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UNIVERSITY OF LOUISVILLE

CHEMICAL SUBSTITUTES

A Dissertation

Submitted to the Faculty of the
Graduate School of the University of Louisville
in Partial Fulfillment of the
Requirements for the Degree
of Master of Science

Department of Chemistry

by

Clarence Elmore Parks

1939

Name of student: Clarence Elmore Parks

Title of thesis: Chemical Substitutes

Thesis Director: Dr. A. W. Homberger

Approved by the reading committee composed
of the following:

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Date: 5-25-39

22 Dec. '39 RYK.

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INTRODUCTION

"Science is the soul of prosperity of nations and
the living source of all progress." --- Pasteur

The word "substitute" usually carries with it some thoughts of cheapness, of inferior or adulterated products and attempted deception. Because of his lack of understanding, the layman usually views chemical substitutes with even greater suspicion and fear. It is the substitution of new materials and processes, however, for the old and less satisfactory that constitute progress. In the world today there are hundreds of men who spend most of their time trying to develop substitutes to meet the demands of a rapidly advancing world---these are the research chemists.

Many a man, smiling at the chemist who "wastes" all of his time studying the antics of the atoms, will proudly claim the ownership of a fine automobile equipped with molded fiber gears, a modern radio with bakelite insulation and control knobs, fine rubber tires that carry his car safely, a molded plastic steering wheel and horn button, nickel and chromium plated decorative parts; nickel-steel alloyed axles, painted with Duco pyroxylin lacquer; lubricated with highly purified oils and greases; and propelled with "high-test" ethyl gasoline. Surely he is proud of it, for he has reason to be, but who has made it possible? Who found out how to make these products and

discovered their uses? It was the man who was "wasting" his time studying the reactions of the atoms, often in unpleasant surroundings of smoke and fumes---the chemist. Not only in the automobile industry has chemistry added to our pleasure and prosperity, but in every other industry.

At one time man had a savage existence. He had to compete with the beasts of the forests for control of the world. By substituting man-made weapons and machines for the natural, he is today master of the land, sea, and air. Without a knowledge of chemistry we would still be but little higher than the savage. This may sound a little exaggerated, but in the last analysis it is true. To be sure there are many other influences that have helped to bring about our civilization, but most of these would be seriously retarded or impossible without some knowledge of chemistry. The great politician and social leaders of the world would be unable to accomplish their appointed tasks without materials developed by chemistry.

Chemistry is new and yet it is very old. It is new as a recognized science---less than a hundred years old perhaps, but some chemical operations were known as far back as written history extends. The fermentation and concentration of juices and the use of sulphur and certain metals are recorded in the earliest records of men. Of course, their manipulations were not called chemistry, but

in reality that is what they were. As we bring our discussion down to modern times, it will be interesting to see how practically every industry today is depending upon chemistry to maintain its operation.

Furthermore, it can be shown that the answer to many of the problems that burden the heads of our government will one day be solved more completely by the chemist. For example, the question of excess farm crops has been partially solved. The surplus can be converted into other useful products which may create an entirely new industry as in the case of the cellulose products. Millions of bales of cotton that one time helped to burden the overcrowded market are now being made into paints, explosives, and fabrics today. On the other hand, the necessities that we import must be made out of our surplus supplies on hand. This is the problem that challenges our chemists in the years to come---to utilize our surplus raw materials and to free this country from foreign controlled markets.

THE METALS

Iron and steel, perhaps, are the most universally and abundantly used of all the metals. They are important beyond our imagination, and yet there was a time when they were little known or used. Long after their discovery, they were not satisfactory because of the lack of the knowledge of chemistry properly to prepare them. The metals today might

well be considered the foundation of our national growth. Our monetary system, construction work, transportation, manufacturing, machinery of any and every description, are depending upon our metals.

The production of the metals from the ores, their purification and tempering are all basic chemical or physico-chemical processes. Modern machinery is depending upon the high grade metals for their long and useful service. It is no longer sufficient to produce high grade pure metals. The requirements of today are much greater. Special metals for the varied purposes must be produced, and this is the task of the chemist. Be that as it may, the fact remains that the substitution of metal for stone was one of the first and most important steps of progress in the history of the world.

The discovery and early use of all of the metals are interesting stories, but one of the most interesting of modern times is that of aluminum. Very recently, in the memory of the older generation living today, aluminum was a laboratory curiosity. It was not rare, but the cost of securing it from its ore was too great, making the metal useless. However, in 1886, Charles Martin Hall discovered the electrolytic process for separating aluminum from its ore. This greatly reduced the price and increased the production from 100 pounds in 1883 to more than 300,000,000

pounds in 1938.

When the airplane manufacturer was given this new, light, durable, non-corroding, white metal, the day of aviation was dawning. Although it did not prove to be thoroughly satisfactory in the pure state, its alloys have enabled aviation to make amazing advances in the last thirty years. If the modern transport planes, which are almost entirely built of aluminum, were still made of iron, which is more than three times as heavy, they would be unable to raise themselves from the ground. These are the kind of substitutions made possible by chemistry that have been responsible for the progress of the world.

All of the metals are important; some of them are more so than others, and some are less important for the reason that the chemist has not yet accomplished his full task. That is, he has not found either a use for them or a method of producing them at sufficiently low cost.

In order to show some of the developments in the metallic field, nickel has been chosen for a detailed account. Nickel might be not considered by some to be of major importance, but very likely this is because they do not realize all of the things for which nickel is used. The fact that it is one of the four metals used in the American monetary system means that it has some very desirable properties.

Nickel has been known for hundreds of years, but its commercial history is short. In fact, it was considered of little value until the nineteenth century when a small vein was discovered in far off Caledonia. Even then, no one had any use for it, and the small supply seemed to be ample. In 1853 a surveyor by the name of Salter noticed that his compass needle was deflected in the area of Sudbury, Canada. By searching the area he noticed some red ore deposits which indicated iron. These were not very important since they were in the wilderness and many miles from a railroad. For thirty years the fact remained only a memory. Then 1883 came, and while the Canadian Pacific Railroad was being built, the crew were making a cut through a hill when they noticed that the rock was different from any that they had seen before. Analysis showed that it contained copper. Nickel was not known to very many people at that time, but copper was known to be valuable, especially since it was close to the railroad. In 1885, a man by the name of Samuel J. Ritchie leased many of the mines and started to mine copper. The ore was sent to two copper smelting plants in New Jersey. After receiving about a hundred car loads, they refused to buy any more because they could not refine it in the ordinary way.

When trouble arises, it is time to consult the trained chemist. At that time a metallurgical chemist by the name

of Robert Thompson was connected with one of the copper smelting companies. After a long research, he discovered that trouble with the copper smelting was due to the nickel present and set to work to find a method of separating it. Nickel had from the very beginning been known to be a factor in the copper smelting industry. In fact, the name "nickel" is said to have come from a German word meaning "devilish imp." Finally, Mr. Thompson and his associates developed the niter-cake process for separating nickel-copper ore, which is still used today. The result of the discovery was the buying of all mines in the district and the formation of the International Nickel Company.⁽²⁰⁾ The substitution of a new method of refining copper for the old has resulted in a new industry and a new metal to help satisfy the world's requirements.

This proved to be only the beginning of a series of changes that have revolutionized the metal industries. About twenty-five years ago there came into being a new process for the concentration of mineral ore. Up until that time the ore had been crushed and put into a large bin where it was shaken or jarred until the heavier ore settled to the bottom. Then the larger particles, being mostly rock, could be removed from the top. The new process, called flotation, developed commercially by the American chemists, has revolutionized the practice of ore concentration. The flotation process works on a principle exactly the opposite of

the older method; instead of the heavy ore collecting at the bottom, it is actually made to float on the top while the lighter rock collects at the bottom. The principle is known to the chemist as wetability. The sulphide ores do not wet as easily as the rock particles, just as a piece of varnished wood will not wet as easily as a piece of unpainted soft pine. By adding to the mixture a small quantity of oil or other chemicals, the wetability of the sulphide ore can be further reduced. When air is blown through the water mixture, the unwetted ore will cling to the air bubbles in an effort to get out of the water. Further treating can prevent the bubbles from bursting easily when they reach the surface. This enables the ore to remain at the top until it can be skimmed off, or allowed to flow over the edge of the vessel, or flotation cell, as it is called.

For many years, it was considered quite sufficient to be able to separate the ore from the rock by this method, but the chemist had noticed that some of the sulphide ores floated more easily than others. Also it was found that some of the chemicals used helped certain sulphides to float more easily than others. Now almost every up-to-date flotation plant practices what is called selective or differential flotation. The sulphide that is most easily floated comes off first; then by stirring, adjusting

the concentration and standing, the next one will come up. By this method, the sulphides of certain metals can be almost completely separated from those of other metals. This method has proved to be especially satisfactory in handling ores that have a high concentration of copper and nickel.

About the same time that Mr. Thompson was developing his niter-cake process, Dr. Ludwig Mond and Dr. Karl Langer discovered an entirely new process for separating nickel from its ore. They were working with the decomposition of carbon monoxide, by passing it through a hot combustion tube, using nickel as a catalyst. One day, when the combustion tube was only warm and the escaping gas was being passed into a flame, it was found to turn the flame greenish-yellow. In order to find out if this was due to the arsenic present, they passed it into another heated tube, expecting it to plate a mirror of arsenic. They were not surprised that it did ~~not~~ form a mirror, but analysis showed the metal to be nickel and not arsenic as they had expected. This was a very interesting scientific fact because up until this time it was not thought possible to volatilize a heavy metal at such a low temperature and convert it back into the solid without its first returning to the molten state.

After further experimentation, it was found that finely divided nickel ore could be united with carbon monoxide gas at a temperature of about 80° C. From this

was developed the Mond or Carbonyl process for refining nickel. One advantage of the process is its simplicity; however, the mechanical difficulties of handling the poisonous gas have to be reckoned with.

In 1914, when the World War broke out, nickel became almost a precious metal. It was in great demand for the manufacture of guns, tanks, machine-guns, armor plating and airplane engines. Because of the untiring efforts of the American chemists in developing our natural deposits, the British-American forces were well supplied.

After four years, the war came to a close and the demand for nickel was at a temporary standstill, because about 90 per cent of the world's supply of nickel had been used in the manufacturing of implements of warfare. Practically all of the large nickel plants were either closed or were running only a few hours each day. It was a critical time for the nickel industry. However, it was not long before the research department of the automobile, airplane, and electrical industries realized its value and absorbed the surplus, because they had found that substitution of nickel-steel alloy for the old carbon type rendered the product free from corrosion and more than doubled its endurance.

Although the war was an accelerating factor in the development of the nickel industry, the roots of the

present consumption extended back to the pre-war.

It is more nearly correct to say that it is a result of the combined study of chemistry and physics which resulted in metallurgy. Metallurgy had developed as an intensive study of the chemistry of metals; then came metallography, with a physico-chemical background, to delve into the structure of metals and to study the changes which could be effected in these structures by the introduction of various elements in combination, and by variations in the quenching process.

In most cases the substitutions in processes and materials are not brought about by the pure industrialist, who is usually satisfied to meet requirements, but rather by research men in our colleges and technical schools. When the war came, many of our industrial plants accepted Government contracts for military supplies. Then the Government inspectors went into the plants and began to reject products right and left because they were below specification. It was then that the foundry-men welcomed the metallurgists in working out these new problems, and the union between the experience of industry and the technique of science was effected. At the same time the Government drafted not only the young graduates, but also the college professors and research men from the technical schools for developing better war supplies. At the close of the war, many of these men remained with the industries and thus the stage was set for a modern attitude toward

production and an enlightened interest in research.

One of the results of this new combination was the production of a new Nickel-Copper alloy which was called "Monel" metal. It is what might be considered a natural alloy, since the nickel comes from the mines combined with copper. The content of the alloy is roughly two parts nickel and one part copper. During the war, the war supplies had consumed ninety per cent of all the nickel produced. By 1929, the production of nickel and nickel alloys for industrial purposes alone far exceeded the war time high for all purposes and at that time less than five per cent was being used for war supplies. (20)

By substituting peace for war, an industry has grown rapidly and become a great blessing to the world.

This new alloy has found wide industrial uses. In 1875, enameled kitchen sinks were developed. They remained unchanged for sixty years and then, in 1935, monel metal sinks were put on the market. They are very bright and tend to produce an attractive kitchen. Another alloy known as "Stainless Steel", which contains eight per cent nickel by weight, is now being used for decorative and cutlery purposes.

For many years, metallurgists had been unable to find a metal which would withstand the corrosive action that steam has on the blade of a steam turbine. However, monel metal is unaffected by it and will last

for many years. About three years ago, the first railroad tank cars were lined with monel metal. This has enabled strong alkali to be shipped in bulk form and has resulted in a saving of a million dollars a year to the rayon industry alone. Other uses of nickel alloys which have resulted directly from the metallurgical research laboratories are: electrical resistance alloys which contain up to eighty-five per cent nickel and are used in heaters, pyrometers, rheostats and household appliances, heat resisting alloys used in electric furnaces, retorts, and in glass making; aluminum alloys containing two per cent nickel, used in making pistons and heads for internal combustion engines; white gold containing about fifteen per cent nickel used quite extensively for jewelry, eye glasses, and decorative purposes. The items mentioned above are just a few of the hundreds of articles that have been improved by substitution of this new metal and its alloys for those with less satisfactory properties.

These chemical substitutions have resulted in an industry that today provides employment for more than 20,000 men, besides providing more than \$50,000,000 to be divided annually among the stock holders. (20)

Its importance is only beginning to be realized and in the near future may prove to be of even greater value.

Nickel is not the most important, the most used, or the most valuable, but it is typical of the advances that chemical substitutions have caused in the field of metals.

CARBON AND CARBON COMPOUNDS

Carbon, one of the most unattractive of all the chemical elements in the free state, has become the chemist's greatest storehouse of power for making chemical substitutions. It is so common in the form of coal, coke, charcoal, and graphite that it could never be suspected of being the most versatile and abundant compound-forming element of them all. The free carbon forms do not hold the interest of the chemist nearly so much as those combined with other elements. There are today something over 250,000 known and isolated organic compounds of which carbon is the principal element.

CALCIUM CARBIDE

In the later part of the 19th century a cotton mill owner, Major J. T. Morehead, was experimenting with a newly invented electric furnace. Working with Thomas A. Wilson, an electrical engineer, he was trying to separate aluminum from bauxite by heating it with various fluxes. One day in 1892, they loaded the furnace with the ore, coke, and lime. The result was a hard mass, with no reduced metal, but when water came in contact with it, a cloud of pungent gas came forth which was found to burn. The hard mass was calcium carbide, and the gas was acetylene. Because of its

brilliant illuminating power and the intense heat produced, the possibilities of acetylene were apparent. Patents were secured with the expectation that acetylene would replace or enrich coal gas and water gas. During the next ten years, several carbide companies were organized, but only one met with great success. This successful company was moved to the Niagara Falls, where a large supply of cheap electricity was available. The other patent rights were bought and the Union Carbide and Carbon Company was organized in 1898.

Prior to 1907, the principal use of acetylene had been for light and heat. In that year, the Linde Air Products Corporation was organized, after the discovery of a method of separating oxygen from the air by liquifaction. Soon the oxy-acetylene blow torch came into existence and the hot flame of acetylene burning in oxygen became available for welding and cutting, which is essential to the modern handling of metals.

Another important step toward the greater usefulness of acetylene was the discovery of the fact that it was soluble in acetone. The gas, when compressed, had been dangerously explosive, but dissolved in acetone, it could now be shipped safely in tanks under high pressure. This discovery resulted in the organization of the Prest-O-Lite Company, which produced one of the

first automobile lighting systems by using small tanks of acetylene.

Strange as it may seem, calcium carbide has become the starting point for innumerable organic compounds. In the early years of the twentieth century, organic research began in earnest. In 1920, the Carbide and Carbon Chemicals Company was organized to consolidate this research and to manufacture synthetic aliphatic chemicals. This was one of the first industries ever to be established for the sole purpose of producing chemical substitutes.

Some of the products made were well known and had to compete with the natural products for markets; others were entirely new as commercial products, while still others were "made to order." By "made to order" is meant that frequently a company would express a desire for a product with certain chemical and physical properties and very often the research chemist would be able to produce just such a substance. To compensate for the special orders, it was frequently found that the new products had properties that suited them for many other uses. In one instance, a special lacquer solvent was developed which later proved valuable as a hydraulic brake fluid constituent. Relying on their research chemists for

expansion, the Carbide and Carbon Chemicals Company added seventy products of commercial value and national benefit to their manufacturing list in ten years.¹⁴

The writer is especially interested in the products of this company since they are a monument to synthetic chemistry. From calcium carbide and liquid air to solvents and resins, the chemical substitutes have solved the nations' problems for new or better materials. Acetylene, with its triple bond arrangement in the molecule, has made it comparatively easy to enter side chains directly into an organic compound. Thus many organic chemicals with wide variation in properties and uses may be traced back to Major Morehead's discovery of acetylene. Only some of the more important ones will be mentioned here.

It will be noticed, by the informed, that many of these products named are the starting point for other organic preparations. The line is never complete, but always one thing leads to another. Ethylene, ethyl ether, ethanol, ethane, diethylene glycol, butane, butylene, butyric acid, butyl acetate, acetone, ethylene glycol, methane, methanol, methyl acetone, and amyl acetate are just a few of the hundreds of compounds that are commercially prepared by synthetic

chemistry and today are necessities in many other industries.

Another descendent of calcium carbide which deserves separate mention is the plastic, alvar. Over two hundred tons of calcium carbide are used in the United States annually in the production of this new substance. Large quantities of carbide are also used in the production of acetic acid and acetaldehyde. When these two substances react under proper conditions, vinyl acetate results. The vinyl acetate is a double bonded compound which will polymerize and form a series of vinyl acetate resins. These are still somewhat undeveloped, but one called gelva has some very desirable properties.

One of gelva's most remarkable properties is its adhesion to porous and polished surfaces. It is said that when a metal plug is cemented to a glass plate by the use of gelva, a section may be pulled from the plate without breaking the adhering bond. Thus it is found to be very useful in assembling glass structures. Gelva is also used as a prime coat for metals, as an aluminum and bronzing vehicle, and in chewing gum and uncrushable velvet. Furthermore, it has been found to be very successful in bonding many different kinds of material, including wood, porcelain, metals, mica, leather,

felt, cloth and cellophane.

When the percentage of the acetate group in gelva is varied and formaldehyde is introduced, a harder, higher melting point material, called alvar, is formed. It is used principally as a thermal molding plastic, from which is made such articles as combs, fountain pen barrels, screw tops for bottles, toothbrush handles, and handles for various other toilet articles. Again, chemistry has produced substitutes that are replacing the natural products because of their beauty and durability.

SOLVENTS

Over two hundred million gallons of carbon compounds are used in the United States each year in the form of solvents.³ This enormous amount of materials is possible only as a result of synthetic organic chemistry. The uses of these solvents vary from the familiar applications in lotions, cosmetics, paints, and lacquers to the huge amounts used in chemical production and extraction that would challenge the imagination. A few years ago, when a solvent was needed, it was necessary to select it from the list of those already known, but today many special solvents are made to order. When the natural solvents were relied upon, it was not always possible to find one suitable, but

through synthetic organic chemistry, a solvent with the desired properties may be had.

Perhaps, early history is the most vivid way to show progress. More than three hundred years ago turpentine, rosin, pitch, and tar were made from the pine forests of North Carolina. This was probably the first solvent industry and one of the first industries of any kind on American soil. A considerable business was developed from these forests, until, in 1890, about forty million gallons of turpentine were refined annually.

Another solvent, which has been known since the earliest records of man, is ethyl alcohol. The fermentation process of producing alcohol from carbohydrates has been in use for centuries, yet radical changes in production and use have taken place in recent years. Although the solvent power of ethyl alcohol was known, it has not been available to commerce in the United States because of an excise tax. This was removed by an act of Congress in 1906 and since then, the consumption has advanced steadily until today the annual output of this solvent is approximately 100,000,000 gallons. Alcohol is used in pharmacy, perfumes, cosmetics, varnish, lacquer, shellac, antiseptics, pyroxalin products, smokeless powder, and chemical manufacturing.

It can truly be considered the cornerstone of the American solvent industry.

One of the oldest branches of the American chemical industry is the destructive distillation of wood, and for many years it was the sole source of the important solvent, methanol. The United States Census of Manufactures states that the value of wood chemical products in 1880 was \$275,000. This value increased steadily until in 1923 it was \$29,695,000. However, since that time, the synthetic manufacture of methanol from natural gas has greatly reduced its value. One of the by-products of wood distillation is calcium acetate, which can be converted easily into acetic acid or acetone. Large wastes accompany the latter operation. However, during the war, the shortage of acetone made it necessary to use this method.

As a result of this shortage, the British Government stimulated chemical research which resulted in the discovery of two methods for the production of acetone. One of these methods starts with calcium carbide as its raw material and goes through the steps of acetylene, acetaldehyde, and acetic acid to acetone. The other is a specialized fermentation process in which a certain species of bacillus is used. During the fermentation process, for each pound of acetone produced, two pounds

of n-butyl alcohol and one third pound of ethyl alcohol are made as by-products. This process, which was put on a commercial basis in this country after the war, was found to have very interesting features.

As the fermentation process became more popular, the great stocks of n-butyl alcohol began to mount. Since twice as much of this product was formed as the desirable acetone, the search for a market for it was a serious problem. About this time a chemist in the lacquer industry found that nitro-cellulose was soluble in butyl acetate which could be made easily from butyl alcohol. Lacquers made with volatile solvents and nitro-cellulose have two distinct advantages over those formerly used. They can be put on more quickly because they dry more rapidly and they withstand weather conditions much longer. The automobile industry quickly took advantage of this new lacquer and the problem of a market for butyl alcohol was changed to the problem of supplying the demand. Almost over night, butyl alcohol became the more important product and acetone the by-product. After this discovery and the loss of the acetic acid business to the synthetic industry, the wood distilling process became of minor importance.

Thus, the solvent industry which began in this country in a very small way, in the distillation of hard wood,

the fermentation of corn and molasses, and the distillation of pine tree gum, is today an outstanding example of chemical substitution. The use of these natural solvents was limited because they were subject to climatic conditions which were beyond the control of man. Today the synthetic products are made from the unlimited resources of the nation, and an abundant, pure, and uniform supply is assured.

At present, the largest consumer of American solvents is the protective coating industry, which uses more than forty per cent of all the solvents produced, excluding the petroleum distillates. In recent years, however, the lacquer industry has been undergoing some drastic changes within itself. Synthetic resin finishes of the phenol-formaldehyde type are replacing the pyroxalin group for many purposes. These lacquers require less solvent and have a greater covering power. The speed of application is equalized by drying at a relatively high temperature. The detrimental effect that the use of the resins will have on the pyroxalin industry cannot be accurately determined at the present time. It has caused little concern as yet, but it is definitely affecting the solvent industry and the cotton farmer.

Perhaps the second largest user of solvents is the

anti-freeze manufacturer. Of course, all anti-freeze mixtures must be completely miscible with water, and this limits the number very definitely. The ones most commonly used are glycerine, glycol, ethyl alcohol, and methyl alcohol. The consumption of these should remain about the same for the next few years unless a more desirable substitute is found.

If the solvent manufacturer had been looking to his old customers for expansion, the present would seem a bit dark, but his research department has not been idle. The new uses for solvents in the rayon, plastic, adhesive, and artificial fabric industries are creating greater demand than ever. One of the newest fields to open for large quantities of various solvents is the refining of petroleum. The selective solvent extraction method of preparing petroleum products was tried as early as 1926, but little progress was made until the last two years. If this method is universally adopted in this country as is indicated, it will take a million gallons of solvents to set the plants in operation. The principal solvents used in these extractions are isopropyl alcohol, chlorinated hydrocarbons, isopropyl ether, acetone, propane, furfural and benzene. Thus it becomes apparent that the industry which has the foresight of the research chemist will never die, because there is always a new use

ACETONE

Artificial silk
Artificial leather
Safety glass
Paints and varnish removers
Pharmaceuticals
Airplane dopes
Cellulose acetate and pyroxylin plastics

Photographic films

Acetylene gas

Liniments

Pyroxylin cements

Dewaxed lubricating oils

Explosives

Synthetic resins

DIACETONE

Lacquers
Anti-freeze
Nitro-cellulose and cellulose acetate plastics
Liquid for hydraulic compression mechanisms

IODOFORM

Antiseptic

CHLOROFORM

Anaesthetic

BUTANOL

Photographic films

Pyroxylin plastics

Lacquers

Ore flotation agents

Patent and enameled leathers

Safety glass

Metal cleaners

Airplane dopes

Detergent

Artificial leather

Penetrating oils

Coated paper

Synthetic flavors

Antiseptics

Stencil paper

Dyestuffs

Anti-foam agent

Polishes

Spirit Varnishes

BUTYL ACETATE

Safety glass

Pyroxylin plastics

Lubricant

BUTYL LACTATE

Lacquers

BUTYL STEARATE

Lubricant

Water-proofing agent

Laminated fibre products

Lacquers

Plasticizer

Polishes

Base for face cream & rouge

BUTYL ACETYL RICINOLEATE

Plasticizer

Emulsifying agent

Lubricant

BUTYLYDE

Rubber accelerators for tires

DIBUTYL PHTHALATE

Insect Repellent

Plasticizer

Fixative perfumes

Lubricant

DIBUTYL ETHER

Solvent

ETHANOL

Anti-freeze	Liniments
Lacquers	Perfumes
Leather dopes	Tonics
Pyroxylin plastics	Toilet Preparations
Pharmaceuticals	Safety glass
Photographic films	Tobacco and tobacco solutions
Artificial leather	Paint and varnish removers
Hydraulic brake & shock absorber fluids	Antiseptics
Dyes	Cleaning fluids
Motor fuels	Artificial silk
Shellac solutions	Polishes
Disinfectants	Transparent and liquid soaps
General extraction and solvent purpose	Ink
	Flavoring extract
	Spirit varnishes

ETHYL ACETATE

Artificial leather

Lacquers

Safety glass

Plastics

ETHYL BUTYRATE

Synthetic flavor

DIETHYL PHTHALATE

Plasticizer for lacquers

Fixative for perfumes

ETHER

Anaesthetic

Solvent

METHANOL

Anti-freeze	Refrigerants
Shellac solutions	Cleaning compounds
Spirit varnishes	Wood stains
Embalming fluids	Pharmaceuticals
Synthetic flavors	Synthetic perfumes
Varnish removers	Paints and varnishes
Dyes	

FORMALDEHYDE

Synthetic molding resins

Fumigant

METHYL SALICYLATE

Medicines

Flavoring

METHYL CHLORIDE

Refrigerant

METHYL ACETATE

METHYL LACTATE

Nitro-cellulose adhesives

Lacquers

METHYL FORMATE

Refrigerant

Insecticide

METHYL AMINES

Rubber accelerator

Dyes

Unhairing of hides

for old products as time moves on.

Perhaps the most important group of solvents is the alcohols. The word alcohol does not refer now to just ethyl or wood alcohol, as it did a few years ago, because there are on the market today twenty-three alcohols which may be purchased in barrel or tank car lots, not including the keto alcohols, the alcohol ethers, and the higher ones such as cetyl and lauryl. The number of alcohols that could be synthesized is almost unlimited, if there was a market demand for them. "The number of isomers of octyl alcohol is calculated at 89, of C_{10} is 507, of a C_{20} alcohol is over 5,000,000, and of a C_{30} alcohol at over 95,000,000. Undoubtedly, a very few of this vast number have any commercial value, but some of those now unknown will have important industrial applications in the near future." 18

From the standpoint of the volume consumed and diversity of uses, the alcohols are the most important industrial organic chemicals. Ethyl alcohol was the first to have an important place in industry since it is the result of a natural fermentation process. However, in recent years, the usage of butyl, amyl, and substituted alcohols has shown a marked increase, because of government restrictions in the manufacture and sale of ethyl alcohol.

One of chemistry's substitutions which seems destined to affect the greatest number of American people is the replacing of natural resources with farm products. The possibility of growing the raw materials for making solvents, plastics, lacquers, fabrics, rubber, and many other essentials is just beginning to be realized. Protecting the farmer by special legislation or government payment for not planting is an honest effort in the wrong direction. All of the protection that the farmer wants or needs is a market for his products, and this must be realized through synthetic chemistry.

One of the most staple crops of the American farmer is corn. It was one of the first with which the research chemist worked, and it has proved to be such a rich source of chemicals that today a large variety, serving practically every major industry, is made from corn. On the accompanying chart will be found listed the uses of these important chemicals and their derivatives.⁵

Of course, at the present time, the country is not depending on corn for all of these essentials, but they can be and are being made from corn. This is further evidence that future economic problems may be solved by chemical substitutes.

ALKALI AND BLEACHES

Less than fifty years ago, practically all of the alkali used in the United States was imported from England. The people were accustomed to the English product and had never made much effort to produce their own product, even though the natural elements necessary were abundant. Alkali and bleaches may not seem to be of vital importance to the casual observer, but if the far reaching results are studied, it is found to be essential to hundreds of industries and to affect the needs of every individual. To see how much we are depending on alkali, we have only to look around us. Our dishes, window panes, clock faces, ornamental vases, and hundreds of other household articles are made of glass, which is the result of heating together sand, lime, and alkali. Our clothes, rugs, furniture, upholstery, and other wollen articles are cleaned with alkali. The cotton clothes, curtains, ropes, and the thousands of other articles made from the millions of pounds of cotton that are made into textiles every year must first be cleaned and boiled with alkali before the finished products are made.

Paper, so common that we fail to think of and realize

the scientific research that is back of its development, is made by boiling wood pulp and rags in alkali. Cellophane, which is the newest of wrapping materials, and rayon, the substitute for natural silk, are quite different from the cellulose pulp from which they are made by boiling with alkali.

Perhaps, the largest consumer of alkali is the soap manufacturer. It is essential in the manufacturing of all soaps, shampoos, cleaning agents, and scrubbing compounds. We today are so familiar with these things that we give little thought to the fact that they are substitutes for the naturally occurring sand and clay that were once used as cleansing agents. For many years soap making consisted of boiling together wood ashes and fat. However, with the advent of chemistry, the industry took on a different appearance and the place of manufacture was changed from the home to special factories. The processes were placed under the supervision of trained chemists, and the result is the fine soaps that we have today. It is not enough now to make good soaps, but soaps and cleaning compounds must be made for every different purpose. Still, alkali is the prime essential.

The usefulness and the extent to which it affects

the lives of our people is shown by the amounts used. In 1934, there were 2,390,000 tons of soda ash and 725,000 tons of caustic soda produced and used in the United States.¹⁵ Since this enormous quantity is used each year, it is well to consider the source of supply. If it were still imported, it would affect the balance of trade, make the United States dependent on other countries, and be a severe handicap especially during the time of war. In the latter part of the nineteenth century, a process for the electrolytic decomposition of salt solutions was developed. In 1892, the Mathieson Alkali Works was organized to make alkali and bleach. A little later the Pittsburgh Plate Glass wanted its own plant to furnish alkali, and they organized the Columbia Chemical Company. These two great plants, along with some others, have brought the alkali business home from foreign markets. The electrolysis of brine is unique in one respect, in that all of the products formed are very commonly used. The three products formed are sodium hydroxide, hydrogen, and chlorine, which are not only valuable as they are, but are the starting point for many important commercial and scientific chemicals.

Just before the beginning of the World War, liquid

chlorine became commercially known. During those trying years, alkali plants expanded and carried an extra burden, in an effort to produce the chlorine that was used as a poisonous gas. Although chlorine was very important in the war, it is no less valuable in time of peace. It is one of the most powerful antiseptics and is commonly used in swimming pools, city water supplies, and for general sanitary purposes. In the textile and cellulose industries the powerful bleaching action of chlorine is needed to decolorize the raw materials. Because chlorine can be economically prepared and is very active chemically, it has found extensive use in synthetic organic chemistry. The uses of chlorine, like those of sodium hydroxide, are so many and important that our lives would not be complete without it.

The other element produced by this very simple electro-chemical reaction is hydrogen gas. It is not poisonous, but highly explosive when mixed with one half its volume of oxygen. Thus ordinary table salt has produced a strange variety of deadly poisons and a high explosive. Hydrogen as a gas is very important as a reducing agent, especially in the hydrogenation of vegetable oils into edible fats which are used as a substitute for butter. Another most important use of hydrogen is in the Haber process for ammonia.

Here, the by-product hydrogen, obtained from the alkali plant, is mixed with nitrogen obtained from the air, and, under proper conditions, the two react to form ammonia. The importance of this discovery cannot be over estimated. After ammonia is formed, it can be made into suitable nitrogen compounds for fertilizers. Plants must have nitrogen for growth, and even though they live in an atmosphere of four-fifths nitrogen, they cannot use any of it. It must be in soluble form in the soil, and only a few plants, called legumes, are able to take it from the air and change it into a usable form. This process becomes even more important in time of war, because the nitrogen of the air is converted to ammonia---to nitric acid---to nitrates which are explosives.

Starting with sodium chloride (table salt) the alkali industry, by the use of synthetic chemistry, has developed products that affect every individual and every other industry in the United States.

EXPLOSIVES AND CELLULOSE

In 1866, Nobel made the first dynamite. It was a wonderful achievement and we today are the recipients of the rewards. Later, he realized the damage that could be done with this powerful explosive and he established the Nobel Prizes, one of which is a perpetual award to the one who contributes the most during the year to world peace. Dynamite has proved to be a wonderful contribution of an honest and constructive chemist. It would have been almost impossible to construct the buildings, bridges, dams, railroad cuts and tunnels, and modern highways without dynamite.

The word dynamite is a general term covering a wide variety of explosives. For the most part, it refers to a mixture of nitro-glycerine and other substances such as sodium nitrate, ammonium nitrate, chalk, sulphur, wood pulp, or similiar materials. The resulting mixture is molded into sticks and wrapped in special water proof paper.

Great progress has been made in the explosive industry since the first discovery of dynamite. All explosives are necessarily dangerous, but, in recent years, the manufacturers have made wonderful advancements in promoting safety for both the factory worker and the user of the products. It is now possible

to get explosives that are safe to use in gassy coal mines and oil wells. One of the greatest steps toward safety is the use of electric detonators. This eliminates the use of the fuse which the worker formerly lit with a match. Much improvement has also been made in caps and the explosives themselves to protect the handler and the user. Recently a company advertised a new explosive that would not react to shock or jar, unless it was far greater than could possibly be encountered in ordinary hauling or dropping.

The forerunner of all explosives has not changed very much in several years. Black powder was discovered by the Chinese before the rest of the world was hardly civilized, and has been in use ever since. However, it has been almost completely replaced now by more powerful explosives. It was discarded during the Spanish-American War for military use and is today used very little for any purpose.

Smokeless powder, which is the principal substitute for black powder, has many advantages over the older product. This powder is made essentially of nitrocellulose or "gun cotton". Sometimes nitroglycerine is added. The name "gun cotton" is well chosen, since it is made by treating cotton linters with a mixture of nitric and

sulphuric acids. Thus the cotton is converted into hexanitrocellulose which is highly explosive. It is usually converted into a colloid with suitable solvent, and then nitroglycerine is added if it is desired. The colloid is pressed through dies into the form of ribbons, rods, or any desired shape, and the evaporation of the solvent allows it to harden. It is then cut into lengths which vary with the size of the gun for which it is intended. The use of the cellulose derivative as an explosive has proved to be a worthwhile substitution for the cotton farmers.

In dealing with nitrocellulose as an explosive, it was only natural that the alert mind of the investigator would see some of its other possibilities. It is today an industry with its full usefulness yet unknown. It has been more or less controlled and operated by the powder companies because they were the first to nitrate cotton commercially, and consequently were better prepared for developing the new industry. We might wonder sometimes why some companies find themselves making such a wide variety of products. Usually it is not because they are trying to enter all of the various fields, but because chemical products have such a wide variation in their usage. It is because of the

fact that one thing has led to another and that each new discovery is a portal to a whole new field of opportunity.

There are several large industrial organizations in the United States today that were not in existence until chemical research had found the new products. As a matter of fact, they are simply a large chemical laboratory which carry out chemical reactions in huge cast iron or nickel-steel tanks instead of glass beakers. One of the most important of these is the cellulose by-products industry. Of course, the natural products, which are principally cotton, wood, and the stalks of all growing plants, have been used since the beginning of time. These contain, in addition to cellulose, small quantities of proteins, fats, and mineral salts which are impurities to the cellulose industry. Cotton is chiefly used as a raw material because of its abundance, purity, and high quality cellulose. The cellulose stalks of plants have been used for many years simply because of their suitable physical structure rather than their cellulose content. The real cellulose industry began only a few years ago when it was discovered that by treating it with various chemicals, especially nitric acid, new and very desirable products were formed.

The use of nitrocellulose as an explosive under the

name of "gun cotton" has already been mentioned, but this is only one of its many important uses. In 1881, amyl acetate was introduced as a solvent for nitrocellulose. This was the beginning of its usefulness as a lacquer. It has found extensive use as a preservative for silver and brass against tarnishing. The viscosity of the solution was so great, however, that it could not be used in spray guns. Through extensive research, butyl acetate was discovered to have remarkable powers with nitrocellulose. It was such an excellent solvent that it would make a solution thin enough to be sprayed and yet carry enough solid to cover in one coat. This proved to be a remarkable discovery for the whole nation. For the nitrocellulose industry, it meant success in another field; for the automobile manufacturer, it meant a better protective coating with less expense, greater endurance, and beauty; for furniture, toys, and everything that requires varnish, it meant an outstanding improvement. For the cotton grower, it meant an outlet for many thousand bales of cotton. The "chemical cotton", which comes mostly from the lint that is left on the cotton seeds after the ginning, could almost be classified as waste, since the fibers are so short that they are not suitable for textile manufacture.

About 1920 another cellulose product appeared on the market under the name of rayon. This new material is said to be the first man-made fiber. It was for a time incorrectly called artificial silk because of its physical resemblance and its use as a substitute for it. However, from a composition stand-point they are entirely different, one being of plant origin, and the other animal. This new material has been welcomed into every American home, in every form, from electric wire covering to curtains and clothing. It gives successful service wherever a beautiful textile is needed. There are two or three accepted processes for making rayon. Some prefer the finished product to be pure cellulose, while others think that some cellulose compound such as the acetate is better. At the present time the production of rayon and other synthetic fibers is about three times the amount of silk used, and almost as much as the wool consumed. More than 160 million pounds of cotton were converted into rayon alone in 1934, and a great deal more was used for other cellulose products.

The universally used transparent wrapping material, cellophane, was first made in France. Although the Swiss chemist, J. E. Branderberger, had been experimenting with cotton in order to produce a highly lustrous finish by depositing on it a film of cellulose from viscose, he found

at first, that it was very expensive and was suitable for wrapping only the most expensive articles. Another disadvantage was the fact that it was not water proof. After it was introduced into this country, the Du Pont research chemists developed and patented a similar product that was moisture proof, germ proof, odorless, non-porous, durable, and strong. This new product has almost all of the properties that could be asked of a perfect wrapping material. It is extensively used today to wrap all kinds of food products in order to protect them from exposure to germs and moisture. The millinery stores find it a great saving in preventing exposure to dust and shop-wear. It has so many uses that sometimes we wonder what we should do without it, and yet it has been here only a few years.

In 1869, Hyall was experimenting with nitrocellulose and camphor in an effort to make a new kind of billiard ball. The result was a pyroxylin plastic, celluloid. It was the first of the synthetic plastics to be discovered and immediately was found suitable for the manufacture of combs, brush backs, false teeth, mirror backs, and a variety of handles. In the sheet form, it became widely used as curtains for automobile windows and photographic films. It made possible the motion picture industry.

Some of the substitutions made by the chemistry of cotton are: cellulose nitrate for gun powder, celloid for wood and glass, pyroxylin lacquer for paint, cellophane for wrapping paper, and rayon fiber for cotton and silk. By these substitutions, chemistry uses several hundred million pounds of cotton annually.

SYNTHETIC RESINS

As in the case of many discoveries, the discoverer often finds something vastly different from that for which he is searching, but far better. Columbus was trying to find a new route to India, but his failure was much more important than would have been his success. Dr. L. H. Baekeland was searching for a shellac substitute, but discovered something that revolutionized many industries and added materially to the nation's raw materials.

It was no secret to the chemical world that when phenol and formaldehyde react, a tough insoluble mass results. For fifty years chemists had been trying to find some useful purpose for it. Also, it was known that many of the homologues of these reagents would produce similar products, yet they were so insoluble,

infusible, and difficult to crystallize that no use was found for them. Some of the best chemists at home and in Europe had worked on these resins, trying to utilize their valuable chemical and physical properties. In 1892, Kleeberg took up the task and spent much time and money on the quest. He tried, among other things, to use hydrochloric acid as a catalyst in the reaction. The result was a paste which quickly hardened into an irregular mass.

This substance had some very desirable properties, such as resistance to acids and solvents. However, it was very difficult to do anything with, and it would not crystallize. Crystallization was thought be essential at that time, so Kleeberg gave it up to work on something else.

Among the other prominent chemists that worked on the subject were Luft, Fayolle, Smith, DeLaire, Lederer, Helm, Knoll, and Labach. All of these had the same raw materials; many of them used similiar methods, and yet their results varied greatly. Most of them made the fatal mistake of using acid, in the condensing process, instead of a base. It was a long hard road as most chemical developments have been.

After successfully solving one of the most difficult problems of the day in photo-chemistry, by creating

velox paper, Dr. L. H. Baekeland started to work with phenol-formaldehyde resins. He did not begin where others had stopped, but started at the beginning and repeated every step of the procedure in order to find any possible errors. As in many research problems, he didn't know for a while what he really was looking for. He thought he was trying to find a shellac substitute, but after several months of experimenting, his eyes were opened to a great vision. He found an indestructible solid with far wider applications than shellac. One of the chief difficulties that Baekeland experienced was the excess foaming when the mass was heated. He found by the use of small amounts of sodium hydroxide that the foaming could be reduced, but still not satisfactorily controlled. In another effort to overcome foaming, he resorted to the use of pressure. This time, when the temperature was raised higher than before, the sticky mass was changed into a clear amber solid which was hard, insoluble, infusible, resistant to acids and oils, and which had taken the shape of the containing vessel.¹⁷

A new raw material, entirely different from anything then in use, had been given to the world to be substituted for the old wherever it was found more satisfactory. This discovery was not the end, but the beginning of a new

industry. All of the plastic materials used up to this time had been of the type that melts with heat and hardens on cooling, but Bakelite, as the new substance was called, was just the opposite. This gave the old time molders a lot of trouble, and it was necessary for Baekeland and the Bakelite Company, which was subsequently formed, to teach them how to use the new product. Bakelite was found to be one of the best electrical insulators; besides, it could be molded into the most delicate forms. The Weston Electric Company was the first to use it; they found it to be far superior to any previously used products. At first, when Dr. Baekeland was trying to find some industries that might use his discovery, he counted forty-three which he thought would find it profitable. Today it would be hard to find forty-three that do not need it.

Half of the things that Bakelite has been used for have grown out of Dr. Baekeland's persistence in trying it on everything around the laboratory. Such substances as cloth, wood, paper, cement, and plaster were found to absorb it and to acquire its useful properties. Many of these materials have proved to be valuable as insulators and gaskets for steam, oil, and solvents. The penetrating quality of Bakelite has opened up an entire new industry known as laminated products. The most common of these synthetic fiber materials are "Bakelite-Dilecto", produced

by the Continental Fiber Company; "Formica" of the Formica Insulating Company; "Condensite-Celoron" of the Diamond State Fiber Company; and the "Texolite" gears of the General Electric Company. These are all made of the same material and owe their existence to the discovery of Bakelite.

It was at the beginning of the World War that Bakelite was recognized as an important manufacturing material. The demand for ignition parts for automobiles airplanes, battleships, and motors of all kinds was enormous. Speed of construction and endurance were the prime factors. Then it was found that this new molding plastic was the answer. Dials, radio fronts, telephones, airplane propellers were made from Bakelite. It has proved to be a satisfactory substitute in places where metals were once thought to be indispensable. In 1914, artificial limbs were made of Bakelite because of its strength, inertness, and exact molding quality. It is also replacing rubber for setting paint brush fibers, and natural resins in making varnish.

As soon as the Bakelite process was patented and the method became known to the world, many other chemists started to work with synthetic resins. Many of the homologues of phenol and formaldehyde have been used

"Cotton seed was garbage in 1860, a fertilizer in 1870, a cattle feed in 1880, a table food and many other things in 1900." (22) Today its manufactured by-products are worth \$500,000,000 a year.

to produce similiar products. However, some other plastics of entirely different origin have been added to the list. The Du Pont Company has developed a substance called "Pyralin" which has added greatly to our list of beautiful things. It is a cellulose product, made principally from cotton and used extensively in the manufacturing of toilet articles. It is a substitute for the combs, brush backs, finger-nail file handles, tooth brush handles, and cosmetic sets and trays. Once the elephant was hunted to the point of extinction for the ivory that his tusks contained, and the ivory thus obtained was so expensive that only the rich could buy it. Even then it would crack and turn yellow with age. Today "~~Pyra~~lin" is made so cheaply that everyone can enjoy its use, and, besides, it is made in all shades and colors. It is more beautiful and enduring than any of the similiar natural products. Not only is it used as a molding plastic, but also is made into coated cloths and laminated products. In addition, it is being used as costume jewelry and other articles of beauty and necessity. The chemical uses of cotton have greatly increased its consumption in the United States and have helped to remove the surplus supply from the market.

RUBBER

A product similiar to the synthetic resins is rubber. It had been known for several hundred years to the savage Indian tribes who were reported to have used little balls of it to play with. However, nothing had been done to try to find a use for it until the early part of the nineteenth century. In 1832, Charles Goodyear read about a shoe company putting "Gum Elastic" on the heels, but the company failed because the "Gum" would melt in hot weather and crack in cold. This served as an inspiration to him and he determined to perfect a "Gum" that would not be affected by the weather and temperature changes. Like many chemists who have contributed greatly to our civilization, he suffered long before he achieved success. He was poverty stricken, sometimes in jail for not being able to pay his debts, and he never lost sight of the thing that he had set out to do. One day in 1839, almost a century ago, quite by accident, he dropped some sulphur into a batch of the gum that he was heating. The result was an elastic mass that would not soften and become sticky in warm weather or brittle in cold. At last, rubber, as it was later called, was a reality. This was just the beginning. He continued his experimenting, and in 1851

he went to Europe to exhibit his specimen in the great International Exposition. He returned and died in 1860 without much reward for his discovery, but the world will continue to be blessed by the contribution of this great man.

After Goodyear's discovery, the rubber industry really began. By the twentieth century it had grown into a large business and was extensively used for covering cloth, shoes, hose, belts for power plants, and other similar uses. The real growth of the rubber industry, however, was simultaneous with that of the automobile. Very little improvement was made in the product after Goodyear's discovery until new demands were made of it for use in the automobile. The plain sulphur-cured rubber had been satisfactory for the simple purposes for which it had been used. When the automobile came into existence, the demand for rubber for insulation of electrical wiring, insulation against vibration, and for tires, became acute. The industry put forth every effort to meet the requirements, and now specific kinds of rubber are made for every purpose. Many chemical compounds are being used for curing rubber, but sulphur is still essential in all vulcanizations. The soft spongy rubber used for insulation and the hard structure used in battery cases and phonograph records are examples of

the extreme ends which it serves.

By far the greatest quantity of rubber is used in the manufacturing of automobile tires. There are more than a hundred million automobile tires running on the roads of the United States daily, and this figure is increasing steadily. Even though rubber is a natural product, it is a substitute for steel in the making of tires and has proven to be far superior in traction and absorption of road shock. After the natural rubber industry became well established and the supply of raw materials was found limited, work was started on the production of synthetic rubber or rubber from other types of plants. Outstanding work was done in this field by the late Thomas A. Edison, who was working on the production of synthetic rubber from milk weeds when he died in 1932. The production of synthetic rubber on a commercial scale and at a price competitive with the natural product will greatly substantiate our national independence, since all natural gum is imported.

The raw material is a milky liquid that comes from the tropical hevea tree, which is commonly called the rubber tree. These trees grow in an area known as the rubber belt which extends about ten degrees north and south of the equator. South America was once the largest producer, but now about ninety per cent of the raw rubber comes from the middle eastern countries of Ceylon, India,

Java, Malaya, Sumatra, and Cochin China. The natives of South America and Africa were the first to gather rubber for the market. They would tap the wild rubber trees, collect the sap, boil it over a fire until it thickened, wind the sticky syrup around a stick, and hold it over the fire until it hardened. This is the way that it came to market. Depending on the natives to gather the latex from wild trees, which were sometimes miles apart, was satisfactory at first when the quantity required was very small. Later when the automobile came and demanded large quantities, the native rubber trees were not sufficient to meet the demand. The great rubber companies of the world planted and taught the natives how to plant and care for rubber trees. Now, with about two hundred rubber trees to the acre, one man can be responsible for more than five hundred trees. Thus the increase in raw material tended to lower the price and to improve the quality of the latex. The British were the first to encourage the planting of rubber trees, and, as a result, today they control about fifty-eight per cent of the world's market. To show to some extent the size and importance of the rubber industry, it was estimated that in 1936, there were 573,522 long tons of natural rubber consumed in the United States alone. To this vast number is added

an untold amount of synthetic rubber and resins that are used for similar purposes. While the tire industry is the largest, there are thousands of other uses for rubber, such as rubber floor tilings for public buildings, garden hose, conveyor belts, heel and soles for shoes, airplane and balloon cloth.

While striving to procure a satisfactory substitute for rubber, chemists have brought into being various gums and resins; most of them are of the Gutta-percha type. Many of the synthetic products have properties much superior to natural rubber. Their resistance to water, oxygen, oil, gasoline, and cracking is often much greater. Furthermore, they can usually be produced at less cost and often are made from products that are otherwise waste. In this respect, it must be kept in mind that one of the greatest services derived from chemical substitutes is a profitable use for waste materials. In the history of our industries the waste products have often become more valuable than the original.

The newest development in synthetic rubbers is Duprene. It is so much like natural rubber that even automobile tires have been successfully made from it. It has some properties superior to those of rubber,

such as resistance to oil, gasoline, and heat. The fact that a substitute for rubber can be made from materials available in the United States is highly desirable in time of war and in maintaining a balance of trade. Independence from foreign market can come only when chemical substitutes have met all of our necessities at home. Koroseal is another synthetic rubber, the hard rubber type of the Gutta-percha class. However, it can be made in forms that vary from a soft jelly to the hardest of hard rubbers. It is used mostly in the molded plastic form. It is especially noted for its resistance to acids and alkalis. In addition, it has remarkable tone reflecting qualities and is used in making some very fine musical instruments. Tornsite is another derivative of pure rubber and has remarkable resistance to acids, alkalis, smoke, and other chemicals. The excellent properties of these rubber substitutes made them valuable manufacturing materials in many industries.

Although rubber is made from naturally occurring gums, it may be classified as a substitute, since it is not used in its original form and has replaced so many materials. From its humble beginning with Charles Goodyear's discovery, it has grown into an industry using 600,000 tons of rubber annually in the United States.

MEDICINE

Since all early medicines were made principally from the roots of certain plants called herbs, it is quite correct to classify all synthetically prepared compounds as substitutes. Most of the medicines in use today are of the latter group and are pure chemical compounds or mixtures of these compounds. However, it is quite true that many of the herbs used were excellent medicines, but there were some serious handicaps to their use. In the first place, any medicine to be satisfactory must be pure and free from unknown and sometimes injurious ingredients. This was not always true of the natural herbs, which were frequently used as they were extracted from the root, stem, or leaf. Another serious handicap that faced the physician was the lack of standardized concentrations. It was very difficult for him to know how much to prescribe. Their lack of uniform potency, and their fluctuation between the two extremes of "worthless" and "dangerous" made them very unsatisfactory. Those familiar with powerful drugs know that the variation of a grain may subject the patient to known danger. It is no wonder that many an early doctor gravely shook his

head after having given drugs of varying unknown strength. However, it was impossible to have medicines of known strength and purity until the chemist became able to make them.

The first great advocate of chemistry in medicine was the renowned Paracelsus. Although he was born in 1493, he had considerable insight into the real value of chemistry. He once said, "The object of chemistry is not to make gold, but to prepare medicines", and the union of chemistry and medicine was cemented under his guidance. Paracelsus declared that the body was made of mercury, sulphur, and common salt, and that illness resulted, when the proportion of these changed; therefore the patient could be cured only by the use of certain chemical medicines to restore the balance. Although he was somewhat mistaken in his chemical composition, it can be readily seen that his idea is chemically and physiologically sound, except in the case of bacterial diseases, which were not discovered until some three hundred years later by Pasteur. No real advances were made in medical chemistry until after the days of Robert Boyle (1627-1691).

Chemistry has also had a part in surgery. Ancient surgery was exceedingly barbarous. The operation was

commonly performed without any anesthetic, and the flow of blood was stopped with a red hot iron. Some substances were already known to produce anesthesia, but most surgeons were not in favor of using them. Although ether was made as early as the thirteenth century, it was not used as an anesthetic until 1842 at Athens, Georgia. Chloroform was discovered to have anesthetic properties by Waldie in 1847. In 1800, Sir Humphry Davy found that nitrous oxide, or laughing-gas, could be used successfully as an anesthetic in dentistry. Thus these chemical substitutes have relieved mankind of much suffering.

In many cases, chemical substitutes have come in the form of improvements, as in the case of the vegetable alkaloids. For example, cocaine has been used for many years as a local anesthetic, but unfortunately it is poisonous and has been known to cause death even in minor operations, such as the extraction of a tooth.

After many years of toil, the chemists were able to determine the structural formula of cocaine. From this formula they recognized three relationships. One part of the molecule resembled nicotine found in our tobacco; another, the deadly poison found in the hemlock, which Socrates was forced to drink; and the third was the particular part that has anesthetic properties.

Not only did the chemists discover this, but they have been able to produce some similiar drugs which have the useful properties without being excessively poisonous. Among these are novocaine, eucaine, and benzyl alcohol. Humanity is greatly indebted to modern chemistry for these substitutes for pain.

Aside from the preparation of medicines and anesthetics for surgery, chemistry has served the medical profession in the form of antiseptics. Without these, all broken places in the skin are exposed to infection which may cause sickness or even death to the patient. It was Louis Pasteur, in the latter part of the nineteenth century, who discovered that bacteria were the cause of most diseases. He isolated the specific germ that caused many of the common diseases. A contemporary, Lister, started the practice of using antiseptics in surgery. The first common antiseptics to be used were carbolic acid (phenol) and corrosive sublimate (bichloride of mercury).

Today there are dozens of antiseptics in common use, and no home is complete without an adequate supply in the house for first aid use.

Not only have chemicals been found that will kill germs after they get started in the body, but also some that will help cause immunity. However, the most satis-

factory immunity is produced by the body itself. When pathogenic organisms enter the body, disease results, if they are allowed to grow and multiply. In general the blood produces substances known as antibodies which tend to destroy the toxin and kill the germs in the body. Working on this principle, the chemists and bacteriologists have been able to produce serums in other animal bodies and use it for treatment in cases of human diseases. A typical case is the treatment of diphtheria, which was once the most dreaded disease of childhood. The virus or toxin of diphtheria is injected into the horse. After several days the horse becomes immune to the poison. Some blood is then drawn from the horse and the antitoxin is made. By the use of this serum diphtheria may be cured or prevented entirely. In Auburn, New York, the death rate was cut from about twenty annually to none in five years by requiring all children of school age and below to be vaccinated with serum. It is quite possible that diphtheria may become a disease of the past. Not only has diphtheria been successfully treated, but also most of the other common bacterial diseases.

Besides its use in helping to prevent and cure diseases, chemistry has helped in diagnosing the case for treatment. If chemistry were taken from medicine,

there would be little left.

MISCELLANEOUS CHEMICAL SUBSTITUTES

One of the greatest responsibilities of chemistry is to find suitable substitutes for our rapidly disappearing raw materials. The United States is blessed with abundance, but that does not mean that our supply will never become exhausted. American industries seem to have a special technique for mass production, and the tons of raw materials consumed look like astronomical data. Some of these quantities may be given as follows:

"Of pulpwood 7,645,000 cords to make paper; 1,039,589 barrels of crude petroleum for gasoline and lubricants; 3,524,682 wine gallons of ethyl alcohol in the manufacture of rayon; 6,346,363 tons of salt consumed each year in our chemical industries; 2,294,183 tons of sulphuric acid to make fertilizer; 76,758,958 tons of coal coked; 104,712,586 gallons of vegetable oils in our soaps." 10

These enormous numbers represent a single year's consumption in the United States. From these figures, the alarmist gets the basis for his serial stories in magazines and newspapers which predict that the supply of certain raw materials will be exhausted in a specified

number of years. Those that are discussed the most are wood, oil, and coal. These are all very essential to our present existence. However, there are several reasons why this dreadful catastrophe may never come to pass. There is always the possibility of utilizing lower-grade materials, discovering new methods of making and utilizing these low-grade materials, or substituting something new and different for the same purpose. Since wood is one of the materials that is being used extravagantly and our re-forestation projects do not equal the consumption, it might be well to analyze this problem. It is safe to assume that wood has long since ceased to be a necessity in the manufacture of furniture, transportation vehicles, and machinery. It is no longer required for fuel, construction material, charcoal, methanol, acetic acid, or acetone. The manufacture of paper and rayon would be more difficult without wood, but not impossible. The cellulose for such purposes could be obtained from annual crops such as corn and the other small grains.

Many of our most cherished raw materials may be substituted when the necessity arises. The use of more than a billion barrels of oil a year may some time exhaust our big oil wells, but the discovery of

the hydrogenation process by Friedrich Bergius is our assurance that we will never be without fuel and lubricants.

It might be well remembered that the scarcity of any material raises the price that the higher price enables the production of competitive products, and that this results in a saving of the irreplaceable supplies. Not only has the use of chemical substitutes helped to conserve the natural raw materials, but it has frequently lowered the cost and made it available for a greater number of purposes.

There are two general classes of chemical substitutes: those that are substituted for another chemical and those that replace a natural product. We have many examples of both groups, and they represent the progress of the world. The first principle of competition between the substitute and the natural product is that the synthetic material must be obtained at lower cost. Furthermore, it must be uniform and dependable if it is to achieve commercial success. Some of the common and successful substitutions for natural products are as follows: lacquers for varnish, vanillin for vanilla beans, rayon for silk, aspirin for quinine, plastics for ivory and horn, and phenolphthalein replacing cascara, aloes, and other cathartics.

Since it is the rule that the chemical substitute

must be less expensive than the material that it replaces, it is worth while to note some outstanding examples. In 1896, indigo was worth \$1.92 per pound on the basis of pure indigotine. Today the synthetic product from coal tar sells for about 75 ¢ a pound and the consumption has more than doubled. Similarly, the price of \$10.00 per pound for best vanilla beans has been reduced to \$4.50 a pound for vanillin.

Another distinct advantage that the synthetic enjoys over the natural is in mass production. The longer a synthetic product is manufactured, the greater the demand; the experience, new methods of production, and the increased production of the raw materials all tend to reduce the price. On the other hand, the increased use of a natural product decreases the supply and usually causes an increase in price. These statements have been verified many times by such industries as wood alcohol, citric acid, rayon yarn, dyes, flavoring, and perfume manufacturers.

THE FUTURE

Although blessed with abundant natural resources, this country was dependent on the outside world for many essentials as late as twenty years ago. Such substances as nitrogen bearing compounds, dyestuffs, camphor, and rubber were not produced in quantities sufficient to satisfy the demands of industry, agriculture, and health.

Today Americans are virtually self sufficient. Thanks to the chemical research and chemical substitutions this country can now produce what that it needs more nearly than any other industrial country. Thus, we have economical as well as political independence. In preceding pages are listed some of the synthetic products that serve man's needs better than the natural products on which he had depended since the beginning of time—products that have influenced our nation's growth and our industrial evolution.

The chemical industry has grown to serve the daily needs of our nation. The industry has not only supplied products to meet our wants, but also provided employment for both labor and capital. The wage earners employed by the chemical industries of the United States numbered in 1935 more than 65,000 and their wages amounted to

\$80,480,665. The total value of the products produced was \$476,502,663. The cost of materials, containers, fuel, and electricity purchased by the chemical industry amounted to \$329,291,117.²

A study of these figures will show the amount of business and the number of people affected by this industry which has resulted from chemical research.

In time of economic depression chemistry has come to the aid of the nation by creating new industries and new jobs for the unemployed. These new developments have broadened the market and bettered the prices for the country's excess raw materials. Last year, for example, the Du Pont Company alone used fifty-one million pounds of cotton linters, seven million pounds of turpentine and rosin, thirty-four million pounds of vegetable oils for conversion into hundreds of useful products.⁸ The chemical industry is also a good customer of the forests and mines, in that it utilizes their products.

In considering the advancements in civilization that can be credited directly to chemistry, we must also remember that the "Age of Chemistry" has only begun. In great research laboratories, such as those maintained by the Du Pont Company, Commercial Solvents

Company, Dow Chemical Company, General Electric Company, National Carbide Company, and others, chemists are continually trying to find new ways to combine nature's raw materials.

When an improved product is made, it gains widespread use and in turn lower prices, increased production, and more employment result. The amount of money spent by our leading industries each year on research probably will exceed twenty-five million dollars. The Du Pont Company alone spends about six million dollars annually trying to improve the products that they now make and to find new ones.

For anyone to try to predict what the future holds for chemistry is a waste of time. It is like trying to forecast the direction a bird will fly from a limb. It will depend on the influence exerted, the opportunities offered, and the demands that are made of it by industry. Although we do not know what contributions chemistry will make in the near future, we have every reason to expect greater and more rapid advancements than have been made in the past, because of the fundamental principles of chemistry that are now known.

At the present time, work is being done in preparing synthetic motor fuels in those countries which

are not blessed with abundance of petroleum. In Germany good results are being obtained by hydrogenation of coal tar. Also mixtures of various anhydrous alcohols are being used. In order not to depend on an uncertain supply of crude rubber, chemists have done much work toward making synthetic rubber from milk weeds and other easily accessible plants. Some of these products are of excellent quality, but at the present time are more costly to produce than the naturally occurring ones.

The future of our nation will be greatly influenced by the chemical substitutes that are developed. These will help to solve our needs, use our surpluses, and keep our nation economically and industrially free.

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