosin, and adhesive for synthetic rubber, was 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.

### Vinyl Ether Technology

The following U.S. Patents deal with various aspects of vinyl ether technology;

VE-1	1,941,108	Production of Vinyl Ethers
VE-2	1,959,927	Production of Vinyl Ethers
VE-3	2,017,355	Vinyl Ethers
VE-4	2,021,869	Production of Vinyl Ether
VE-5	2,066,075	Vinyl Esters of Carboxylic Acids and their Production
VE-6	2,066,076	Producing Vinyl Ethers
VE-7	2,118,863	Mixed Polymerization Products
VE-8	2,118,864	Polymerization Products from Vinyl Esters
VE-9	2,157,347	Production of Vinyl Ethers Derived from Carbohydrates
VE-10	2,157,348	Production of Aliphatic Vinyl Ethers by means of Acetylene
VE-11	2,118,945	Mixed Polymerization Products
VE-12	2,118,946	Mixed Polymerization Products
VE-13	2,153,993	Process of Producing N-Vinyl Compounds
VE-14	2,228,365	Process of Producing Vinyl Esters
VE-15	2,978,450	Production of Vinyl Compounds
VE-16	2,716,666	Production of anthranlyl vinyl ethers

## 6. Mercaptan Reactions

Mercaptans, react with acetylene to give products analogous to those derived from the oxygen alcohols.

M-1	2,073,589	Production of Ethane Dithio Ethers
M-2	2,081,766	Thioethers and their Production
M-3	2,094,467	Production of New Thio Ethers
M-4	2,098,759	Production of Thio-Ethers
M-5	2,105,845	Production of Organic Sulphur Compounds
64	3,394,193	Preparation of Mercaptoalkanols

## 7. Reactions of Aldehydes with Acetylene

Aldehydes including but not limited to formaldehydes, acetaldehyde, propionaldehyde 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



The butanediol 1,4 (n-butylene glycol) can be recovered from the aqueous solution and be dehydrated in one step to butadiene over a phosphate catalyst.

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 tetrahydrofuran and then the latter to butadiene.

A key concept in the making of compounds via Reppe chemistry is the ability to convert acetylenic bonds (triple bonds) into ethylenic bonds (double bonds) and into fully saturated materials. The preparation of saturated compounds is relatively easy and can be accomplished using standard hydrogenation, but stopping at a double bonded material is quite a bit more complicated. A series of patents collectively called Technology for Converting Compounds of the Acetylene Series into Compounds of the Ethylene Series, was issued to Dr. Reppe. Specific catalysts capable of selective reaction were developed along with processes for their use. Typical are the following patents.

SH-1	2,207,071	Process of Converting Compounds of the Acetylene Series into Compounds of the Ethylene Series
SH-2	2,207,070	Process of Converting Compounds of the Acetylene Series into Compounds of the Ethylene Series
SH-2	2,267,749	Process of Converting Dihydroxy compounds of the Acetylene Series into Dihydroxy Compounds of the Ethylene Series

#### 8. Tetrahydrofuran

Tetrahydrofuran is an important new building block in synthetic chemistry, as well as 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 from it. 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 tetrahydrofuran in said solution by the addition of a small amount of  $H_3PO_4$  and maintaining the pH at least 2 and distilling the mixture at a temperature of about 260-300° C. and a pressure of 60-100 atm; the THF (tetrahydrofuran) 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 (Volfatite). THF

THF-1	2,251,895	Production of Tetrahydrofuran
THF-2	2,251,835	Production of Tetrahydrofurane from 1,4 – Butylene Glycol
THF-3	2,251,292	Production of Tetrahydrofuran

Butanediol 1,4 is also the starting product for the war time blood plasma substitute. By oxidation of its hydroxy-groups to aldehydes by simple spraying over a Cu catalyst at 200° C. by well-known Cannizzaro reaction, there is produced gamma hydroxybutyric acid and butyrolactone by reaction with liquid ammonia at 250° C. gives alpha pyrrolidene

## 9. Lactams

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 1/2 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.

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 dehydrogenation of pyrrolidine gives pyrrol.

## Conclusion

Despite the fact that Reppe chemistry is rather old, the technology is very impressive as to what type of products can be made and it's versatility.