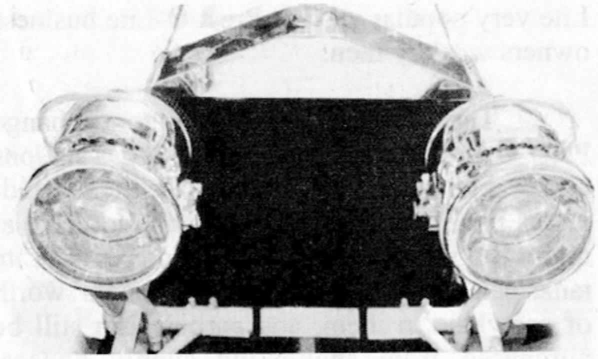


Gas Lights for Motoring

by Bouvard Hosticka

Part II - Fuels

Acetylene:

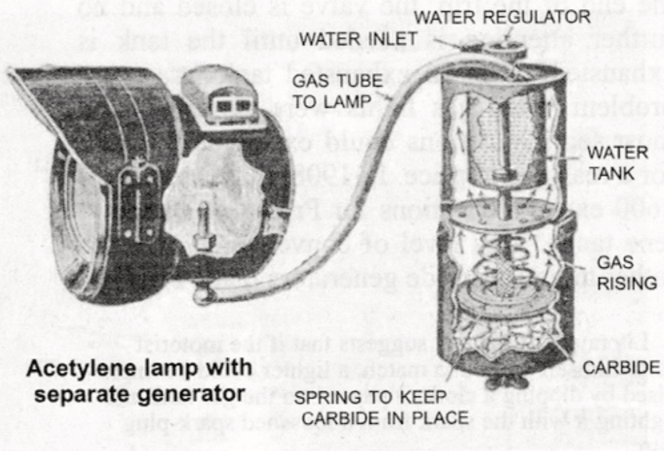
Until modern times, all acetylene (C_2H_2 or more properly, $HC \equiv CH$) was produced by the reaction of calcium carbide with water ($CaC_2 + H_2O \Rightarrow C_2H_2 + CaO$, then another step: $CaO + H_2O \Rightarrow Ca(OH)_2$ i.e. slaked lime). Acetylene is characterized by having a triple bond between the carbon atoms which makes it a high energy, unstable, and very small molecule[1]. Calcium carbide is itself a high energy material so there are no natural deposits of carbide. Instead, carbide is produced by melting and reacting calcium oxide (CaO i.e. lime) with carbon (coke or anthracite) in an electric-arc furnace ($CaO + 3C \Rightarrow CaC_2 + CO$). This reaction is endothermic and the energy of the carbide and ultimately the light from acetylene lamps is electrical in origin. It is no coincidence that the first carbide plant in North America was at Niagara Falls at a time when electricity was easy to produce but difficult to transmit.

It takes about two kilowatt-hours of electricity to produce one pound of carbide. When reacted with water, this pound of carbide will produce about five cubic feet of acetylene.

1 The small size of the molecule results in the low viscosity of acetylene which is about half that of air. This becomes important when using certain types of flow meters.

A lamp using one cubic foot of acetylene per hour will produce about 50 candle-power of light. Electric incandescent lamps produce roughly one candle-power of light per watt of electric power (purely by coincidence). So for 2000 watt-hours of electricity consumed at Niagara Falls to make one pound of carbide, you get the same amount of light from the acetylene produced as you would get directly from 250 watt-hours of electric light. Thus, the efficiency of storing electrical energy in the form of carbide is 12% if used exclusively for lighting as flame. (Where mantels are used, the efficiency is closer to 60 %.)

Even though calcium carbide is a high energy material, it is mechanically and thermally stable and can be broken up with hammers or thrown into a fire with no chance of an explosion. The only concern in handling carbide is that it must be kept dry and away from humid air when stored. Otherwise acetylene will be produced during storage which, if in a closed container, can build up explosive pressures, decompose explosively, catch fire, or all three. Acetylene can be produced at the point of use with small generators or in industrial plants that fill storage tanks. Using acetylene generators mounted to the side of a car, or as part of the lamp itself (self generating lamps), adds an extra level of charm to running under gas lights. There is gratification in loading the carbide and water in the generator, setting the water drip rate to produce the right amount of gas, and cleaning the generator of the residual gunk after use. There is also the continual worry about the



Acetylene lamp with separate generator

water freezing and damaging the beautiful brass-work of the generator. (Solutions of alcohol in water can safely be used as antifreeze in a generator.) The water-carbide reaction is exothermic so both the generator and gas will get hot, hence the cooling water jackets in many generators. The amount of heat produced by generating acetylene from carbide is about one-fifth the heat that would be produced by burning an equal weight of coal. The quest of a perfect acetylene generator kept many engineers employed during the early days of motoring. A simple drip of water onto a basket of carbide tends to create a region of spent chemicals while running on smooth roads with the drip always hitting the same part of the bed of carbide. The lights will dim just when conditions allow for fast driving. But when a rough road is encountered, the carbide in the basket is well shaken causing the slaked lime to fall from the bed exposing fresh carbide. In addition, the drip splashes around making generation efficient, and the lights brighten just when you cannot drive rapidly. Schemes for shaking the basket, lowering the basket gradually into a tank of water, using a diving bell, wicks, or other means to overcome this shortfall as well as attempts to provide automatic regulation to keep a constant brightness of the flame distinguished various manufacturers' generators from each other.

Using acetylene stored in a tank eliminates most of the fussing and fiddling associated with gas lights. All that is required is open the doors of the lamps, open the valve on the tank, light the lamps with a match, and adjust the brightness of the flame with the valve[2]. At the end of the trip, the valve is closed and no further attention is needed until the tank is exhausted. Even an exhausted tank was not a problem when gas lights were prevalent and most service stations could exchange the tank for a reasonable price. In 1908, there were over 2600 exchange stations for Prest-O-Lite acetylene tanks. This level of convenience over the rather tedious carbide generators made Prest-O-Lite very popular and the Prest-O-Lite business owners wealthy men.

The days of being able to exchange Prest-O-Lite tanks or buy carbide at gas stations are long gone, and the users of acetylene headlamps have a dilemma if they wish to drive at night. But all is not lost. Many old Prest-O-Lite tanks can be found that have a few hours' worth of acetylene in them, and carbide can still be purchased from spelunking supply houses. Modern acetylene tanks can be installed vertically, or some old horizontal tanks can be certified.

Copper Acetylide:

Acetylene can react with copper to form explosive metallic acetylides, if used with copper plumbing. This possibility has been known since before 1885, but it does not seem much of a concern in lighting systems. The low pressure of lighting systems as opposed to industrial plants relieves many of the problems of acetylide, and keeping the gas dry (not easily done with small carbide generators) further reduces the chance of acetylide formation. The gas from a generator as found on an automobile is usually saturated with water, and it tends to condense out when the warm gas hits the cool pipes leading to the lamps. Water traps just downstream of the generator and others near the lamps are used to keep the system clear of standing water but the gas is not really dry. To be in accordance with theory, all metal in an acetylene system should be either yellow brass, aluminum, or iron so that copper acetylide cannot form under any combination of moisture and pressure. In practice, no alloys containing more than 70% copper should be used in high pressure systems, and this should also be observed on low pressure systems when generators are used without some scheme to desiccate the gas. Common copper tubes and fittings can be used on the low pressure side of Prest-O-Lite systems, and the original plumbing on some cars is plain copper.

2 Literature of the day suggests that if the motorist finds himself without a match, a lighter could be improvised by dipping a cloth or paper into the gas tank and lighting it with the spark from a loosened spark-plug wire.

The Dissolved Acetylene System:

The scheme for safely storing highly unstable acetylene in tanks is a remarkable invention. Although it was first tried in France, it was perfected by Gustaf Dalen in Sweden to provide lights for remote lighthouses. Mr. Dalen was awarded the Nobel Prize for physics in 1912 for his work.

The Problems:

Acetylene itself is unstable, and a shock can cause it to decompose into hydrogen gas, carbon, and a lot of heat. Once started, the reaction can cascade into a continuous decomposition reaction heating the resultant hydrogen gas and producing pressures that no practical tank can withstand. The total quantity of gas does not change as a result of decomposition, but the elevated temperature increases the pressure of the gas. Decomposition eventually leads to an explosion, if there is sufficient acetylene around to sustain the reaction. It is easier to define 'not-enough' than 'sufficient' for the set of conditions that can lead to a decomposition explosion. Acetylene gas with a pressure less than two bars will not sustain the decomposition reaction even though there might be local decomposition[3]. The soot often seen inside torch heads and hoses indicates that decomposition has occurred, but if the hose did not burst and the torch is not blown to pieces, the reaction did not get out of hand. All acetylene gas regulators are designed to keep the pressure from ever exceeding two bars. This gives us one way to handle acetylene safely: i.e. limit the pressure. Lamps operate at about 2½ inch water column over atmospheric pressure (1 bar) so that the acetylene in the plumbing (and generator) of the car is about half that needed to support an explosion. Another way to prevent an explosion is to limit the volume of gas that has a pressure above two bars. Even if a decomposition reaction gets started, it cannot spread beyond the available volume of gas. To this end, high pressure plumbing should be small diameter, and the free volume of the high pressure side of regulators is limited. It is interesting to note that the British Navy experimented with using liquid acetylene in bottles at 50 bar for lights on navigation buoys[4]. This is the worst possible thing to do by our modern reckoning since liquid and solid acetylene are just as unstable as the pressurized gas. There were no explosions incidental to the experiment. Tests were done where the tanks were repeatedly dropped from 20 feet onto a steel surface with no explosions. But when hit with a 'crushing blow,' an explosion occurred. At the turn of the century (1899) the British Home Office considered any acetylene stored at more than 20 inch water column pressure as falling under the Explosives Act. Just because some tests show that it did not explode under certain circumstances does not mean that it is generally safe.

Acetylene can be dissolved in acetone to the extent of 23 volumes of acetylene (gas) per volume of acetone (liquid) per bar of pressure at 70°F. For comparison, carbon dioxide can be dissolved in water to form fizzy drinks to the extent of less than two parts CO_2 to one part water by volume at one bar pressure. The solubility of a gas in a liquid is linear with pressure. Dissolving the gas in acetone is the key to safely storing acetylene, but it is only half the story. Consider a standard Size B tank that has a physical volume of 0.28 cubic feet. If this were filled with acetone saturated with acetylene at two bar pressure (the safe limit), you could extract out only 6.4 cubic feet of gas (remember that when the tank is 'empty' it still has one atmosphere of pressure in it). This would give about four hours of lighting with two 3/4 cfh burners. With a purely liquid acetone-acetylene system, it is not practical to take it to high pressure since the solution shrinks as the acetylene is drawn off creating a free volume of high pressure gas

3 When dealing with acetylene, the BAR seems the appropriate unit of pressure. One bar is 14.5 psi or roundly one atmosphere pressure. During this discussion, bars are referenced to a vacuum and other pressures are referenced to atmospheric pressure. One psig is equal to 27 inches of water column pressure.

4 As with all gases stored as liquids in bottles, these acetylene tanks held a two-phase, saturated state where the pressure is defined by the temperature, not by the quantity of liquid or gas in the tank. The 50 bar pressure represents a temperature of about 82° F.

which is explosive. In reality, Size B tanks hold about 40 standard cubic feet of gas with safety[5]. So a more complicated scheme than just dissolving the gas in acetone must be used.

If the tank were completely filled with a porous substance, the free volume of acetylene that is within any pore would be so small that if a decomposition reaction started, it would not generate much heat or pressure and thus the decomposition would be isolated to the particular pore where it started. The pores also have a huge surface-to-volume ratio so it is effectively cooled by the pore walls and its neighbors. If decomposition starts, it cannot spread beyond the few adjacent pores. This is the other half of the scheme. The tank is filled with a porous mass which has between 80% to 90% free volume that is divided into a myriad of small pores, each a few microns in diameter. The acetone is adsorbed on the surface of these pores like water on a damp sponge. The acetylene is then dissolved in the adsorbed acetone.

Almost everything imaginable has been tried at one time or another for the porous mass. Corn cobs, diatomaceous earth, fire-brick, asbestos, and modern calcium-silicate are a just a few masses that have been tried. Mr. Dalen developed the AGA Mass which was the standard through most of the 20th century consisting of a concrete filled with charcoal and asbestos. The charcoal gives high porosity while the asbestos strengthens the cement. It is important that the porous mass fill the entire tank with no voids or cracks for it to be effective. A crack or settling of the mass can lead to large open volumes where free acetylene under full bottle pressure can accumulate. Such cracks in the porous mass have led to explosions. Modern regulations in the U.S. require that the mass be tested once sometime between its 5th and 20th year from date of manufacture (or before 2011 for older tanks).

It is a simple matter to calculate the amount of acetone within a properly filled tank.

[5] The 40 cu. Ft. rating for a Size B tank is the amount that is delivered by the tank. Since there is about 5.6% residual gas left in the tank when empty, the tank holds closer to 42 cu. Ft. when full.

A Size B tank with a free volume of 0.28 cubic feet (cu. Ft.) holds 42 standard cu. Ft. of acetylene under a pressure of 18 bar (250 psig) at 70°F. Thus the amount of acetone is equal to: 42 cu. Ft. acetylene divided by 23 cu. Ft. acetylene per cu. Ft. acetone per bar, divided by 18 bar which gives 0.10 cu. Ft. acetone. The solution of acetylene in acetone at 18 bars occupies about 1.8 times the volume of pure acetone so the liquid portion of the system is about 0.18 cu. Ft. The solid portion of the mass is generally about 0.04 or 0.05 cu. Ft. which leaves 0.05 cu ft of free space within the pores to hold gaseous acetylene. The only effect of having less than the rated amount of acetone in a tank is that the tank will hold less than its advertised quantity of acetylene when at 'full' pressure. It is worth noting that as the gas is drawn off, the absolute pressure falls linearly with the amount removed, but since the bottle is empty when it still holds one atmosphere of pressure, the half-way point between a full bottle at 250 psig and an empty bottle at 0 psig is 140 psig rather than 125 psig as might be expected.

The solubility of acetylene in acetone is a strong (inverse) function of temperature. It is more soluble at low temperatures than at high temperatures so the pressure in the tank is also a strong function of temperature. The normal gas laws do not apply to acetylene tanks. A full tank is defined as being at 250 psig at 70°F (with the appropriate amount of acetone). The same tank will read 150 psig at 32°F and 350 psig at 100°F. At 0°F, the pressure in the tank will be half of what it is at 70°F but this has little effect on the amount of gas that can be extracted from the tank, or in turn, how long the lamps will run on a tank. It is the amount of acetylene in the tank when it is empty that is important. The amount of residual gas is small at 70°F and twice as much at 0°F but still a small amount. A Size B tank will light a pair of ¾ ft burners for 27 hours at 70°F or 25 hours at 0°F.

It takes a considerable amount of time for the acetylene to come out of solution and defuse through the porous mass to the valve where it can be drawn off and used for lighting. The warmer it is, the faster it comes out of solu-

Figure 7. ***Advertisement from a January 1905 issue of Motor Age. This is a very early mention of dissolved acetylene for automobile use and shows the minimum duration of 14 hours based upon the maximum draw rate of seven percent of the nominal volume per hour.***

tion (think back to CO_2 in fizzy drinks). The safe sustained withdrawal rate for cylinders at room temperature is generally given as 7% of the full volume per hour before entrainment of acetone in the gas becomes a concern. This is why a the 1905 advertisement in Figure 7 for dissolved acetylene states that it provides 14 to 80 hours of illumination depending on the size of the tank and the number and sizes of the burners. The 14 hours corresponds to a 7%/hr withdrawal rate and is the fixed minimum burn time for any dissolved acetylene system. The 7%/hr rate is at room temperature, but at freezing temperatures, the safe withdrawal rate is only about 4%/hr. A Size B tank can thus support a pair of lamps even in winter and is the size used on most cars[6].

Drawing acetylene from solution is endothermic, and the bottle absorbs heat and cools when gas is slowly drawn off. This cooling together with the time that it takes for the gas to come out of solution results in a low pressure reading on the tank during use that will recover when the tank is allowed to warm to equilibrium after the gas is shut off. Putting the acetylene into solution evolves heat, and the bottles tend to get hot and must be cooled while being filled for this reason.

S.K.

6 There was a Short B size made especially for running board or tool box mounting that held about 30 cu. Ft.

Next Month:
Fuel Tanks for Gas Lighting