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Rubber Plantation, 1944 Style

By ERNEST GRABILL, CH.E. III

"Of all critical and strategic materials, rubber is the one which presents the greatest threat to the safety of our Nation and the success of the Allied cause. Production of steel, copper, aluminum, alloys, or aviation gasoline may be inadequate to prosecute the war as rapidly and effectively as we could wish, but at the worst we still are assured of sufficient supplies of these items to operate our armed forces on a very powerful scale. But if we fail to secure quickly a large new rubber supply our war effort and our domestic economy both will collapse. Thus the rubber situation gives rise to our most critical problem."

That was how the Baruch Rubber Survey Committee put it when it reported to the Nation that its fate depended upon a rubber supply. With 35,000,000 automobiles registered in the United States, it required three-fourths of the total rubber used in this country to keep them rolling. Yet, it took a disaster like Pearl Harbor and the few months ensuing, when 90 per cent of our rubber supply was cut off, to make the average American realize how vital rubber is to our national economy and to the prosecution of a war.

Practically overnight, the materialization of huge quantities of rubber from nowhere in particular became an extremely important problem. Since it was clear that the problem was one which we alone had to solve—our Allies could not supply us—every possible source of rubber was investigated, and investigated thoroughly. The reader may remember the numerous experiments made on the Russian dandelion, on the Guayule plant, and many other potential sources to which we might turn. But every investigation, from the standpoint of speed and quantity, pointed to the one answer: "synthetic" rubber.

The name "synthetic rubber" is an unfortunate misnomer, as there is no such thing as synthetic rubber, but the term is the only one which adequately describes the product resembling rubber in springiness and appearance. Experimental work has been done on synthetic rubber in the last fifty years, but the vast supplies of natural rubber discouraged use of the synthetic material. In fact, not until the last ten years or more, has serious work been done on synthetic rubbers. Germany and Russia led the experimentation, but as early as 1925, the late Father J. A. Nieuwland of Notre Dame University and a young chemist by the name of Bolton, now Chemical Director of E. I. du Pont de Nemours & Company, became interested in the subject of synthetic rubber. Only a short time before, the noted Dr. Kurt Gottlob, Germany's eminent rubber scientist, had said that synthetic rubber was no longer practicable from the technical stand-
This flowsheet shows the process for the synthetic rubber being produced on a large scale at the present time.

Natural rubber is thought to be a polymer of about 15,000 units of isoprene, having the formula:

$$\text{CH}_2=\text{C}—\text{CH}=\text{CH}_2$$

Chloroprene, then, substitutes a chlorine atom for the methyl group on the second carbon atom:

$$\text{CH}_2=\text{C}—\text{CH}=\text{CH}_2$$

Cl

Chloroprene is a more desirable "rubber" than rubber itself, in that natural rubber is a hydrocarbon; it is soluble in other hydrocarbons of its own kind. When a halogen such as chlorine is substituted in the molecule, it becomes insoluble in these hydrocarbons. Thus chloroprene, or neoprene, as the commercial du Pont product is called, is decidedly superior to natural rubber where it is to be used around greases, oils, gasoline, and chemicals.

You may ask why neoprene is not being used more in the Government rubber program. The answer is that every ounce of neoprene being produced today is allotted for essential military and civilian needs, but that neoprene does not measure up to one of the requirements for the program—that of cost. Neoprene requires for its production very large amounts of electric power, being comparable to aluminum in this respect. The construction of neoprene plants requires large tonnages of structural steel, copper, bronze, and special corrosion resistant alloys. For these reasons the quantity of neoprene involved in the Government synthetic rubber program is limited to that required for purposes for which the more readily available synthetic rubbers are inadequate. Neoprene production is now about ten per cent of the prewar rubber consumption.

Having eliminated, one by one, the various synthetic rubbers, the search narrowed down to the butadiene "rubbers", Buna-N and Buna-S. A conference of government officials and representatives of the leading oil, rubber, and chemical companies was held in the summer of 1940 to discuss the possible production of a synthetic rubber of the butadiene type polymer if the need should arise, as it did a year later. It was there that it was decided that Buna-S would be the synthetic made in any large scale program because of five reasons:

1. It can be made quickly.
2. It is a type with which rubber-processing companies already had some experience, and it could be processed with present factory equipment.
3. It provides good tire life.
4. It is useful for other things besides tires.
5. It is made from raw materials that are plentiful in America.

Buna-N was decided against because there was no cheap way of producing acrylonitrile, the important co-polymer with butadiene (the "N" part of Buna-N) and producing it quickly.

Buna-S rubber is made from two main ingredients, butadiene and styrene. Butadiene is a gas (boils at $-3^\circ\text{C}$) and styrene is a clear liquid.
boiling at 146°C. Butadiene itself polymerizes
to give a rubber-like substance:
\[ x(CH_2=CH-CH=CH_2) \rightarrow \]
\[ -CH=CH-CH=CH_2 | CH_2 \_ etc. \]
But butadiene rubber built up in this way is too
stiff; it isn't soft and pliable like natural rubber.
A more desirable product is obtained if we in-
corporate into this structure other kinds of
units, styrene units giving us the most economical
and best all-round synthetic, everything being con-
sidered. The polymerization
\[ x(CH_2=CH-CH=CH_2) + y(C_6H_5-CH=CH_2) \rightarrow \]
\[ -CH=CH-CH=CH_2 | CH_2 \]
butadiene + styrene \( \rightarrow \) butadiene units
unit unit
takes place with ease and the resulting product
is crude Buna-S. \((x \text{ and } y \text{ in the above equation}
\text{ are usually in the ratio of about six to one, i.e. six}
\text{molecular units of butadiene to each unit of)}

The alcohol process had three important ad-
\[ \text{vantages:} \]
\[ \text{(1) It could be applied with the smallest} \]
\[ \text{amount of critical materials for the plant.} \]
\[ \text{(2) It could be put into production in the} \]
\[ \text{quickest possible time.} \]
\[ \text{(3) It would produce butadiene of exception-
\text{ally high purity.}} \]
It probably should be emphasized here that the
ethyl or "grain" alcohol required for this pro-
cess is obtainable from many different sources.
It is available from the fermentation of natural
products: potatoes, sugar, molasses, grain, or
farm and wood wastes. It is made synthetically
from natural gas, refinery gas, or petroleum.
Thus our rubber plantation of 1944 and the
future may be anything from an oil well to a
cornfield. The end result will always be high
quality butadiene. (Incidentally, if all the alcohol
were made from the fermentation of corn, one
plant in West Virginia would require the yield
of about 520,000 acres or 800 square miles each
year.)

Alcohol is shipped to a butadiene plant by rail-
road tank cars or by barge. It first passes through
two sets of converters where catalysts convert it
into crude butadiene. The crude butadiene is
then purified by distillation and washing until
it is over 98.5 per cent minimum purity. Be-
because butadiene is a gas at ordinary tempe-
\[ \text{ratures, it must be kept cool and kept under pres-
\text{sure to facilitate handling it as a liquid.} \]
The production of styrene depends upon one
raw material—coal. From the distillation of
coal, benzene is obtained. From coal gas (or
petroleum gas) ethylene gas is derived. These
are the two basic ingredients of styrene. The
benzene and ethylene are combined to produce
ethyl benzene. Then by the use of heat, pres-
sure and catalysts, ethyl benzene is converted
into its chemical "cousin", the liquid styrene.
\[ \text{(Continued on page 20)} \]
At the polymerization plants, these two chemicals, butadiene and styrene, are polymerized into the long chain polymer of Buna-S rubber. One of the major differences between Buna-S and natural rubber is that a pure gum stock prepared from Buna-S possesses much lower tensile strength than one made from natural rubber. But the incorporation of various carbon blacks produces much greater reinforcement in Buna-S than in the case of natural rubber. Consequently, practically all Buna-S contains some form of carbon black. It is essential for good milling, as Buna-S does not smooth readily on the mill. A cool mill is necessary and overmilling must be avoided. Buna-S requires lower sulfur and higher acceleration ratios in its vulcanization than natural rubber. The thiazole accelerators seem to be the most satisfactory type, the rate of cure being nearly the same as for natural rubber. The sulfur ratios lie in the range from 1.75 to 2.25 (based on 100 parts by weight of Buna-S). Higher concentrations lower elongation and tear resistance and harder, stiffer stock result. Lower concentrations produce stocks having lower efficiency.

A co-polymer of Buna-S has been produced showing a tensile strength of 4000 pounds per square inch, although materials being made available commercially in the future will show tensile strengths of 2500-3500 pounds per square inch. At the present, the production of readily processable polymers is done at somewhat of a sacrifice in tensile strength. While this looks serious to the inexperienced person, it ought to be stressed that the application of laboratory tests for rubber to these new "synthetics" without considering that they are new and different materials will lead to mistaken conclusions. Actual wear tests made on tires made from a high-tensile strength polymer show no difference from those made on tires from polymers of low-tensile strength but of equal plasticity. As compared with natural rubber, Buna-S is more heat resistant, less tear resistant, has about equal flex-cracking resistance, and has much greater resistance to aging as tested by the Geer oven, oxygen bomb, air bomb, and natural aging tests. The average synthetic truck tire is now good for about 10,000 miles and the average synthetic passenger car tire is good for about 20,000 miles. It can be seen from these figures that there is room for much improvement and it should be stated here that the laboratories of these great new plants are working day and night to improve the quality of rubber for war, and subsequently for peace.
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