SYNTHETIC RESINS FROM PETROLEUM

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INTRODUCTION

The word "resins" is very broad and is used to describe many different materials occurring naturally or produced synthetically. These range from the gums or hard resinous lacquerlike substances found in trees and plants, to synthetic substances and to the color bodies absorbed by decolorizing clays from petroleum fractions or other oils.

According to this latter meaning, all plastics can be considered. Even in restricting the original meaning of the word "plastic": material of a certain elasticity and softness that may be molded; to the modern sense: a polymerized substance, made by combining certain chemicals and transforming them under heat and pressure into a new substance. We know today that the greatest majority of the synthetic plastics can be manufactured from petroleum more or less completely through pure chemical compounds obtained from petroleum as products or by-products.

As hydrocarbons are present in every fraction of crude oil from the gases to the solids, every part of petroleum offers the possibility of chemical synthesis, and may be regarded as a potential brick for the plastic chemist. But this study will be confined only to the resins which can be obtained directly from petroleum or its fractions.

The naturally occurring petroleum resins which are asphalt-like in nature, will not be part of our study, but we will be interested in the field which is between these two extremes. There we find many by-products or even crude products of a more or less complex nature which may be treated or condensed to form resins of undetermined structure. The purpose of our study will be to disclose more fully the properties and preparations of these resins.

The subject of resins from petroleum is old because bitumen was the third plastic to be developed, after casein and shellac. It is a cold molded plastic which can be molded only under pressure. Along the same line asphalt base plastics were developed for electrical devices in the early days of the plastic industry. In recent years those plastics occurring naturally in petroleum have not been used very much, but the possibility of employing petroleum as a cheap and abundant material to produce resins directly, seems interesting.

RESINS BY OXIDATION OF PETROLEUM

Oxidation can be applied to petroleum and its distillates to give rise to a great variety of products including resins and asphaltic materials, depending upon the conditions of oxidation.

Brooks (1) reveals that cracked gasolines have sometimes given trouble due to the oxidation of the drying oils by air with the formation of resinous substances. Such resins can be obtained in the form of honey yellow, alcohol soluble material, and it is possible that this nuisance can be turned to profitable account by study of the problem. Always, according to Brooks, the nature of other natural resins or copalacids hold out the promise that the polycyclic hydrocarbons of lubricating oil distillates and the heavier fractions of gas oil can be oxidized to commercially valuable resins. So a cheap process of oxidation which would give resins as the principal product, and from which the black asphaltic matter could be separated if formed, would be valuable. Thus far, however, no high grade resin appears to have been made by such method, because there is formation of black asphaltic products. For synthetic resins the most interesting reactions are those yielding asphaltenes and asphalt-like bodies and carboxylic acids.

By vapor phase oxidation of heavy petroleum distillates it is possible to obtain acids of the aldehyde or hydroxyaldehyde type mixed with aldehydes of

various molecular weights.

According to Smith and Cooke (2) in their report to the U.S. Bureau of Mines, a highly unsaturated gasoline can be oxidized more easily than a saturated sample, therefore it seems probable that aldehydes are formed in gasoline largely by oxidation of olefins or similar compounds. According to (3) J. H. James' patents on saponification of the products of oxidation with alkalies, brown or yellow resins are formed by condensation. In fact the mixture obtained by catalytic oxydation contains w-aldehydo-derivatives of acids C_{12} to C_{15}, together with aldehydes and hydrocarbons. Only the former are converted into soaps by treating with caustic alkali; KOH for example, after having been fractionated. If the soaps are separated and treated with an excess of dilute hydrochloric acid (4% HCl) resinification of the liberated acids take place. These latter resins are used in varnishes and paints.

The liquid phase catalytic oxydation of hydrocarbon oils gives resinifiable acids. Schaal (4) obtained liquid acids by air-blowing petroleum in the presence of alkalies, these acids, on vacuum distillation, furnish a residue of a resinous nature. Solid acids from this same procedure form asphalt-like masses with calcium or magnesium oxides. Esters of the latter acids are somewhat resinous in character and can be used in making varnishes or as substitutes of waxes, pitch or asphalt. According to Charitschoff (5) Shaal's method yields naphtenic acids with asphaltogenic acids. The latter are viscous polynaphtenes which are pseudo-acids, apparently tribasic. Their origin is probably bicyclic condensation products, which are easily decomposed to resins by heat or the action of concentrated alkaline solutions.

The high boiling petroleum fractions such as the lubricating distillates, the turbine or transformer oils, give resins on exposure to air. They are acids which are brown, hard and brittle in the dry state, and are soluble in the lower aliphatic alcohols, chloroform, pyridine, benzene, and slightly

soluble in ether.

Tar oil, paraffin and montan wax give acids of high molecular weights by oxidation. Experiments have been performed by Wilhelm Schneider (6).

a. A sample of tar oil boiling from 200° to 300° C. is freed from phenols and solid paraffins. Then its composition is:

$$\text{unsaturated} \text{ - - - - - - - - } 50\%$$
$$\text{naphtalene} \text{ - - - - - - - - - } 30 - 40\%$$
$$\text{paraffin hydrocarbons - - - } 10\%$$

In treating with air at 30 atmospheres pressure and 200° C. about half of the tar oil is precipitated as a solid asphalt. In the presence of a dilute Na_2Co_3 solution an alkali soluble product is formed with a 55% yield. When isolated it is a sirupy liquid, insoluble in petroleum ether with a density greater than one. It appears to be similar to Charitschoff's polynaphtenic acids.

b. Lignite paraffin of m.p. 53° oxidized in presence of a sodium carbonate solution at 170° C. under 30 atmospheres gives 46% of water insoluble monobasic fatty acids. Alcohols and aldehydes, like the hydroxyacids, are present only in traces. The mechanism seems to be the formation of acids of high molecular weight, loss of Co_2, reoxidation, and so on, forming the whole homologous series. Those fatty acids are brown in color and have an average molecular weight of 271.

c. The American paraffin oil gives also water insoluble acids; $C_nH_{2n}O_2$ (n = 13, 15, 17, or 19). The reaction is accelerated by iron, copper, and manganese salts--and not by alkalies.

d. The montan wax is hard to oxidize and gives low yield of water insoluble acids. Schmidt (7) oxidizes paraffin wax with air at $100 - 120^{\circ}$ C. to obtain resin acids and fatty acids. Mercuric oxide is a catalyst for the reaction. According to Chernozhukov (8) the products of the oxidation of petroleum having acid values between 60 and 110 give resins by loss of carbon dioxide and

condensation of the resulting unsaturated hydrocarbons.

In two patents, G. S. Petrov (9) explains how to obtain artificial resins by the condensation of aldehydes and the acids obtained by oxidation of petroleum distillates in the presence of amines.

By destructive oxidation of paraffin wax one obtains crude acids, and by pressing them it is possible to obtain dark colored liquids, which are acidic in character and insoluble in petroleum ether. Martin Luther and Robert Held (10) propose in their patents to heat them with an aliphatic compound containing at least two OH groups such as glycerol or other polyhydric alcohols to a temperature of 150° to 210° C. A catalyst (lead oxide or sulphur) may be used. After a short heating, materials resembling linoxyn or artificial rubber are obtained and can be used in linoleum or rubber mixtures. In place of the liquid acids it is possible to use the unsaturated aliphatic acids obtained by the dehydration of the oxidation products of paraffin hydrocarbons or waxes. The esters of these acids and glycerol, sorbitol or other polyhydric alcohols are heated while oxygen or air are passed through them. A diluent such as a petroleum distillate, carbon disulphide, or carbon tetrachloride is suitable, and substitutes for linoxyn or rubber are obtained.

According to Burwell (11), a petroleum distillate of 36 to 40° Baume, and distilling mainly at 260 - 360° can be oxidized in liquid phase with air or other oxygen-containing gases at 100 to 155° under 150 to 350 pounds per square inch with or without a catalyst (manganese oleate or 0.1% of iron or copper). There is formation of hydroxy-carboxylic acids insoluble in petroleum and in water, which are shellac substitutes.

M. Katz (12) showed that it is possible to oxidize Alberta bitumen by air blowing. During the operation there is dehydrogenation by removal of hydrogen as water, and then polymerization which is accelerated by the sulphur of the bitumen and gives a substance similar to rubber.

Koetschau (13) found the possibility of preparing resins from high boiling petroleum distillates. He subjects a transformer oil (sp. gr. 0.915 and molecular weight, in benzene, 293) to the action of ozone at 12° C. Ozonides of mean molecular weight 663, which corresponds to the formula $(C_{19}H_{20}O_6)_2$, are obtained in a 25% yield. They are solid or semi-solid substances, insoluble in petroleum ether, and at higher temperature they change to a red colored resin.

Resinous substances are produced by oxidation of petroleum hydrocarbons (vaselins and paraffins) by the action of certain chemical oxidizing agents. Yellow vaseline, when mixed with concentrated sodium hydroxyde and potassium permanganate and shaken for three days, gives a sludge which gives an oil on dissolving in dilute sulphuric acid. Upon heating on the steam bath with concentrated sulphuric acid the oil evolves SO_2 and gives an apparently crystallin mass, insoluble in all ordinary solvents. Liquid paraffin when oxidized in alkaline solution with permanganate until insoluble, leaves $M_{n2}O_3$ remaining. The insoluble mass which is formed gives a soft resin when dissolved in dilute hydrochloric acid. If first oxidized in alkali solution with permanganate and then by further reoxidizing by acid solution of the oil recovered from the alkaline oxidation of the paraffin oil, a brittle resin softening at 75° C is formed. Chlorine can form resins with paraffin oil, potassium bichromate favors the formation of solid products; but with it the reaction becomes violent and must be carefully conducted around 100° C. The yields are about 75% of resinous brown fatty acids.

K. Eisenmann and F. Bergmann (14) patented the following process. By bleaching the montan wax with chromic acid free organic acids are obtained and by partial neutralization and esterification respectively to salts and esters, they give a mass. This mass can be used as a binder with iron powder to give a product useful in the manufacture of magnetic cores.

Petrov's varnish is the calcium salt of oxidized vaseline dissolved in turpentine; it is suitable for all kinds of interior painting, since it is not very fast to moisture.

The work of Bestuzhev (15) shows that aromatic hydrocarbons produce asphaltic compounds which are easily carbonized, and naphtenes produce acids mainly with intermediate reaction products. Bestuzhev shows that under mild oxidation with nitric acid naphtenes give only acids, but with stronger acid and higher temperature the oxidation is more energetic and polymerization products as resins and asphalts are produced.

E. Kleiber and P. Gilardi (16) in a British patent propose to treat petroleum with nitric acid or sodium peroxide in the presence of soda lime or sodium acetate as oxidizing agents. The neutralized liquid which is thus obtained, is distilled over colophony. The resulting distillate is heated under pressure with a dilute alkali and separates into three layers. Both of the upper layers are treated with a rubber promoter (glacial acetic acid, formaldehyde or raw rubber) and by addition of acetone or alcohol to the sirup like mass, an elastic mass is obtained and it can be vulcanized. The third layer can be used as a copal substitute in making varnish. The same authors in a French patent (17) propose another method to treat the products of the oxidation of petroleum by nitric acid or sodium peroxide. Of the two layers obtained after oxidation, one is composed of octanaphtenes, which on treatment with sulphur are transformed to m-xylenes. The other layer, having a turbid aqueous appearance, is transformed by oxidation with fuming nitric acid to cyclohexanes and passes to adipic acid. The latter is mixed with the m-xylenes which are also converted to adipic acid. Terpenes are then added and after heating to about 150°, isoprene and butadiene are formed, from which artificial rubber is obtained.

K. Hielsen (18) in a patent proposes to oxidize the hot asphalt oil or

asphalt pitch with air in the presence of an oxygen transmitter, such as oxides of nitrogen. A catalyst may be added, for instance, manganese dioxide or nitric acid. Thus rubber-like substances are obtained.

RESINS BY CONDENSATION WITH VARIOUS COMPOUNDS

Reaction with Formaldehyde

This reaction was discovered by Nastyukov (19) and was first used to determine quantitatively the aromatics. This first test involved the mixing of the petroleum distillate with an equal volume of concentrated sulphuric acid added by small portions. Then slow adding of one and a half volumes of aqueous formaldehyde. A precipitate was formed, which after washing with petroleum ether and ammonia water was a brown powder. The product was named formolite, and the reaction became known as the "formolite reaction". It involves the precipitation of a certain class of unsaturated hydrocarbons in the oils and certain cycles (naphtenes, C_7H_{16}, C_8H_{18} and cyclohexane) in the form of amorphous compounds through the action of sulfuric acid and formaldehyde upon them. The highest yields were obtained at about 0° C. This formolite reaction had been studied by many authors, from the point of view of the analyst for the determination of the aromatics. We will consider its use only for the production of resins. Two cases are to be considered:

a. Case of light distillates.

The most satisfactory resins with regard to color and melting point have been prepared by refluxing mixtures of the hydrocarbon, formaldehyde and zinc chloride in glacial acetic acid. The ratio of the components varies somewhat with the molecular weight of the hydrocarbon used. The solutions are refluxed for 6 to 18 hours, depending upon the reactivity of the hydrocarbon used and the melting point desired. The crude resin which generally starts to separate

from the solution after 0.5 to 2 hours of refluxing may be recovered by cooling

or "finished" by dissolving in an inert hydrocarbon; and stripping to about

250° C. under a 20-inch vacuum. The four components of the reaction are: the

hydrocarbons employed, catalysts, solvents, and aldehydes.

Hydrocarbons

They are of importance for the reaction rate and the color of the final

product. There are substances which cause the resin to be dark in color.

It may be small amounts of compounds such as olefins, peroxides, sulphur and

nitrogen compounds, and possibly the structures of the hydrocarbons become more

complex, oxidation and other deleterious side reactions take place. It is

therefore advisable to take good cuts of petroleum distillate by fractionation

and then pretreat with aluminum chloride, percolate through clay and distill

over caustic. The fraction of the refinery distillates boiling between 135°

and 270° show the best results. The various cuts have very different reac-

tivities due to their chemical structure and composition. The least reactive

probably consists mainly of tri- and tetra-substituted benzene rings, whereas

the more reactive consist principally of disubstituted benzene and naphtalene

derivatives. Since at least two positions of the benzene ring must be free

for multiple condensation, these results would be expected. The resins may be

modified by the addition of phenol or alkylated phenols to the feed stocks

prior to the condensation or preferably after the reaction has proceeded nearly

to completion, since the phenols are more reactive. In this manner it is

possible to vary the solubilities and heat reactivities of the final product

almost at will.

Catalyst

The choice of the catalyst is largely determined by the effect on the color

of the final product. First sulfuric acid (95%) and phosphoric acid (85%) in glacial acetic acid were used as the reaction medium. The resins formed from a 137° to 140° C. hydrocarbon but were very dark-colored. Anhydrous hydrogen chloride in acetic acid is not a catalyst but zinc chloride added to the mixture gives a violent reaction producing a black, charred-looking resin. Zinc chloride in acetic acid as a 10% solution gives a reasonable reaction rate without excessive color formation. Anhydrous ferric chloride is an even more active catalyst than zinc chloride; a 2% solution in acetic acid gives the same reaction rate as 10% of the latter. The other chlorides (Al, Ca, Mg, Sn, and Hg) are of no value.

Solvents

The use of a solvent in the formolite reaction is not an absolute necessity. However it makes a smoother reaction, which is more easily controlled. Glacial acetic acid appears to be one of the best. Among them are: propionic acid and chloracetic acid. Dichloracetic is more active.

Aldehydes

Paraformaldehyde is interesting because it contains very little water. Gaseous formaldehyde may also be used and also formalin. The resins prepared from highly aromatic light petroleum distillates and formaldehyde are amber to pale in color, are very brittle, and have melting points up to 140° C. They are neutral hydrocarbons containing a trace of oxygen and possess molecular weights of 700 and higher. They can be used in paints and varnishes, where they give a good viscosity to the oils and do not interfere with their drying properties. In the varnish films they give a medium hardness and toughness and a good alkali resistance, but they are not especially resistant to hot and cold water. The films have good color and adhesiveness while possessing an intermediate gloss and are subject to slight yellowing with age.These resins

are very soluble, and are insoluble only in the lower alcohols and petroleum ether.

b. Case of heavy distillates.

Cracked oils, tars and tar distillates may also be condensed with formaldehyde in a manner similar to the one used for light distillates. The only difference is that precautions to be taken with regard to color formation are relatively unimportant. This is true because the raw materials are dark in color to start with. An even better source of raw material is the highly aromatic portion of lubricating oil which can be separated by extraction with phenol or nitrobenzene in the modern processes of refining. They give resins reddish to amber in color.

According to Nastyukov's patents (20), the crude distillates are treated with a mixture of four volumes of sulphuric acid and two volumes of 40% formaldehyde to form a hardened condensation product. The reaction mass is diluted with water and treated with steam to remove light volatile hydrocarbons and filtered. The precipitate is neutralized and washed, then dried to a brown powder. It is freed from the adsorbed saturated heavy hydrocarbons by extraction with cold solvents like benzene or gasoline. This formolite is used alone or mixed with artificial resins or other plastics to manufacture molded articles.

Ormandy and Craven (21) in treating cracked gasolines with formalin in the presence of an electrolyte obtained brown resins, whose consistency varied from a sticky oil to a hard gum. The reaction product was isolated by evaporation of the gasoline and drying the residue in a steam oven. The yield is roughly proportional to the bromine number of the liquid hydrocarbons.

Reaction with Methylal

V. F. Herr (22) found that methylal forms condensation products with the aromatic constituents of petroleum or its distillates. The reaction is

similar to Nastyukov's formolin reaction. Methylal is even superior to formalde-hyde because it acts as a solvent as well as a condensing agent. One part by weight of the oil is dissolved in two parts of methylal and four parts of concentrated sulphuric acid are introduced as a thin stream. The reaction product is separated by pouring the liquid mixture into water, neutralizing with ammonia and filtering. If the liquid is kept cool during the reaction, the product is soluble in chlorobenzene. On the other hand, if the liquid is allowed to become hot and is finally heated on a water-bath for half an hour, a larger yield of an insoluble product is obtained.

Reaction with metallic halides

In his researches G. Torossian (23) found that when anhydrous stannic chloride is poured into a crude sample of petroleum or any of its distillates, a precipitate is instantly formed. Its color, quantity, and physical and chemical properties depend upon the particular fraction of petroleum at hand. Red, orange, yellow, gray, brown, dark brown, and black precipitates are produced from various distillates. There is a polymerization of the oxygenated bituminous constituents of petroleum. This is seen from the fact that the reaction is vigorous and highly exothermic, only a small amount of the reagent is required to produce a bulky precipitate from a heavy crude distillate. The distillates treated with tetrachloride are easily filtered in a suitable filter press and come out as a clear yellow oil. In all cases, and especially with petroleum distillates containing sulfur compounds, distinct improvement in color and odor of the oils is observed. Considering the nature of the action of the tetrachloride, its action on crude petroleum products cannot be explained on the assumption that it is solely chemical in nature. To be sure, chemical compounds are formed when petroleum impurities come in contact with tetrachloride, and polymerization also takes place, but it seems that some physical factors

must enter into the process of precipitation of bulky, tenacious, or plastic bituminous bodies from the crude petroleum or its heavier distillates. The fact that such small quantities of tetrachloride are required to bring down bulky precipitates from the heavier distillates, combined with the fact that although in adding the reagent to a heavy sample all particles of reagent and oil are not brought into close contact at once, the precipitation is almost instantaneous, indicates that the process is physical as well as chemical. It appears that, once the tetrachloride has brought down part of the impurities, the rest will follow as a result of disturbed equilibrium. The tetrachloride seems to react primarily with the oxygenated bituminous bodies, sulfur compounds, unsaturated organic acids and terpinenes, found in petroleum. Terpinenes especially enter into a violent reaction, forming yellow and brown precipitates.

J. Le Nobel (24) treats dark petroleum asphalts with a catalyst-like anhydrous aluminum chloride, zinc chloride, boron fluoride and ferric chloride to eliminate asphaltenes, as amorphous insoluble materials, from the asphalt. The light asphaltic products thus obtained can be used for varnishes and paints.

A patent of the Standard Oil Company (25) gives the following method to prepare stable resins. Petroleum tar is distilled at 150 - 350° at low pressure (1 mm) to remove the oily matter. The residue is agitated at 100 - 180° with 1 - 10% of aluminum chloride for about two hours. The reactive constituents are condensed or polymerized and the yield of resin is increased by adding unsaturated hydrocarbons. The resin is purified either by extraction with a selective solvent or by treating its solution in a hydrocarbon solvent with concentrated sulphuric acid and evaporating the solvent after neutralizing.

N. Zelinskii and V. Smirnov (26) in breaking the heptanaphtene fraction of Baku petroleum (b. p. 101 - 102° C.) with aluminum chloride at 100 to 140° in sealed tubes, obtained a yellow non-distillable resin along with gas
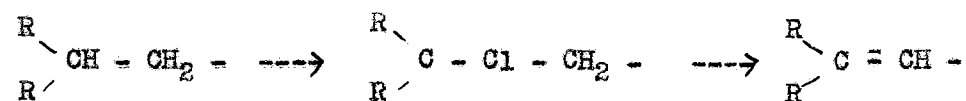
and liquid unsaturated hydrocarbons.

Reaction with Sulphur and Sulphur Chloride

When heated with sulphur the saturated hydrocarbons of paraffin commence to evolve hydrogen sulphide at 150°. At 200° C. the reaction occurs and at 230° hydrogen sulphide is evolved along with carbon disulphide. After seven hours of treatment a brownish black mass is formed and extracted with carbon disulphide and ether, giving resinous and asphaltic substances of unknown constitution. It seems that both condensation and dehydrogenation reactions take place. These substances resulting from sulphurizing paraffin hydrocarbons may be added to rubber before vulcanizing.

J. Meigs (27) investigated the reaction of sulfur monochloride on hydrocarbon oils and on bituminous and tarry substances. The saturated hydrocarbons yield chlorinated compounds with evolution of hydrogen chloride, while the unsaturated hydrocarbons polymerize.

E. Lorand (28) studied also this reaction between sulfur monochloride and the hydrocarbons. Heat development, change of color of the solution, effervescence and the escape of hydrogen chloride mark the reaction. The higher boiling the fraction, the more violently it reacts when mixed with sulfur monochloride. In his work, Lorand found that the reaction is much more general than Meigs supposed. Tests had been run on both single hydrocarbons and petroleum fractions, and it appeared that it is a general reaction of unsaturated hydrocarbons, which consists probably of chlorination and subsequent condensation or polymerization. This author showed that pure hydrocarbons and petroleum fractions breed from their unsaturated constituents and do not react in giving resins. So the action of sulfur monochloride is quite different with saturated and unsaturated hydrocarbons. The sulfur monochloride is a general reagent for the unsaturated chain, and with the saturated straight chains a chlorination occurs. By continued heating to a higher temperature

probably two neighboring carbon atoms lose a molecule of hydrogen chloride and form a double bond. Furthermore, the resulting compound undergoes polymerization and condensation.

$$\begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} CH - CH_2 - \quad \dashrightarrow \quad \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} C - Cl - CH_2 - \quad \dashrightarrow \quad \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} C = CH -$$

According to Lorand the formation of triple bond can occur:

$$\begin{array}{cc} - C & \equiv C - \\ | & | \\ \boxed{\begin{array}{cc} H & H \\ Cl & Cl \end{array}} \\ S & S \end{array} \quad \dashrightarrow \quad - C \equiv C - \; + \; 2 \, H \, Cl \; + \; S_2$$
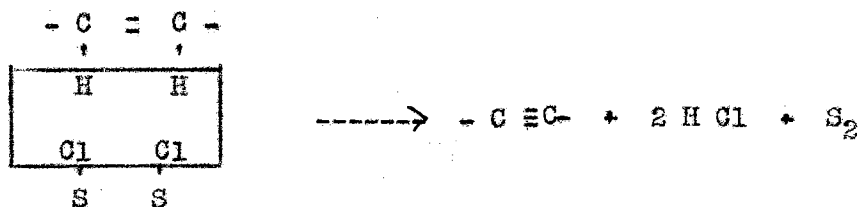
R. Hernels (29) obtained asphaltic bodies by treating petroleum distillates with sulphur or sulphur monochloride. A mixture of eleven parts of tar, two parts of resin, and 1 part of sulfur is heated to the melting point of sulfur and then 11 parts of powdered lime are added to the brown, thickened mass. The resulting product was a brown, opaque, resinous mass, insoluble in water.

L. Landsberg, in treating the oils from dry distillation of acid sludge by sulfur in presence of a catalyst-like sulfur monochloride or copper powder, obtained an insoluble sulphur product.

H. Knight (30) heated residual hydrocarbons (asphalt, pitch, bitumen) with 1% of sulfur to 204° C. Then he added metallic oxides (Al, Cu, Fe, Pb) and earthy substances (talc, aluminum silicate, calcium carbonate and silica) to assist dehydrogenation and subsequent hardening. Finally he heated the entire mixture to 300 - 350° to effect reactions between the oxides and the hydrocarbon material. The resulting plastic was described as non-porous, non-adsorptive and resistant to acid and alkali corrosion. It could be molded in various forms and was adapted for making pipes and conduits.

A. Mury (31) recommended the following method to convert residues from the distillation of crude petroleum into asphalt-like substances. The former were heated in presence of a dehydrogenating agent capable of eliminating sufficient

hydrogen to dehydrogenate petroleum to unsaturated hydrocarbons, which by a subsequent heating under sufficient pressure and temperature, condensate.

Another procedure (32) comprised distilling crude oil at 274° C. Calcium carbonate is added to neutralize any sulphuric acid formed. The residue was treated at 250° C. with sufficient sulfur to give the desired consistency.

In a patent, Egloff (33) suggested to heat cracked pressure distillates or pressure distillate bottoms with 5 - 10% of sulphur or sulphur compounds at 260° and a pressure of 50 pounds per square inch for about six hours, the more volatile vapors being continuously removed.

RESINS FROM ACID SLUDGE

In refining petroleum distillates with sulphuric acid, large quantities of acid sludge are obtained, its formation being at a maximum in the drastic treatment of heavier fractions for white oils and medicinal paraffins. However, even in the less severe treatment of lubricating oils, sludges are formed which tend to become solid. Hydrocarbons responsible for such are not true unsaturates, such as are present in cracked distillates, but are more likely polynuclear naphtenes with unstable groupings or bridge structures. Concentrated or fuming sulphuric acid reacts with these hydrocarbons to form oxygenated, condensed or sulphonated products. Acid sludge consists of a mixture of unchanged sulphuric acid, oil, viscous or solid oxygenated and resinous substances and sulphonic acids. Many attempts have been made to utilize acid sludge in the preparation of resins, asphalts, and paint bases. Possibly because of the sulphurous nature of the initial material, no high grade products have been made therefrom.

L. Singer (34) proposed to treat the acid sludge by a fractional washing with solvents such as methylic alcohol, ethyl alcohol, acetone, and certain chlorohydrocarbons. The washing should be done with two or more solvents—

the later washings contain resins.

L. Landsberg (35) uses a first washing with gasoline to remove remaining oils, and a second with water to remove the sulphuric acid. The asphalt-like product obtained is suitable for use as a combustible for forming explosives with oxidizing salts as potassium chlorate. Mixed with petroleum residuum, tar, creosote, or other substances it forms a road binder or a substance to impregnate wood or other fibrous material for roofing.

Berntrop and Van Ledden Hulsebosch (36) stated that solidification of petroleum residues is effected by intimately rubbing together, for a prolonged time, a mixture of them and resin with slaked lime and water until a tough mass is produced which will harden on standing. This can be molded by pressure into a firm body.

A. Adiasiewitsch (37) prepared resinous material from lubricating oil residuum by blowing with air at 150° - 200° C. and subjecting the material to a simultaneous discharge of electricity.

C. J. Burkley (38) heats together five parts of gilsonite and six parts cylinder oil to 175°, then subjects the mixture to air blowing under pressure of about ten pounds. The temperature is raised to 225° and the blowing lasts three hours. The product is a tough plastic, homogeneous material with a dull luster. It can be used as an electrical insulating varnish.

W. Daitz (39) makes a hard asphalt from residues obtained in treatment of mineral oils, by mixing with magnesium oxide and water to neutralize the free acid and then blows air at 150 - 170° C. The possibility of employing acid sludge in the manufacture of drying oils, varnishes and lacquers has received some attention. It had been proposed by Millochan (40) to make a paint oil, capable of drying to a varnish-like finish by extracting sludge with water, neutralizing the oily and resinous residue and removing the separated oil.

Zaloziecki (41) dissolves the neutralized residue in a mixture of alcohol

and benzene, oil of turpentine, or tar oil to give a lacquer.

J. C. Bird (42) suggests diluting the sludge with water to approximately 25% concentration, warming to 100° C. and treating with a halogenating agent as sodium chlorate. The resin thus formed, is translucent when hot and can be drawn into long silky threads possessing a coppery luster. On cooling, it becomes friable and can be ground to a powder. The resin dissolves in alcohol and evaporation of the solvent yields reddish brown scales similar in appearance to shellac. It can be employed in the manufacture of phonograph records, as an insulating media, and as a constituent of molding powder. According to W. Demann (43), oil-refining acid sludges may be treated:

a. with bleaching earth such as fuller's earth, silicagel, or animal charcoal.

b. with substances which may coagulate or resinify, such as phenol, sodium phenolate, formaldehyde, and alkali silicates.

c. with water and a heavy benzine, benzene, tetralin, and like substances of strongly aliphatic or polymethylene character.

Thus a resin is formed which is separated from the acid and other associated liquids.

L. Bolgar (44) mixes equal quantities of petroleum asphalt or tar residue and sludge and heats to 120° C. After agitation the temperature is raised to 250° C. and maintained until complete decomposition of acid compounds. The liquid product is added with various filling materials (sand, rock flour, clay, steatite powder) and pressed into the desired form.

According to L. d' Antal (45), petroleum residues mixed with animal or vegetable oils may be subjected in a like manner to the action of sulphuric acid above 120° C. Volatile components are removed by distillation and a plastic or elastic residuum is obtained.

RESINS FROM CHLORINATED PETROLEUM HYDROCARBONS

There are two different ways for producing synthetic resins from chlorination of petroleum. Sometimes the chlorinated derivatives of high boiling petroleum fractions are resins or resin substitutes. In other cases the elimination of hydrogen chloride from the chlorinated hydrocarbons yields hydrocarbons of varying degrees of unsaturation, which can be polymerized to resins.

Paraffin, ceresin, montan wax and petroleum oil can be chlorinated to a high degree by dissolving in carbon tetrachloride and introducing chlorine. In this way paraffin containing 70% of chlorine, gives a transparent solid substance, which is resistant to acids and alkalies. Chlorinated ozokerite is scarcely effected by fuming nitric acid at 300° C. under pressure. But in spite of this resistance, chlorinated aliphatics exhibit a tendency to split off hydrogen chloride on long standing. Apparently the chlorine atoms are not bound so firmly.

Geller (46) uses soft chloroparaffin resins and hard chloroparaffin resins in a chewing gum base. Blakeman (47) also uses chlorination products of drying oils, paraffin wax, and naphtalene in paints.

C. Ellis (48) uses chlorinated asphaltic petroleum oil alone or with other chlorinated chemicals to produce a fire-proof insulator suitable for coating wires. Another flame-proof, flexible electrical insulation is based upon the chlorinated hydrocarbons from solvent naphta, and wax and asphalt.

Wickenden (49) used a mixture of chlorinated petroleum asphaltum and chlorinated vegetable oils, serving as a toughening agent to produce an acid resisting paint or varnish.

Chlorination and Dechlorination

Cracked tar of petroleum origin obtained in liquid or vapor phase cracking

is used as the preferred raw material. The tar is subjected to distillation under high vacuum or with steam and a lower vacuum by which means about 85% of the tar is obtained as distillate. The distillate is chlorinated slowly with agitation at substantially room temperature until 10 - 15% of chlorine has been absorbed. The chlorinated product is then heated in a still up to about 350° C., first at atmospheric pressure and then under vacuum. The treating simultaneously removes as overhead products the chlorine in form of hydrochloric acid and an oily material. Only traces of chlorine is found in the hydrocarbons carried overhead and in the residue. If the bottom remaining in the still is cooled to about 100° C. and then agitated with about three times its weight of a selective solvent such as naphtha, from 0 to 15% of hydrocarbon insoluble material can be separated and the final resin recovered by distilling off the naphtha either at atmospheric pressure or under slight vacuum. When a lighter colored product is desired, the naphtha solution is treated with 95% sulphuric acid before the final distillation. The acid sludge is separated and the solution neutralized either by contacting with fine clay or by washing with water or dilute alkali. The yield of resin is on the average 15% of the tar distillate and will depend on the degree of chlorination. The more thorough the chlorination, the higher will be the softening point of the resin. The latter is above 30° C. and usually between 70° and 105° C. as determined by the ball and ring method. Increased chlorination, however, also increases the hydrocarbon insoluble material and consequently decreases the yield. The final resin is an unsaponifiable solid, odorless and tasteless, and has a yellow to reddish brown color. It is soluble in naphtha, drying oils, esters, and aromatic solvents, but not in water, lower alcohols or acetone.

Among practical realizations we find that a fraction from Caucasian petroleum boiling from 68 to 73° C. can be chlorinated to yield dichloromethylcyclopentane. The latter is dissolved in glacial acetic acid and treated with a small proportion of sulfuric acid. Elimination of hydrogen

chloride and subsequent polymerization of the resulting methylcyclopentadiene probably occurs. When the dichloroderivative is dissolved in two parts of acetic acid and boiled with 20% of zinc chloride, hydrogen chloride is evolved and a resin precipitated.

Bielouss and Gardner (50) chlorinate petroleum oil until it contains 34% of combined chlorine. Then they dechlorinate by heating at about 220 - 240° C. without catalyst to obtain a drying oil. If the temperature during dechlorination rises above 250° C. resinous and asphaltic substances are found. When dechlorination has to be accelerated superheated steam in presence of a solvent for the chlorinated material, as kerosene, can be used with catalysts as metallic iron, zinc or aluminum, or their oxides.

According to H. Gardner (51), dechlorinated oil, such as chlorinated and dechlorinated petroleum products are mixed with high boiling glycerides, and by distillation give a drying oil and a hard and brittle resin as a residue. The latter can be used in varnishes. The same dechlorinated oils (52) employed with sulfur and rubber can be added with fillers or pigments (lampblack, zinc oxide, or barium sulphate) to give tough molded articles, which may be vulcanized.

The Standard Oil Company (53) has patents on the chlorination of the distillate boiling above 150° from a cracked petroleum tar. Then dechlorination by heating under a vacuum to 350°; the resin is extracted by a solvent such as naphtha, and then decolorized. S. Fulton, the author of these patents, gives the following details: The cracked petroleum fraction boiling between 300 - 660° F. (1 mm. pressure) is the raw material for synthetic resins. Chlorine is bubbled through the distillate, while it is agitated at room temperature, until 10 - 15% is absorbed. Distillation of the product eliminates chlorine as hydrogen chloride and also any volatile oily components. Only traces of chlorine are found in the residue, which is dissolved in naphtha, filtered and

the solvent evaporated. A lighter colored resin may be obtained if the solution is treated with sulphuric acid and neutralized before removal of the solvent.

E. Hultman (54) suggests to use a mineral oil boiling above 205° C. and treat it at temperatures below its boiling point with a polymerizing agent (cerium oxide or dioxide). The product is cooled to 17° C. and subjected to the action of an activated reducing gas (such as methane and carbon monoxide contacted with nickel or platinum at 205° C.) and finally to a halogenating agent as chlorine or bromine. A soft and rubbery, vulcanizable material can be readily separated from the bulk of the oily mass.

J. Morrell and G. Egloff (55) describe a process for producing resins from the polymerized hydrocarbons, contained in cracked petroleum distillates. These constituents, after being separated from the distillates, are mixed with phenols, cresols, tar acids or other compounds, then heated to 500° F. and chlorine introduced. The viscosity of the product is regulated by the proportion of chlorine employed.

A patent of C. Krauch and M. Muller (56) - Cunradi - shows that the hydrocarbons resulting from the destructive hydrogenation of oil or coal can be treated by a dehydrogenating catalyst such as chromium oxide at 500° C. The product obtained is treated with aqueous hydrochloric acid, passed over barium chloride. The resulting olefins are treated with chlorine and dechlorinated by splitting off hydrogen chloride. The resulting unsaturated hydrocarbons are polymerized with sodium to give resinous or rubber-like substances.

CHLORINATION AND CONDENSATION WITH METALLIC HALIDES

As in the previous method, high boiling distillates of predominantly aromatic structure are chlorinated at moderate temperatures and treated with from 2 - 10% of a metallic halide such as aluminum, ferric or zinc chlorides. Heating at 75 - 100° C. for ten hours usually suffices to complete the reaction.

After decomposition of the catalyst, unreacted material is removed by distillation up to 320° C. at 1 mm. pressure, and the residue is treated to improve its color, melting point, etc. This treatment consists of a selective extraction of the resinous material with a hydrocarbon solvent which may be followed, if desired, by agitation with concentrated sulfuric acid and neutralization with clay or caustic. The yield of resin is usually within the limits of 20 - 50%, and the products have a softening point in the range of 90 - 125° C. as determined by the ball and ring method. A modification of the process consists in the addition of aromatic hydrocarbons such as benzene, naphtalene, to the chlorinated distillate before condensation.

RESINS FROM CRACKED DISTILLATES

Hydrocarbons oils which had been subjected to cracking or thermal decomposition, differ from corresponding fractions from crude petroleum. Unlike crude oils, cracked products contain unsaturated hydrocarbons as monolefins, diolefins, and olefins having aromatic substituents. This is because cracking hydrocarbons under pressure produces a high boiling residue as well as products of lower molecular weight than the original feed stock. The tar residue is formed by cyclization and condensation, with the evolution of hydrogen or hydrocarbon fractions rich in hydrogen which go to satisfy the hydrogen requirements of the light cracked products. As far as can be determined by the methods at present available, cracking coil tar consists essentially of compounds with highly condensed ring structures, the higher molecular weight fractions being resinous in character. Investigations of this product by the methods developed for determining the general composition of asphalts, show that it contains asphaltenes, resins and oil, along with a small percentage of acidic compounds. Cracked distillates, especially cracked gasoline, because of the unsaturated hydrocarbons may be regarded as a potential source of synthetic resins. Resinous

and gummy substances can be obtained by oxidation of such hydrocarbons, particularly by exposure of cracked gasoline to air or oxygen, though as yet of no practical value, it appears to have some possibilities.

It was also found that highly cracked distillates obtained from the pyrolysis of hydrocarbons formed resins when treated with various catalysts. It was discovered that the resins are largely a function of the diolefine content of the distillate, but highly cracked distillates contain other resin forming hydrocarbons. And the proportion of unsaturated hydrocarbons in a cracked gasoline, for example, depends upon the temperature and duration of cracking, and the pressure. Further investigation showed that the type of hydrocarbon present in the cracked distillate greatly influences the character of the resin obtained.

All this introduces the problem of producing a distillate with a maximum amount of resin-forming constituents and determine the cracking conditions most favorable for their production. At the same time a resin with uniform properties should be produced from a raw material containing numerous hydrocarbons of varying character. For example, high temperature (600° C.) cracking at approximately atmospheric pressure, yields gasoline with a relatively large proportion of olefins. At lower temperatures and super-atmospheric pressures, distillates with a smaller percentage of unsaturates are produced. It has been found that high temperatures and low pressures are in general the best conditions for producing resin-forming distillates. They contain:

1. straight chain and cyclic olefines.

2. straight chain and cyclic diolefines.

3. aromatic and substituted aromatics with both saturated and unsaturated chain.

4. unchanged paraffins.

The study of cracking under different conditions in order to produce a cracked

distillate containing uniform proportions of the desired constituents from which commercial resins could be synthetized reveals the following facts: A distillate of uniform character can be obtained by carefully selecting the proper type of hydrocarbon to be cracked and exercising close control over the cracking conditions. Then rigid specifications must be maintained in the cracked distillates on boiling ranges, specific gravities, refraction indices, and average molecular weights. This, along with control of the olefins content.

If a peculiar distillate fails to meet the required specifications it can be blended with another distillate or its deficiencies can be corrected by addition of various substances. After meeting the specifications the distillate is immediately converted to resin for it has been observed that there is a tendency for oxidation and polymerization to proceed if left in storage.

For practical realizations, perhaps the most successful method of utilizing olefins in cracked distillates is by controlled polymerization. An example is the action of aluminum chloride on gasolines containing monolefins, diolefins, and aromatics.

By standing in contact with air for long periods of time, cracked gasolines give a semi-fluid, brown and sticky mass. It is designated as "gum" because of its appearance and consistency, reminding one of natural gums. Its formation is accelerated by bright sunlight or rise in temperature. It also can be produced by evaporation of cracked gasolines in the presence of air.

Schonbein (57) was the first to note that slow oxidation of oils. Then many authors studied it. Smith and Cooke indicated oxidation of hydrocarbons to aldehydes and polymerization of the latter to give the gums and resins in cracked gasoline. Moisture and light accelerate these reactions. At first it was thought that phenol-aldehyde resins were formed, but the absence of phenols led to the conclusion that aldehydes alone are responsible for resinification. The gum,initially sticky, becomes harder on standing and

prolonged drying gives a hard and brittle resin.

Brooks (58) and Mardles and Moss (59) indicate that along with aldehydes, ketones, and acids, organic peroxides are involved in the oxidation, giving the gums in cracked gasoline, during the early stages. Many authors propose different methods to extract resins from cracked distillates. The material thus obtained is thick, sticky, and reddish brown, and does not seem to have much commercial interest. It is extracted rathermore to purify the gasolines or the oils. But if the resins formed during the cracking of oils are not so good in quality it is possible to synthesize some from the same distillates by polymerization.

RESINS BY POLYMERIZATION OF CRACKED DISTILLATES

When petroleum is cracked, along with the distillate, gaseous hydrocarbons are produced, containing isobutylene. It is separated and polymerized over metallic halides as aluminum chloride, boron chloride, or boron trichloride to give polyisobutylene, having molecular weights as high as 300,000. The trade names are Vistanex in the U.S.A. and oppanols in Germany.

The polymerization of simple monolefins does not yield resinous polymers of high molecular weight, the products being mostly oily or viscous liquids. On the other hand, controlled polymerization of conjugated olefins and diolefins furnishes high molecular weight resinous polymers. So particular fractions of cracked gasoline can be used in raw materials to manufacture these resins.

In reacting such a distillate with aluminum chloride for example, which promote both condensation and polymerization reactions, the following four main reactions take place:

1. Polymerization of olefines to form high boiling oils. Sullivan and his coworkers (60) studied the reaction to prepare lubricating oils with superior qualities. This reaction alone is detrimental in the formation of resin,

as high boiling oils reduce the melting point of the resins and cause them to be tacky. However, olefins must be present in the distillate to take part in the following two reactions.

2. Combination of olefins with aromatics to form substituted aromatics when treated by aluminum chloride. A part of the olefins present in the distillate described react to form branched chain aromatics. This reaction does not stop with the monosubstituted compound but if there is an excess of olefines present, di- and tri-substitutions may take place. Also the amount of aluminum chloride is a factor in this reaction.

3. Polymerization and condensation of diolefins and olefins to resins. When a very pure diolefine is treated with aluminum chloride, no violent reaction takes place. But if a small amount of olefin is present with the diolefine, reaction starts immediately and continues violently. This reaction can be controlled by adding the aluminum chloride in small portions with agitation and drastic cooling. A point is soon reached after which further additions of aluminum chloride complex is decomposed; for example, by the addition of ammonia, it is found that two polymers result, one soluble and the other insoluble in organic solvents. The soluble polymer may vary from a viscous oil to a hard resin, depending upon the proportion of olefins and diolefins employed and the subsequent treatment to which the product is subjected. If the oil is removed, there results a hard resin which ranges in color from a light straw to a dark brown.

In cracked distillates containing diolefines and olefines, with an excess of olefines, the resulting resin is very soft, being sometimes a semi-viscous oil. In this case practically no insoluble polymer is found. The hardness of the resin, therefore, can be controlled by adding diolefines to such a mixture. If it is observed that a large amount of insoluble polymer is formed with a peculiar mixture, the yield of soluble polymers can be increased by the addition

of olefines.

4. Combination of diolefines with substituted aromatics and subsequent polymerization of these products to resins. This reaction is probably similar to that of combination of olefines with aromatics. However, the intermediate products from the diolefines polymerize to resins in the presence of the aluminum chloride complex. Here again two polymers are formed, a soluble and an insoluble. By study on pure compounds it has been found that in this reaction the more substituted the aromatic nucleus, the greater is the tendency for reaction to take place. In fact, no appreciable amount of resin is formed from a diolefine and pure benzene.

As a conclusion to this discussion, it has been found that cyclic olefines and cyclic diolefines follow the same reactions as the straight-chain olefines and diolefines. Nevertheless, with cyclic compounds the reaction is much more vigorous and the resulting resin is harder and of a better character.

Practically, the polymerization is carried out in vessels, which are equipped with adequate cooling coils, since much heat is liberated in the reaction. The catalyst, anhydrous aluminum chloride, is added in a finely divided state in a small continuous stream so as to avoid local heating as much as possible. The stream of catalyst is under control at all times, and toward the end of the reaction the rate of addition may be increased slightly. In fact, in the formation of resin, an important factor is the amount of catalyst used. With all other conditions the same, the iodine value, yield, and color can be influenced by this factor alone. The yield of resin increases with increase in catalyst to a certain point, where the curve then flattens out and the addition of more catalyst does not increase the yield of resin. There is also a decrease in iodine number of the resin formed with increasing amounts of catalyst. The iodine values also reach a point where they flatten out, beginning at about the point where the maximum yield is reached.

After a time a point is reached where no more heat is evolved with further addition of catalyst. In practice it is best to maintain a constant temperature in the reaction vessels. The distillate darkens in color as polymerization proceeds and at the end of the reaction it has changed to a dark reddish brown color. The viscosity and specific gravity of the distillate have also markedly changed, the material at the end of the reaction having increased in specific gravity from 10 to 15%.

The effectiveness of the catalyst is believed to be proportional to the amount of it that goes into solution. About six hours are required for complete polymerization. The reaction mixture obtained is treated with an alkali to break down the aluminum chloride complex, and the resin remains in solution while there is precipitation of the aluminum hydroxide and the alkali chloride. There is also formed in this precipitate an insoluble organic polymer. By filtration the inorganic material and insoluble polymer can be separated from the resin solution.

The insoluble polymer by repeated treatments with diluted hydrochloric acid 10% and subsequent washings, gives a white granular material, insoluble in all organic solvents and which tends to depolymerize when heated.

The soluble polymer is the one which is of technical interest. Its solution is distilled under reduced pressure to remove the solvents at as low a temperature as possible, and then steam is passed directly into the molten resin. An amber colored resin is obtained after the removal of the high boiling oils by the steam. As the resin is a mixture of higher oils and hydrocarbon resin, its hardness depends upon the amount of oils present. So by controlling the time and temperature of the steam treatment, the hardness of the resin can be controlled up to certain limits. Samples are taken from time to time during this operation, and, when the desired hardness is reached, the steam is shut off, and the molten resin is run into shallow pans and allowed to cool. The

resulting resin is now suitable for various industrial applications and the
type of resin required may be produced by control of the factors of resin form-
ation.

The obtained resin is amber colored, hard and brittle. Its melting point
is between 130 - 240° F. It is soluble in all hydrocarbon solvents and is
insoluble in methanol, ethyl alcohol, and acetone. This resin is practically
neutral with an acid value of 0.1 to 2.

Other investigations revealed that the nature of the final product can
be varied by employing different proportions of two cracked distillate fractions,
one boiling at 25 - 50°, the other at 125 - 180°. The insoluble polymer
referred to above, can be converted into a useful resin. The white granular
material can be heated at 300° out of contact with air to give a light amber-
colored resin, which is soluble in drying oils, benzene, gasoline, and naphta.

Until now we only mentioned aluminum chloride as a catalyst for the
reaction of polymerization, but in the literature other catalysts are mentioned.
Among metallic halides there are iron and zinc chlorides with chlorides of
antimony, indium, titanium, and tin. Such organic compounds as sulphonic acid,
propylalcohol saturated with hydrochloric acid, ethyl sulphate, and aniline
hydrobromide, along with aluminum silicate and active clays are all catalysts of
the polymerization giving resins with quick drying properties, so they have an
intensive application either alone or in combination with the glyceride oils
in the varnishes industry.

The industrial resin manufactured by the process described above is named
Santoresin. We already said a word about its application to make varnishes,
but it exhibits a tendency to bleach on exposure to light.

This resin also finds application in molded products. For this purpose
it is milled with an inert filler such as wood flour, cotton linters or the like.
The molding mixture thus prepared is then molded under heat and pressure.

Articles molded from this resin are thermoplastic, that is, they can be reshaped
by reheating and pressing. However, when sulphur is added to the molding
mixture a true thermosetting compound results, which is completely hardened
by molding under heat and pressure.

Using the same type of reaction the following authors found derivated
processes: Dunham (61) obtained a resin by conducting hydrocarbon vapors
having 5 - 10% of diolefines, through bauxite, fuller's earth, animal or vege-
table charcoal or porous clay, heated to about 200° C. The resin, representing
a nearly quantitative conversion of the diolefines, was molten at this temper-
ature, plowed through the contact mass, and was withdrawn. It solidified to a
brittle substance, in appearance somewhat resembling the darker varieties of
colophony. The resin is suggested to varnish manufacture, for insulating com-
positions and may be vulcanized with sulphur.

J. Morrell and G. Egloff (62) suggest to remove the resinous substances
from cracked distillates by an adsorbing medium such as carbon, fuller's earth
or bentonite. Then these removed substances are subjected to the action of
oxidizing agents as air, oxygen at slightly elevated temperatures, and to the
polymerizing action of heavy metal salts such as ferric, zinc, or stannic
chloride, to produce hard resins which may be employed for varnish, insulating
films, or fillers.

A modification of the above procedure (63) is to mix polymeric hydro-
carbons obtained from cracked distillates with a phenolic compound as phenol,
cresols, or tar acids. Then heat to 150° in the presence of an oxidizing gas
such as air, ozones, or oxides of chlorine, until the mixture has reached the
desired viscosity and the product is then allowed to cool. It is suitable for
molding under pressure. The same authors recommend in another patent ultra-
violet or actinic light as a promoter for the action of the oxidizing agent.

Amber colored resins are obtained by treating petroleum distillates

containing a large proportion of olefins with 90 - 95% acid at 95 - 105° F.
removing the acid sludge and steam distilling it after neutralization. Such
resins may be hardened by treatment with cresylic acid or formaldehyde in the
presence of ammonia (64).

The many resins that are by-products of the refining of gasoline cannot
be used to give commercial plastics. They are usually used as raw materials
for the production of asphalts, and it is difficult to remove the sulfuric
and sulphonic acids or sulphuric esters.

E. Kleiber and P. Gilardi (65) polymerize mineral oil directly by agitation
with sulphuric acid and a small quantity of caoutchouc which acts as a priming
agent. An elastic mass, capable of vulcanization is obtained.

MISCELLANEOUS PROCESSES

L. Auer (66) proposed heating oils containing unsaturated hydrocarbons
with electrolyte as mineral or organic acids, their metallic salts, or organic
metallic compounds. Heat and pressure may be employed. The resulting mass
may be submitted to the action of ultra-violet rays. The resins obtained find
application in the manufacture of varnish, rubber, soap, or candles.

According to R. Arnot (67) the mixing of tar and asphaltic bitumen with
a cracked distillate boiling above 190° C. give a composition which is fluid
and suitable for use without heating. The unsaturated hydrocarbons under the
influence of atmospheric oxygen will resinify and polymerize between those of
the tarry substances and the cracked distillate. So the mixture is suitable
for use on roads, where it hardens after use.

De Giron (68) developed the following process: He prepares an aqueous
solution of the fermentation products of hay or molasses. A mixture of water,
chopped hay and sugar of equivalent weight of molasses is allowed to ferment
for about two weeks in a covered receptacle at room temperature. After straining

through a 1 1/8 inch mesh, the liquid is mixed with uncracked petroleum fractions, boiling at 280 - 370° C. at atmospheric pressure. Fractions 300 - 350° C. are preferable. The mixture is aerated in direct sunlight, preferably at 30 - 40° for 70 - 80 hours until water is evaporated. The material thus prepared is either mixed with a base as 1 - 2% of magnesium oxide and 0.5 - 1% of sulphur monochloride or with 1 - 6% sulphur and heated to 115 - 120° in the latter case, to give a rubber substitute used in tire manufacture.

H. Winkelmann (69) by blowing with air mixture comprising an asphalt, a petroleum of flux and rubber, obtained a compound suitable for molding electrical insulators or battery jars and also useful as compounding ingredient in rubber goods.

Recently, the United Gas Improvement Company (70) built a pilot plant, whose crude oil is cracked under atmospheric pressure by spraying it on to refractory bricks heated to about 1100°. The cracked product is a mixture of: ethylene, butadiene, isoprene, piperylene, cyclopentadiene, styrene, methyl-styrenes, benzene, and its homologues, with numerous other unsaturates. Separation and purification has been difficult to achieve, but by distillation it has been possible to obtain pure products as styrene, which can be used in the manufacture of plastics.

The natural gases coming along with the crude petroleum, can be a source of raw material for resins. The study of the gum deposits in gas distribution systems reveals the presence of these substances which are able to yield resins. Nevertheless no industrial development for the recovery of these resins has been realized until now. In fact, these resins do not present much practical applications. But in refining crude oil, refinery gases are obtained, which can be used to manufacture formaldehyde and ammonia, intermediaries for the manufacture of numerous plastics.

The cracking and pyrolysis operations give different gases, the most

important being: acetylene, ethylene, and propylene. All of these gases are intermediary in the production of synthetic resins. According to the recent developments in certain plants for plastics, more and more cracked gases are used as raw material.

Recently such plants as the Jefferson plant at Port Neches (71), have ethylene units where the refinery gases are first treated by diethanolamine to remove carbon dioxide and hydrogen sulphide. This feed stock is then combined with the effluent from the cracking heaters, compressed and separated in fractionating towers, some of which are operated under low temperatures, requiring refrigeration for cooling and condensing. Propane and ethane are used as refrigerants. This type of unit produces a purified ethylene stream, an aromatic distillate, and a hydrocarbon polymer stream. The ethylene can be polymerized to give the well-known "polythenes". Recent patents describe the polymer yielded as of particular toughness. But this field of the refinery gases is just opened to the industrial utilization and very few realizations are known among the public.

CONCLUSION

At first coal and coal tar were considered the basic raw materials for the organic industry and more particularly for the plastics and synthetic resins industry. And in the beginning of this industry petroleum was considered as being of little industrial use for a starting material. In course of time the industry has begun using materials such as asphalt and bitumen.

Since World War II the rapidly expanding demand for plastics and synthetic resins has raised their original raw materials to the rank of essential products. It is nowadays admitted that the oil industry presents the plastic industry with an abundant supply of relatively cheap raw materials.

This study has shown the possibilities of certain fractions of petroleum

for use as a starting material for manufacturing useful resins. On the contrary the petroleum fractions we considered, were usually waste products or products of little commercial value. And the first thought that comes to mind will be the cheapness of the produced synthetic resins.

The discussion emphasized the interest of the reaction of metallic halides on petroleum distillates.

The products of petroleum cracking appear to be of great importance in the manufacture of synthetic resins and plastics. This, because crude oil contains only traces of oxygen, no nitrogen and only a very small proportion of sulphur, which can easily be removed on cracking, which produce pure products free from these adultering compounds. The cracking should be run for the production of a distillate with a maximum amount of resin-forming constituents. High temperatures and low pressures are in general the best conditions for producing such resin-forming distillates.

The cracked gases have been mentioned. We saw that it is possible in some cases to manufacture resins directly from them; but usually they are only one of the raw materials used to manufacture a certain plastic. It seems that rapid advances are made in using gases as a starting point in resin manufacture.

However, this account showed that the production of a uniform product from the heterogeneous hydrocarbons present in petroleum fractions is exceedingly difficult. Nevertheless, possiblities are wide open with certain fractions, or by-products of certain treatments, and who shall say which unknown hydrocarbon fraction of today will not be one of the reigning monarchs of the plastics world tomorrow?

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