

UNITED STATES PATENT OFFICE

2,510,550

PRODUCTION OF METHYL ACETYLENE AND
MAGNESIUM ALCOHOLATESAlva C. Byrns, Los Altos, Calif., assignor to
Kaiser Aluminum & Chemical Corporation, a
corporation of DelawareNo Drawing. Application April 7, 1945,
Serial No. 587,205

5 Claims. (Cl. 260—632)

1

This invention relates to chemical processes involving the alcoholysis of magnesium carbide.

Objects of this invention include the production by such alcoholysis of methyl acetylene and of various magnesium alcoholates, and other objects will be apparent on reading this specification.

Difficulties have been encountered in hydrolyzing magnesium carbide by means of either water or acid, and in fact, the difficulties have increased with increase in concentration of the acid. Difficulties have also been met with in alkali hydrolysis. For instance, when water is used as the hydrolytic agent, reaction proceeds so energetically that the material may be heated to incandescence. There is the further disadvantage that gelatinous magnesium hydroxide is produced which prevents penetration of the hydrolyzing agent to the center of the particle with consequent loss of yield. With acid, and even more noticeably with alkali, hydrolysis, considerable hydrogenation of the methyl acetylene occurs due to traces of free magnesium metal which are left at the end of reaction.

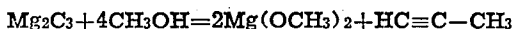
According to this invention it has now been found that the above objects can be attained and the above disadvantages largely avoided by hydrolyzing magnesium carbide by means of a substantially anhydrous alcohol. The presence of small amounts of alcoholate or hydrocarbon in the alcohol is not objectionable.

The magnesium carbide, Mg_2C_3 , which is used in this reaction may be from any available source. It is a stable carbide and its method of preparation as well as its characteristics and behavior are described in the article on magnesium carbides by Rueggeberg, Jour. Am. Chem. Soc., Vol. 65, 602-606 (1943). The magnesium carbide may be prepared for example, by the reaction between magnesium metal and hydrocarbons at elevated temperatures, a range of about 1280 to 1320° F. being generally preferred, with butane or pentane ordinarily being preferred as the hydrocarbon. Natural gas can also be used, as well as other hydrocarbon gases. Some magnesium carbide corresponding to the formula MgC_2 is usually formed but at the temperatures indicated the proportion is very small. Some cracking of hydrocarbon occurs with the formation of a carbonaceous deposit, and some olefins may be formed. The Mg_2C_3 prepared as described always contains, therefore, some impurities, the major proportion thereof being carbon, but the carbide content is usually about 80%. Based upon the magnesium used the yield may be made to approach 100%, so that the magnesium metal content of the product is below 1%. The presence of nitrogen causes some of the magnesium metal to be converted into nitride. When this is not desired, the presence of nitrogen should be avoided. However magnesium nitride reacts readily with

2

methyl alcohol, liberating ammonia gas and giving a solution of magnesium methylate in the methyl alcohol. Such nitride reacts also with the other alcohols as referred to herein. When the magnesium alcoholate is not sufficiently soluble additional solvent therefor is required. The carbothermic dust resulting as a by-product in the production of magnesium metal may be used as the source of the magnesium carbide Mg_2C_3 and thus makes available magnesium values in a by-product of the manufacture of magnesium metal. Such carbothermic dust results where a reaction mass including an oxygen compound of magnesium is caused to react with a reducing agent yielding vaporous products of reduction such as Mg and CO vapors, and the vapors issuing from the reduction zone are extremely rapidly chilled by means of a hydrocarbon gas or other inert chilling agent from a temperature above the dissociation point of any magnesium compound that could otherwise be formed, to a temperature at which the elemental magnesium will not react to form a magnesium compound and will remain in the elemental form. Although specific sources of magnesium carbide Mg_2C_3 are referred to, it is to be emphasized that it may be obtained from any source thereof.

Methyl acetylene and magnesium methylate are produced simultaneously by reacting, for example, one gram of the magnesium carbide Mg_2C_3 with thirty milliliters of commercial absolute methanol (methyl alcohol) in the presence of one milliliter of carbon tetrachloride or similar organic halide, such as chloroform, methylene dichloride, etc., which activates or catalyzes the alcoholysis. The reaction proceeds at room temperature according to the following equation;



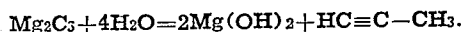
The methyl acetylene is a gas and the magnesium methylate is soluble in the excess of methyl alcohol present, so that separation of the two products is simple. The concentration of the magnesium methylate in the methyl alcohol can be controlled by the proportions of such alcohol present and in this example amounts to about one mol. per liter at room temperature, or more at higher temperatures. The magnesium methylate is crystallized from the solution by chilling, for example to 32° F. or 0° C., with 3 to 4 mols. of methanol of crystallization present. The solution may be recycled when desired, and the presence of some alcoholate in the alcohol for reaction is not disadvantageous.

The proportions of materials used as given above are preferred and they can be varied when it is desired to produce either or both of the products mentioned, but it is generally preferred that the amount of carbon tetrachloride or other activator present does not exceed about five percent. Other alcohols can be used in place of the

methyl alcohol, with the production of the corresponding alcoholate and methyl acetylene in each instance, according to the general equation $Mg_2C_3 + 4ROH = 2Mg(OR)_2 + HC \equiv C - CH_3$, where R designates an alcohol-forming radical. Methyl, ethyl, isopropyl alcohols, ethylene glycol and glycerine, and other alcohols can be used for the alcoholysis of this invention.

Some of the magnesium alcoholates are not as soluble in the corresponding alcohol as the methylate and some may be practically insoluble, and this may result in the formation of an insoluble film of magnesium alcoholate on the surface of the magnesium carbide, which may slow down or interfere with the progress of the reaction. The reaction can then be generally made to progress by the presence of enough solvent for the magnesium alcoholate produced to dissolve it sufficiently to permit the reaction to proceed. Such solvent can be a sufficient excess of the alcohol used.

The alcoholysis reaction is somewhat similar to the hydrolysis reaction according to the equation $Mg_2C_3 + 2H_2O = 2MgO + HC \equiv C - CH_3$ or the equation, if more water is present,



However, such use of water is unsatisfactory because the reaction is too vigorous, and it is even more vigorous if an acidic reagent is used. The reaction mass becomes too hot under some conditions resulting in incandescence, causing decomposition of the magnesium carbide Mg_2C_3 and also of the liberated methyl acetylene. The violence of the reaction can be toned down by diluting the water used with alcohol, that is using an alcohol containing only a small amount of water. The reaction proceeds as an alcoholysis reaction when anhydrous alcohols are used, for which the presence of a catalyst is generally desirable. The reaction of the carbide or nitride with methyl alcohol is mild and easily controlled, and the same is generally true for other alcohols.

Magnesium alcoholates, as is true of magnesium methylate, generally react with any water present to yield magnesium hydroxide and the corresponding alcohol; and when less water is present than is required to form the hydroxide, basic magnesium methylate is apparently formed, and this seems to be the case with respect to some other magnesium alcoholates; so that the presence of water is to be avoided as much as is expedient when it is desired to produce magnesium alcoholate.

Magnesium methylate is useful as a dehydrating agent, particularly for alcohols as well as for other materials; for reaction with alkyl halides to produce ethers; for reaction with fatty acids to produce the corresponding magnesium soaps; for reaction with water to be hydrolysed thereby to produce a chemically pure or United States Pharmacopeia grade of magnesium hydroxide; and for such other purposes as may be desired. The same is more or less generally true of other magnesium alcoholates. The magnesium hydroxide so prepared is very pure; and when calcined yields magnesium oxide which not only is very pure but has exceedingly high surface activity. The methyl acetylene is useful in making resins and propionaldehyde and it has other uses as well, although it has hitherto been more or less of a laboratory curiosity.

The magnesium alcoholate may contain impurities, depending on impurities present in the reagents used to make it. To purify it, the alco-

holate may be dissolved in an excess of the corresponding alcohol, or in other solvent, with the application of heat where it is desired to produce a more concentrated solution, the solution filtered off, and the solute recovered by crystallization or by evaporation of the solvent.

A reaction of alcohol also occurs with the magnesium carbide Mg_2C_3 to produce magnesium alcoholate and acetylene, according to the general equation



where R represents an alcohol-forming radical. This is of interest, for example, when working with carbothermic dust which frequently contains, beside Mg_2C_3 , an appreciable amount of MgC_2 . The mixture of acetylene and methyl acetylene obtained in such a procedure can be treated to recover each constituent separately, when so desired.

What is claimed is:

1. The process of making a magnesium alcoholate and methyl acetylene, which comprises the alcoholysis at room temperature of magnesium carbide corresponding to the formula Mg_2C_3 with an alcohol which is substantially anhydrous, in the presence of an organic halide catalyst.

2. The process of making magnesium methylate and methyl acetylene, which comprises the alcoholysis of magnesium carbide corresponding to the formula Mg_2C_3 with substantially anhydrous methyl alcohol in the presence of a small amount of carbon tetrachloride as catalyst, to form a solution of magnesium methylate in methyl alcohol and gaseous methyl acetylene.

3. The process of making magnesium methylate and methyl acetylene, which comprises the alcoholysis of about one gram of magnesium carbide corresponding to the formula Mg_2C_3 with about thirty milliliters of substantially anhydrous methyl alcohol in the presence of about one milliliter of carbon tetrachloride, to form a solution of magnesium methylate in methyl alcohol and gaseous methyl acetylene.

4. A process of making a magnesium alcoholate and methyl acetylene, which comprises the alcoholysis of magnesium carbide corresponding to the formula Mg_2C_3 with an alcohol which is substantially anhydrous, in the presence of an organic halide catalyst.

5. A process for making a magnesium alcoholate, which comprises reacting an alcohol with compounds selected from the group consisting of magnesium carbide, corresponding to the formula Mg_2C_3 , and magnesium nitride, said reaction being carried out under substantially anhydrous conditions and in the presence of an organic halide catalyst.

ALVA C. BYRNS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,287,088	Cohen	June 23, 1942

FOREIGN PATENTS

Number	Country	Date
279,095	Great Britain	Oct. 14, 1926

OTHER REFERENCES

Zeitschrift fur Physekalische Chemie, vol. 73, pages 513-528 (1910). (Article by Novak).
Contardi "Chemical Abstracts," vol. 31, 4265 (1937).