is that there is no easy road to efficiency in government. All of us—scientists, business men and lay public—must take an active and continuous interest in government—federal, state and local. We must inform ourselves on the issues involved in succeeding campaigns. We must elect honest, public-spirited and able servants. We must if possible make public office-holding—all along the line—a high calling, a worthy and rewarding career for any one. But this can not be fully accomplished until the federal government is so organized as to permit and foster thinking on the part of our representatives in terms of the national welfare as a whole rather than in terms of sectional and local special interests.

WARTIME CHEMICALS FROM NATURAL GAS. II

By Dr. GUSTAV EGLOFF
DIRECTOR OF RESEARCH, UNIVERSAL OIL PRODUCTS COMPANY, CHICAGO, ILLINOIS
PRESIDENT, AMERICAN INSTITUTE OF CHEMISTS

With the number of research men in the field of synthetic rubber, with expenditures of millions of dollars yearly, one can feel confident that synthetic rubber tires will evolve with a life of at least 100,000 miles or, expressed another way, the tires may well outlive the motor car.

As far as the author is concerned, synthetic rubber in the United States is here to stay and will be a permanent industry during the next peace period. With the fall of Singapore our greatest source of natural rubber was cut off. Natural rubber (December, 1941) cost about 22 cents per pound. The price ranged through the years from 3.5 cents to over one dollar per pound. It can be stated that synthetic rubber in mass production will cost less than 15 cents a pound.

Does this mean that natural rubber will not have its uses? As far as tires are concerned, it will not have the dominating position it has held heretofore. One may be certain that as good as synthetic rubber is to-day, it will be far surpassed by that yet to come. The properties of the rubber desired will be under close chemical control based upon the high purity of the components started with, catalyst and precise conditions to yield the finished product. Natural rubbers vary widely in properties, due to many factors. Producers of natural rubber depend upon the life cycle of the rubber tree, climatic and soil conditions, while the chemically produced rubber will have the exact properties for which its structure and use was designed. Natural rubber contains a number of unknown components, whereas synthetic rubber has one, two or three components of known characteristics.

Natural gas is an important source of high explosives. Natural gas in some parts of the country is being cracked into hydrogen, which is combined with the nitrogen from the air, producing synthetic ammonia. The ammonia is readily oxidized with air into nitric acid. Combination of the ammonia and nitric acid produces ammonium nitrate.

In World War I the maximum toluene production was at the rate of 15,000,000 gallons a year, and practically all came from coal carbonization plants to derive coke for steel making, with toluene as a by-product. The toluene production in World War II from coal carbonization is at the rate of over 25,000,000 gallons a year. According to published reports the demand for toluene is from 250 to 300,000,000 gallons a year—the difference between the volume of toluene from coal and the total demand will come from petroleum, *i.e.,* ten to twelve times as much from petroleum. In comparing the two wars the increased demand for toluene is from sixteen to twenty times. On a T.N.T. basis World War I called for 150,000,000 pounds, whereas the present war calls for 3,000,000,000 pounds a year. Benzene is readily converted into carbolic acid or phenol through chlorination and hydrolysis. Combine the phenol with nitric acid and pictric acid is the result, a high explosive, and when synthetic ammonia reacts with picric acid, ammonia picrate is formed, another high-grade explosive. The ammonium picrate is relatively stable, but when picric acid is used, it reacts readily with iron to form iron picrate, a very unstable compound that has a habit of exploding when least expected. That is what happened in a number of plants in World War I.

Many natural gases contain hydrogen sulfide, which when oxidized with air is converted to sulfuric acid necessary in so many arts, particularly high explosives. A number of commercial units are producing sulfuric acid based on hydrogen sulfide or elemental sulfur produced from natural gas as a starting material. So we have sulfuric and nitric acid, both produced from natural gases, raw materials necessary for high explosives needed in this present war, some of which are on a scale over twenty times that of World War I.

An important substance in war is glycerine for the production of trinitroglycerine, the commonest form of which is dynamite. The main source of glycerine has been in the splitting of fats to glycerine and fatty acids in the soap-making industry. As is well known, a campaign is on for the conservation of cooking fats of all kinds which has been requested by our government. These fats have many uses, one of them being the manufacture of soap and glycerine. A few years ago a glycerine-making process was developed by the petroleum industry starting with propane or propylene, which are chlorinated and then hydrolyzed to glycerine. The glycerine is then nitrated to trinitroglycerine.

Nitroparaffins from natural gas may well develop into one of the newer and valuable sources of high explosives. Methane gas when nitrated produces tetranitromethane. This compound is the most destructive explosive known to man. This product is a very high explosive, extremely difficult to handle. About twenty years ago in a university laboratory in Switzerland, they were working with tetranitromethane, which is usually a reaction product of toluene nitration in small concentrations. Ten grams of tetranitromethane killed ten individuals, wounded twenty and nearly wrecked the building. Unfortunately, no commercial process has been worked out to make this product available for use by our forces. Fig. 1 shows the importance of nitro compounds in the manufacture of explosives.

Nitro Compounds[2]

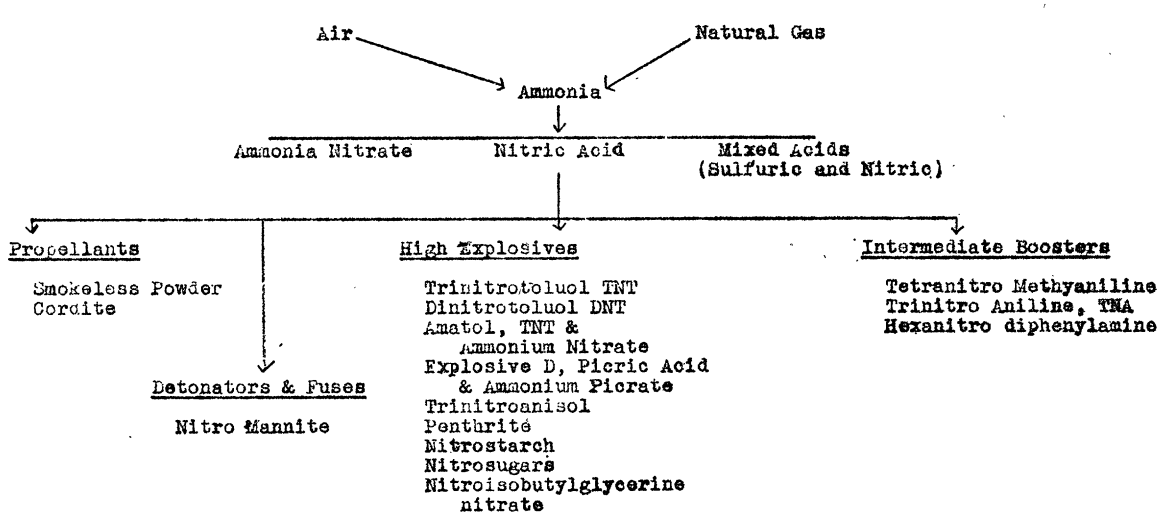

FIG. 1.

Anesthetics are vital in a world at war. One of the primary needs of the medical profession has been anesthetics which do not have post-operative dangers due to pneumonia and nausea. Ethylene has been shown to have properties superior to those of ether and nitrous oxide. Deep surgical anesthesia is readily induced by ethylene and insensibility to pain comes rather quickly. A general feeling of well being and comfort with no harmful after effects is present when ethylene is used. Cyclopropane, although known since the year 1882, was still a laboratory curiosity until the end of 1930, when it was first applied in human anesthesia. It has been rather widely adopted since as being one of the safest anesthetics. Cyclopropane produced from either propane or propylene by a series of chemical reactions is less explosive in the hospital than either ether or ethylene.

Olefins have been investigated as fruit-ripening agents and for use in inducing an accelerated plant growth. The first gas to be utilized for this purpose was ethylene, which was first used in an impure form —the fumes from a kerosene stove were found to be effective in bringing about the ripening of citrus fruits. Ethylene was the agent responsible for the ripening.

Ethylene and propylene stimulate potato growth, and have been found to shorten the growth season for tomatoes, grapefruit and oranges. The German Botanical Society reports that up to a 100 per cent. increase in the yield of potatoes can be obtained when the seeds are treated with ethylene gas. "The tubers of plants grown from seed potatoes which had been exposed for twenty-four hours to atmospheres containing 7.5, 15 or 30 per cent. gas at 65° F. were more numerous, larger and richer in vitamin C. It is claimed that this process is cheaper than the application of hormones."

Researches by the Russians on butylene gas showed a stimulating effect on the maturing time of such trees as the walnut, peach, apple, cherry, plum, apricot and pear. In periods when the season is too short to allow the full maturing, due to winter weather being so prolonged that flower formation and fruit setting are delayed, butylene may be used to hasten the growth period. The procedure adapted to plant treatment consists of enclosing the trees in tents or gastight covers for about two weeks before the normal or desired leafing, *i.e.*, start of the growth cycle. Butylene is passed into the tent in about one part per 100,000 parts of air, at temperatures between 69° and 100° F. for a period of one to two hours.

Another method for ripening fruits is to use pentylenes, hexylenes and heptylenes from cracked gasoline. Addition products of the unsaturated hydrocarbons derived from cracking, such as ethylene di-iodide, ethylene butyrohydrin, ethylene acetohydrin and ethylene formohydrin are also used as agents for furthering the ripening of fruit.

The skin of the green fruit absorbs the olefin or olefin derivative, destroying the chlorophyl. The advantage in using liquids as ripening agents is that they are absorbed and continue their action after removing the fruit from the liquid; after storage under normal conditions, the ripening is complete.

Natural gas hydrocarbons can be used as basic materials for the synthesis of plastics after forming olefinic hydrocarbons. There are three basic reactions which in various combinations are used to produce plastics from the derived hydrocarbons; they are oxidation, halogenation (mostly chlorine is used) and polymerization. Stemming from these reactions, the entire plastics industry has built up new materials and replacement products for many structural materials and rubber. Fig. 2 shows some of the derivatives of the unsaturated hydrocarbons from natural gas.[2]

The materials which are outlined in the chart have many uses besides plastics as the intermediates shown are a typical cross section of the chemicals derived from natural gas. The finished plastics, as well as the intermediate compounds, find use as paints, varnishes, addition products for lubricating oils and molded materials. Their intermediates are used as solvents, cleaning agents, and as additives for various types of products.

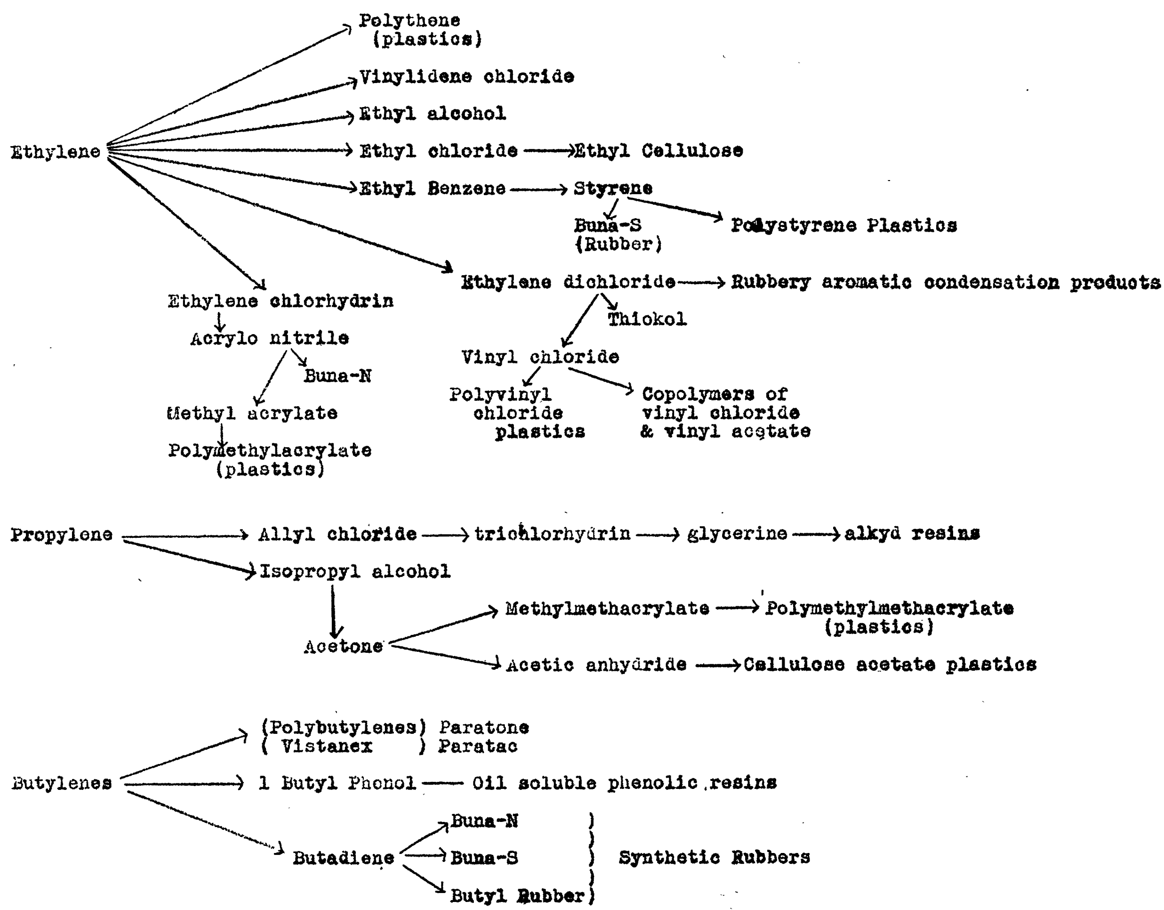

FIG. 2.

The coming importance of plastics can not be overemphasized at this time, since airplane manufacturing is calling for more of the plastics for use in plywood planes. Steel now used in many places is being replaced by plastics. In the war industries where the fabrication of planes takes place, the methylmethacrylate resins are used as the transparent non-shatter-

[2] R. L. Wakeman, *Nat. Petroleum News*, July 23, 1941, p. R-226.

able parts where great visibility is necessary, and this will undoubtedly be used by the automobile industry after the war is over. A high degree of visibility from all over the motor car will be worked into the new design requiring less supporting frame work, and a clear vision rooftop with sliding window will undoubtedly take the place of present designs. In fact, the motor car of the future may well be substantially all plastics.

At the present time any of the components necessary for the manufacture of plastics of all types can be made from natural gas. One of the important substances for the Bakelite type of plastic manufacture is formaldehyde, made largely from the methanol or wood alcohol by the catalytic reaction of carbon monoxide and hydrogen at high pressures. For a number of years formaldehyde and methanol have been produced from the oxidation by air of natural gas. This process can be readily expanded to produce all the formaldehyde necessary in the ever-expanding Bakelite program. The phenol or carbolic acid and cresols, etc., are also potentially available from natural gasoline.

One big field of research and development that merits discussion is carbon monoxide and hydrogen or the water gas reaction to form hydrocarbons. In the United States we have over 2.6 trillion cubic feet of natural gas yearly production. This gas contains about 90 per cent. of methane which can be converted into carbon monoxide and hydrogen by high temperatures in the presence of steam. In Germany the Fischer-Tropsch process has been developed to produce oil from carbon monoxide and hydrogen at the rate of about 15,000,000 barrels a year. The hydrocarbons produced are methane, ethane, ethylene, propane, propylene, butanes, butylenes, gasoline, gas oil and Diesel oil to solid paraffin wax. The reaction takes place in the presence of a catalyst, which may be oxides of nickel, chromium or cobalt, using temperatures of 400° F. and pressures of the order of 200 pounds.

The gasoline produced by the water gas reaction is poor in quality with about a 40 octane rating. The gasoline has to be cracked thermally or catalytically into higher octane fuel. The gasoline fraction boiling up to 300° F. contains olefins which polymerize with each other to form lubricating oil. These lubricating oils are produced commercially in Germany and some of them are high grade. The balance of the gasoline fraction, the paraffins, hexanes, heptanes, octanes may be thermally cracked under controlled conditions to make more olefins which in turn are converted into lubricating oil by polymerization. A portion of the synthetic oil is a high grade Diesel oil with octane number of over 100. The Diesel oil fraction is blended with lower grade Diesel oils to improve its quality.

Paraffin wax, which is also derived from the water gas reaction, is oxidized with air to make fatty acids. The fatty acids are reacted with potassium or sodium hydroxide, and soap is produced. The last report out of Germany is that one small cake of soap is allotted per inhabitant per month, and much of it comes from this paraffin wax. In 1938 and previous years also, conversion of paraffin wax from the water gas reaction, coal carbonization, and petroleum, was carried out forming fatty acids. In addition, these fatty acids are combined with synthetic glycerine to make fats for food. Glycerine and soap are produced (U. S.) from the splitting of fats, but the Germans are reversing the process in order to produce edible fats for food. It is not the type of fats to which we are accustomed, but it is helpful under the critical food conditions existing in Europe.

An enormous amount of research is going forward in a study of natural gas and gasoline to enhance their importance in the war effort—through solvents, plastics, high explosives, acetylene, synthetic rubber, lubricating oils and aviation gasoline. As a matter of fact, if one starts with methane gas alone, all the known synthetic products that man has produced in organic chemistry can be derived, and there are over 500,000 different ones. Any synthetic product desired can be produced at a price; the hydrocarbons are all potentially available to be converted into the manifold products that man requires in a modern world.

SCIENTIFIC EVENTS

THE GUJARAT PREHISTORIC EXPEDITION

ACCORDING to *Current Science,* Bangalore, India, a press communiqué from the director-general of archeology in India makes the following report:

The Archeological Department has recently organized an expedition for the study of the prehistory of Gujarat with the cooperation of a number of institutions and scholars. Although the department has hitherto organized systematic work on a large scale at sites belonging to the historic and prehistoric periods, particularly in Northern India, the occurrence and sequence of the earlier stone age cultures were not brought within the purview of its activities. Much interest has recently been taken in this subject, particularly since the British-American expedition led by Dr. De Terra, of Yale University, worked on