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PROCESS FOR THE DEHYDROGENATION OF GASEOUS AND LIQUID PETROLEUM HYDROCARBONS

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2 Claims. (Cl. 106—221)

Applicant has had a number of patents granted him on oxydehydrogenation processes pertaining to petroleum hydrocarbons. Also in patent application, Serial No. 561,158 of September 4, 1931, the following description of processing for the production of unsaturated hydrocarbons from more saturated ones occurs:

"I have found that it is possible partially to oxidize the hydrocarbons by the use of oxygen, in other words to oxidize the hydrogen to form water without oxidation of the carbon content of the molecule.

"In order to carry out the experimental 'runs,' a high pressure resistant cylinder was filled with nitrogen gas at about fifty to seventy pounds pressure per square inch. A pump circulated this gas, to which oxygen was added in the desired percentage, at the rate of about one liter per minute (at fifty to seventy pounds pressure) through a heated reaction chamber through which the hydrocarbons were also circulated.

"Two series of experimental 'runs' were made.

"In the first 'runs' the hydrocarbons were circulated through the reaction chamber at the rate of five grams per minute, whereas oxygen was mixed with the circulating nitrogen in such percentage that approximately .3 of a gram per minute of said oxygen was circulated. The pressure in the reaction chamber was fifty pounds and the temperature thereof 375 degrees C. In twenty minutes 100 grams of hydrocarbons and 6 grams of oxygen had been circulated. The resulting products, including, among others, oxidized hydrocarbon and H_2O, showed a 2% carbon dioxide (CO_2) yield.

"In the second series of 'runs' the percentage of oxygen was increased so that 1 gram per minute thereof was circulated with the 5 grams of hydrocarbon and with the nitrogen at the same pressure and temperature in the reaction chamber. In twenty minutes 20 grams of oxygen was circulated. The resulting products showed a 7% carbon dioxide yield.

"In each case the contents of the gas reaction chamber, pumps, reservoir, etc., approximated 22.4 liters, or practically the volume occupied by one-gram-molecular-weight of gas at normal pressure. Since the final pressure in each case was about 60 pounds, approximately 4 moles of gas were in the reaction chamber pumps etc., at the end of each 'run.'

One molecule CO_2 weighs 44 grams.

$2\% \times 44 \text{ grams} \times 4 \text{ moles} = 3.5 \text{ gms } CO_2$

$7\% \times 44 \text{ grams} \times 4 \text{ moles} = 12.3 \text{ gms } CO_2$

Respectively, therefore, in the two 'runs' 3.5 gms of CO_2 and 12.3 gms of CO_2 were formed.

"Since, in all, in the first 'run' 6 grams of oxygen was used and in the second 'run' 20 grams of oxygen was used, the percentage of oxygen used to form the respective amount of CO_2 is as follows:

$$\frac{32}{44} \times \frac{3.5}{6} = 0.42 \text{ or } 42\%$$

and

$$\frac{32}{44} \times \frac{12.5}{20} = 0.45 \text{ or } 45\%$$

"Thus, about 42–45% of the oxygen used combined with carbon at the above temperature of operation, whereas, excluding a very small percentage, a matter of a few tenths percentage of oxygen found in the residual gas, the greater percentage, or let us say about 58%, combined with the hydrogen. If each atom of carbon in the hydrocarbon molecule had combined with it originally two atoms of hydrogen, which in turn would combine with half a molecule of oxygen, the total oxygen used for oxidizing the carbon atom and hydrogen atom combined with it should be raised 50% or to a total of 21%. Thus, with a CH_2 group of the hydrocarbons

$$CH_2—1\tfrac{1}{2}O_2—CO_2(42\%O_2)—H_2O(21\%O_2)$$

"If we consider the carbon atom as having 3 atoms of hydrogen combined with it, the above figures would be, of course, somewhat altered; for instance 10½% more oxygen would combine with the CH_3 group (½ of 21%—10½%).

"In other words, about 26½% (100—42—31½) in the CH_3 group to 37% (100—42—21) in the CH_2 group, of the oxygen utilized acted selectively to oxidize the hydrogen. At 200 to 300 degrees C., practically all of the oxygen used acted selectively, no carbon dioxide, or at most only a few tenths percent (this small percentage might well be within the limits of error of my analytical method) were found in the residual gas."

The catalytic materials used were a mixture of finely divided copper and iron oxides with asbestos as the carrier, the preferred catalytic combination being made up of the above oxides secured by aqueous alkaline precipitation of their hydrates from their soluble sulphates in equimolecular proportions, with suitable washing and drying of the hydrates to produce the pure oxides.

In his application Serial No. 383,930 of March 17, 1941, the following paragraphs relative to dehydrogenation with the use of metal oxide catalysts occur in the description:

"In the above connection applicant fused together about eighty percent of antimony and twenty percent of antimony trioxide. The fused mass was subsequently crushed. The coarser particles, not passing through a 50-mesh screen, were used as a catalytic material for selective oxidation or dehydrogenation with the use of oxygen and the fines for similar work when em-

ploying nitric acid. Such fusions were made with copper and ferric oxide and with the addition of tin. Tin, of course, aids greatly in reducing the melting or fusion point of the mass, but of course such point must not be carried below that to which the catalyst is to be subjected. Also, tin in some cases appeared to prevent adequate fusion between the metal and its oxides.

"In dehydrogenation work using air at about two hundred and fifty degrees and fifty pounds pressure and the metallic oxides fused catalysts just described, practically ninety-nine percent of the gas acted as a dehydrogenation agent or in other reactions with the petroleum hydrocarbons, only one to two-tenths percent carbondioxide being found in the residual gas. The reaction tube used in this work was about six feet long and one and one-half inch inside diameter and was filled for the first two-thirds with a fusion mixture of five parts antimony by weight to one part antimony trioxide, and the last third with a fusion mixture of three parts antimony to one part of its oxide. The first fusion mixture rapidly reduces the oxygen content, initially that of air or twenty percent, to about ten percent, and the second fusion mixture utilizes the residual ten percent, without burning or formation of carbondioxide, so that very high speeds of reaction can be brought about even at relatively low operating temperatures. About five to six liters per minute of air were forced through the tube and 10 c. c. per minute of petroleum oil. Copper or ferric oxide fusion mixtures were similarly employed."

Also part of a sentence, relative to dehydrogenation with the use of metal oxide catalysts, taken from the above application reads as follows: "the employment of new catalytic condensation agents, and finally the use of catalysts made up from the fusion of the metallic oxides described in Patent No. 2,224,603, with the pure metals themselves."

Finally in this patent application descriptions occur covering the employment as catalysts for oxy-dehydrogenation work of the oxides of metals and of the metallic elements themselves, which form lower and higher oxides, as antimony, copper, iron, silver, tin, bismuth, cobalt, chromium, manganese, cadmium, lead, molybdenum, mercury, nickel, tungsten and vanadium. The above two applications were permitted to expire. In his application Serial Number 373,322 of January 6, 1941, the following descriptive matter occurs:

"In his applications Serial Numbers 333,389 of May 3, 1940, now issued into Patent Number 2,274,204 of February 24, 1942, and 370,005 of December 5, 1940, applicant describes processing for the selective oxidation of hydrocarbons, both liquid and gases. Copper and iron, their oxides and hydroxides, were used as catalysts for dehydrogenation processes.

"Applicant has found now that the combination of metal and oxide of nickel, cobalt, manganese, antimony and tin may be used in place of copper and iron and it is practically certain that other metals may be similarly substituted.

"In place of copper iron oxides, nickel, cobalt, tin, antimony and chromic oxides have been satisfactorily substituted as also molybdic, tungstic and vanadic acids or their anhydrides, actually, of course, oxides. Mercury and arsenic have been eliminated from our study because of their idiosyncrasies respectively to liquify and to poison.

"Hydroxides, as ferric hydroxide, copper hydroxide, chromic hydroxide, etc. may be satisfactorily substituted for oxides. It goes without saying that salts that would decompose under the operating conditions to oxides might be substituted for the respective oxides.

"From the operational data it will be seen that the elements under consideration cannot be classified under a single group or even several groups of the atomic table. Applicant has chosen at least one element from a group for experimentation thus far completed. There is one property that is common to all the metals or elements that have been found operationally serviceable to the processing. The metals under consideration constitute the group of so-called common elements known to form lower and higher oxides. They also constitute the same group of metals or elements that applicant found serviceable in selective oxidation of petroleum hydrocarbons to unsaturated hydrocarbons when he employed nitric acid for such oxidation purposes. Description of this processing is contained in his Patent No. 2,224,603 of December 10, 1940. In his nitric acid oxidation processes applicant now also is using a combination of metallic oxides and metals.

"Applicant has employed not only metals and oxides in the powdered or finely divided state, suitably supported, as on asbestos, but also the so-called granular and wire forms of both metals and oxides.

"An example of his operation when using powdered or finely divided constituents in his catalytic combination is the following: one hundred and fifty grams of powdered copper, fifty grams of copper oxide and thirty-five grams of ferric hydroxide were mixed and spread on two hundred grams of asbestos fiber and cemented thereto by an aqueous colloidal aluminum hydrate. Employing the above catalytic combination at about three hundred degrees centigrade, practically no carbon dioxide was found in the residual gas when operating with seven percent oxygen and ninety-three percent of nitrogen. When operating at the above temperature and with twenty percent oxygen and eighty percent of nitrogen, about 0.5 percent carbon dioxide and 0.5 percent oxygen were found in the residual gas. Thus, even when using air, about ninety-seven percent selective oxidation was established. Operations, although not as good as the above, at much lower temperatures, as low as one hundred twenty-five degrees centigrade and as high as four hundred degrees centigrade showed selective oxidation.

"Generally speaking, selective oxidations or dehydrogenations when using the optimum temperature or operation and finely divided catalysts and air, or about twenty percent of oxygen and eighty percent of nitrogen, of from ninety to ninety-nine percent efficiency were secured. Even when operating with rather coarse granular copper and ferric oxide, or so-called scales, at about two hundred fifty degrees centigrade in the exit gases there was found about nine percent of oxygen and one percent of carbon dioxide so that better than fifty percent of the oxygen of the air employed had reacted with hydrogen and only five percent with carbon. At about three hundred degrees centigrade, using the same catalytic combination, about four percent of oxygen and two percent of carbon dioxide were found in the exit gases. Thus at the latter temperature about seventy percent of the oxygen

had reacted with the hydrogen and ten percent with carbon and twenty percent remained unutilized.

"This dehydrogenation work was carried out in a chrome nickel iron tube, about six feet long, 1½" internal diameter, heated by electric resistance furnaces. In the above noted case, the tube was filled with five kilograms of granular copper and two hundred fifty grams of iron oxide scales. Copper oxide was not used, as under the operating conditions it is gradually reduced to copper. A superatmospheric pressure of from fifteen to sixty pounds was employed. A petroleum fuel oil of about 0.87 specific gravity was used. This was passed through the reaction tube at the rate of about one liter per hour and air was forced through the tube at about four liters per minute. Operating similarly as described, but with the catalyst made up of three kilograms of granular copper, one kilogram of rather coarse iron turnings and two hundred fifty grams of iron oxide scales at about two hundred fifty degrees centigrade, no carbondioxide was found in the residual gas but the latter showed a twelve percent oxygen content. At three hundred degrees, about three-tenths percent carbon dioxide and two percent oxygen were found. Thus iron requires a higher operating temperature but the formation of carbon dioxide is kept at a very low figure.

"It was found, unfortunately, that the so-called iron oxide scales gradually disintegrate at the operating temperatures described, so that the latter would not be serviceable for commercial operation. In employing finely divided particles of the catalysts and a carrier, as asbestos fiber, the former have to be cemented to the carrier, as with calcium silicates, aluminum hydroxide, etc. The method is not wholly satisfactory. To get perfect cementation without vitiation of the catalysts has been found difficult. Therefore, applicant employed the granular form of catalysts noted and was very gratified and surprised to find that even with these larger aggregates of the catalytic materials relatively excellent results were secured. As noted, however, granular copper oxide and iron oxide scales disintegrate. He therefore tried fusion of ferric oxide with molybdic trioxide, the anhydride of molybdic acid, using from fifty to seventy-five percent of the ferric oxide to fifty to twenty-five percent of the molybdic anhydride. Similar fusions were made between ferric oxide and antimony oxide and ferric oxide and silver vanadate. These fused materials are more or less granular or easy to disintegrate and after breaking up the fines are discarded and the material obtained on a twenty-mesh screen used for the catalyst.

"In using chromium, molybdenum, tungsten and vanadium oxides in conjunction with ferric and other metal oxides, chromates, tungstates, etc. possibly are formed. However, these act similarly to the oxides, or as if they were in separate physical and not chemical combinations, so that such possible chemical combinations should remain inherent to the processing of applicant. The same general statement would, of course, apply to manganates and plumbates. On the other hand the barium salts of tungstic and molybdic acids were tried and found practically valueless in applicant's dehygrogenation work. It is thus only the combination of metallic oxides and metals already outlined that act with high efficiency in the dehydrogenation processing described.

"The rate of flow of oil through the reaction tube may, of course, be altered at will and in accordance with the percentage of unsaturation or dehydrogenation desired. The rate of flow of air through the tube was varied at from one to five liters per minute. Usually, about four liters were used. Above five liters the tube when using the asbestos carrier was liable to plug and local heating influenced the results. No very marked differences in results were found when using such variation in the flow of gases. The better catalytic combinations are hence highly efficient. In commercial bubbling towers for the granular forms of catalysts and suitably rotating housings for the carrier cemented catalysts exceptional dehydrogenation efficiencies should be secured. Applicant has operated at atmospheric to two hundred fifty pounds superatmospheric pressure, but the relatively low superatmospheric pressures used, when all points are considered, are probably the most commercially suitable.

"Using seventy grams of nickel powder, thirty grams of chromic oxide, the green oxide, spread on one hundred fifty grams of asbestos fiber as carrier, at two hundred fifty degrees and thirty pounds pressure, the residual gases showed no carbon-dioxide content and nine percent of oxygen; at three hundred degrees four-tenths percent of carbon dioxide was found present in these gases and no oxygen.

"Employing one hundred grams of powdered antimony and fifty grams of finely divided antimonic oxide spread on two hundred grams of asbestos fiber as carrier at two hundred fifty degrees and about fifty pounds pressure, no carbon dioxide and nine and two-tenths percent oxygen were found; and at three hundred degrees also no carbon dioxide and one and two-tenths percent of oxygen.

"With the use of seventy grams of powdered tin and thirty grams of the anhydride of tungstic acid spread on one hundred eighty grams of asbestos fiber, no carbon dioxide was found and nine percent of oxygen; at three hundred degrees there was found six-tenths percent of carbon dioxide and eight-tenths percent of oxygen was left in the residual gas.

"It will thus be noted that antimony proved an excellent catalyst. Silver, gold and platinum come fully within the category of metallic elements found efficient by applicant, but because of high cost he has conducted no experimentation with the latter two elements, although he used a silver as a catalyst in considerable experimentation in his nitric acid selective oxidations. The cheaper metals give nearly one hundred percent effective dehydrogenations as by the processing described. The rarer elements, such as osmium, titanium, thalium, etc. should probably also serve efficiently for the dehydrogenation work described, but it would appear rather absurd to induce higher costs into operational work when the same has been established practically one hundred percent efficiently by lower cost methods.

"Finally, for his oil dehydrogenation work, about two hundred grams of ferric oxide were fused with one hundred grams of silver vanadate, one hundred grams of molybdenum trioxide and one hundred grams of antimony oxide. The mass was broken up and the fines passing through a twenty-mesh sieve discarded. The remainder of about three hundred seventy grams was mixed with two and one-half kilograms of granular copper and two and one-half kilograms of granular nickel and the reaction tube filled with this

catalytic combination. At two hundred fifty degrees centigrade and fifty pounds pressure, three-tenths percent carbondioxide was found in the residual gases and eight and eight-tenths percent of oxygen. At three hundred degrees about one and two-tenths percent of carbondioxide was found present and six-tenths percent of oxygen. Air was passed through the reaction tube at the rate of about four liters per minute and oil of 0.87 specific gravity at the rate of about one liter per hour. Judging from the use of the finer powders studied, crushed antimony lumps and ferric oxide fused with antimony oxide should act similarly to the above catalytic combination or possibly even more efficiently.

"A catalytic combination made by precipitating onto an asbestos fiber copper oxide and iron hydroxide from their sulphates used in equimolecular proportions by an aqueous sodium hydroxide was employed for selectively oxidizing a commercial butane gas. About fifty grams of ferric hydroxide and the same weight of copper oxide were deposited on one hundred and fifty grams of the asbestos fiber and, after drying, one hundred grams of powdered copper was further added to make up the catalytic combination.

"Using the above combination and operating at about two hundred twenty-five degrees centigrade and thirty pounds superatmospheric pressure, neither carbondioxide nor oxygen were found in the residual gas, so that the twenty percent oxygen and eighty percent nitrogen oxidizing mixture had acted one hundred percent selectively. Air was forced through the reaction tube at about four liters per minute and the butane gas at about one and one-half liters per minute.

"Applicant has found that the catalysts act the same with the hydrocarbon gases as with petroleum hydrocarbon oils, only that considerably lower temperatures must be employed with the gases. Various gravities of oils were employed from kerosene to fuel oils of 0.92 specific gravity, however, without the necessity of making practically any changes in the operations. This was true even with the mixture of about half gasoline and half kerosene.

"The unsaturated or dehydrogenated petroleum oils produced have been condensed with resins to give drying oils. For these condensations, applicant has used double chlorides, as those of cadmium and sodium and potassium and copper. He has found these to act similarly to solid acid phosphates and solid hydrogen metallic phosphates. To free these oils from a red discoloration, applicant has found that aldol is very efficient.

"As an example of making an oil of this sort, a dehydrogenated oil, in which about three percent unsaturation had been produced, from a 0.87 specific gravity petroleum oil, was distilled under vacuum. Distillation took place between eighty and two hundred ninety-five degrees centigrade. In this oil heated to about eighty to ninety degrees, there was then dissolved of from five to ten percent of a natural resin, a white colophony resin being generally employed, and about thirty grams of finely divided cadmium and potassium chloride were added. The oil was held at the above temperature for about forty-five minutes under powerful stirring and filtered off from the catalysts. Both lower and considerably higher temperatures were also used for these condensations, but at too high a temperature darkening of the oil becomes excessive. Instead of using distillation the dehydrogenated oils were washed with a dilute aqueous solution of sulphuric or phosphoric acid and finally with a small percentage of aldol. The latter has proved an excellent basis for purification of these dehydrogenated oils. A light lemon-yellow drying oil was produced having excellent drying oil properties.

"Chlorinated petroleum hydrocarbons may be subjected to the processing described by applicant and he has carried out extensive work of this nature. Also operating with the preferred catalysts described and with five percent oxygen and ninety-five percent of nitrogen at four hundred degrees centigrade and thirty pounds superatmospheric pressure, a ninety-nine percent selective oxidation was secured, and even at one hundred twenty-five degrees with air and butane considerable dehydrogenation took place. Finally, it may be said that the dehydrogenation steps may be carried out fairly successfully even at atmospheric pressure and it is quite probable that subatmospheric pressures might be used. Applicant made no study of this latter point, as he deemed it was of no commercial advantage over other processing described. Applicant has not given one percent of the dehydrogenation analyses carried out, but he believes that he has given a sufficient number and representative variation of these fully to establish his basis of operation and invention. It goes without saying that temperatures and pressure and catalytic combinations could be multiplied ad infinitum without digressing from the fundamentals of the invention described. As an example, for instance, he added five percent of oxygen to air in order to operate with percentages of oxygen higher than twenty, but the relative carbondioxide then rises rapidly and he cannot see that any advantage would be gained by the latter procedure, as air is a pretty cheap commodity."

Oxy-dehydrogenation of butane to give butylene is described in applicant's Patent No. 2,274,204 of February 24, 1942. For this work a mixture of iron and copper hydroxides was used. Applicant has tried his metallic antimony, 80%, antimony oxide, 20%, fused or "slagged" catalysts for similar dehydrogenation of butane and obtained very analogous results. This oxy-dehydrogenation of butane with a flow of about three liters per minute of the oxidizing gas, consisting of 7% oxygen and 93% nitrogen, at about two hundred and twenty-five degrees and fifteen pounds superatmospheric pressure, and a flow of gas of about one liter per minute of butane practically no carbondioxide and only a few tenths percent of oxygen was found in the residual gas.

The "slagged" antimony-antimony oxide catalysts above noted, and elsewhere more fully described in the specifications, after use for a few weeks on oxy-dehydrogenation of petroleum oil unfortunately tends to disintegrate. The tensile strength of antimony is apparently too low for continuous operation. A catalyst made up of seventy grams metallic antimony, thirty grams copper and fifteen grams antimony trioxide, all three fused together showed considerable better tensile strength and finally one made up of forty grams antimony, sixty grams copper and twenty grams antimony oxide had good tensile strength and has been employed satisfactorily for the period of a month on oxy-dehydrogenation of a 0.87 specific gravity fuel oil. About once a week this catalyst was heated to about six hundred degrees and air passed over it or forced through the reaction tube to oxidize any carbon or other deposited organic material. Chromic oxide in

conjunction with antimony trioxide has been similarly "slagged" with both antimony and copper to give these metal, metallic oxide catalysts. The latter had been found excellent on petroleum hydrocarbons, ranking up with the best of the catalysts noted and on which analyses of products have been given. Applicant will not give all these analytical data as he believes that he has illustrated by such data the possibly more than sufficiently or too fully already, when considering the length of these specifications. Fusion of other metals as iron, silver, nickel and manganese, more especially with antimony and chromic oxides, was carried out. The catalytic properties of the "slagged" catalysts were found excellent in all cases tried. Seventy grams copper, thirty grams antimony, fifteen grams antimony oxide were fused to produce a catalyst of the type noted. When using three to four percent of chromic oxide the porous slag separated on top of the fused mass was found excellent for the last stages of dehydrogenation or when the oxygen had been reduced to a very low percentage.

The unsaturated or dehydrogenated oils were mixed with resin esters of linseed, tung and soya bean oils to enhance viscosity to give drying oils of excellent quality. For instance, about eighty-five percent of a 0.87 specific gravity dehydrogenated oil was mixed with ten percent of linseed (2 parts) oil condensed with colophony resin (1 part) and five percent of soya bean oil similarly condensed with colophony resin. Also the vegetable oils mentioned were condensed with phenol formaldehyde and phenol furfural resins and these condensation products mixed with dehydrogenated oils, likewise for drying oil purposes. The oils thus produced dry quickly and make good surface coatings with all the common pigments tried. Some of the pigments used were ferric oxide, white lead, titanium oxide, lithopone, "titanox," red lead, chrome yellows and greens and Prussian blue. From fifty to two hundred and fifty percent of pigments on weight of oil were employed.

These dehydrogenated oils were also treated with glycerine or ethylene glycol and the resins noted as also with the resin esters of vegetable oils mentioned. Molecular rearrangements or condensations occur; the viscosity of the drying oil is increased and its weathering quality enhanced. For instance, the combination noted of eighty-five percent dehydrogenated oil, ten percent linseed oil colophony resin ester and five percent soya bean oil resin ester was heated to one hundred and fifty to two hundred degrees with three to five percent of glycerol for about three quarters of an hour in a closed vessel and the oil thus produced and while hot was filtered by suction to free from a small percentage of deposited material. Likewise seven percent of colophony resin, or five percent of a phenolic formaldehyde resin and three to five percent of glycerine was similarly condensed with the unsaturated or dehydrogenated oil by heat as just noted. Combination of resin and resin ester condensations was also carried out as likewise condensation with natural and phenolic or furfural formaldehyde resins. Copal and dammar resins were likewise substituted for colophony resin and found satisfactory. In all cases excellent drying oils were obtained. Small percentages of catalysts, as "solid" phosphoric acid, or, metal hydrogen phosphate, as copper hydrogen phosphate, cadmium and potassium chlorides in combination, or other metallic chlorides and bromides, as ammonium bromide and cadmium chloride, were found valuable in aiding these condensations.

Possibly the best drying oil was synthesized by condensing some four hundred grams of a 0.91 specific gravity petroleum or fuel oil, in which about three percent of unsaturation had been established, with four hundred grams of butylenes, twenty grams of glycerol, fifty grams of colophony resin, twenty-five grams of a phenolic formaldehyde resin, twenty-five grams of soya bean oil and fifty grams of tung oil. The resins were dissolved at about seventy degrees in the unsaturated hydrocarbon oil and vegetable oil mixture and the catalyst of "solid" copper hydrogen phosphate was thoroughly stirred with the oil and resin reaction mass which was then passed into the reaction tube. About four hundred grams of a commercial butylene gas were subsequently forced into the tube and nitrogen gas, to raise the pressure to about two hundred and fifty pounds. The reaction was carried out during about an hour at about one hundred and fifty to two hundred degrees. Of course other temperatures might be employed. The oil while still hot was nevertheless withdrawn from the reaction tube and freed from the catalyst and any precipitated matter by filtration with the use of suction. Applicant found in his earlier work on drying oils that butylenes and other gases of the olefinic series if suitably condensed with other oils and resins gave drying oils with very exceptional weathering properties.

To enhance the weathering quality of these oils when used for metal surface coatings to the pigments used a small percentage, as one percent, of an acid or hydrogen metal phosphate was added. For instance one percent of ferric hydrogen phosphate was added to the ferric oxide used in making up a pigmented oil or paint when using the pigment noted. When using a red lead one percent of a lead hydrogen phosphate was added to the pigment. Also diethyl phosphate, about one percent on weight of oil, was found valuable for a similar purpose. A separate patent application however covers this latter finding.

Finally the butylene gas synthesized, as well as commercial butylene, was polymerized to products similar to gasolene that is distilling at about the same temperature range, by means of borontrifluoride mixed with an inert gas, as nitrogen, and at superatmospheric pressure. Although the work was started at about minus fifty degrees centigrade, or at about the temperature of dry ice, it was found that with suitable dilution of the borontrifluoride by nitrogen and at suitable superatmospheric pressure the gasolene products could be produced at room temperature or fifteen to twenty degrees. For instance 5 to 25% of borontrifluoride, by volume, was mixed with 95 to 75% nitrogen and passed through the butylene gas condensed to the liquid state by nitrogen at from 200 to 2000 pounds pressure. The gaseous mixture of borontrifluoride and nitrogen was then bubbled through the condensed gases which were thereby polymerized to liquid products as determined upon opening of the reaction vessel. As commercial butylene gas contains other unsaturated hydrocarbons, as propylenes and amylenes, and practically complete polymerization occurred these other unsaturated hydrocarbon gases must have condensed similarly to the butylenes. Other fluorides and chlorides, as those of

chromium, silver and copper, were tried as the catalytic material in place of borontrifluoride but the results were comparatively poor. Of course other percentages of borontrifluoride might be employed and other inert gases, as carbon dioxide, might be used in place of nitrogen as a diluent gas.

I claim:

1. In a process for the fabrication of synthetic drying oils the step of subjecting petroleum oils to oxygen and an inert gas at superatmospheric temperatures and pressures in the presence of a metallic element and the oxide of a metallic element, the metallic element and the metal oxide being chosen from the group of metallic elements with commonly known higher and lower oxides and consisting of copper, iron, nickel, cobalt, silver, tin, bismuth, antimony, cadmium, chromium, manganese, lead, mercury, molybdenum, tungsten and vanadium and their oxides and finally the step of heating for establishment of reaction the said unsaturated dehydrogenated petroleum hydrocarbons with a polyhydric organic alcohol containing not over three hydroxyl groups, an oil soluble natural resin and a vegetable drying oil condensed with the said resin.

2. In a process for the fabrication of synthetic drying oils the step of subjecting a petroleum oil of about 0.87 specific gravity to air at from one hundred and twenty-five to four hundred degrees centigrade at superatmospheric pressure in the presence of a metallic element and the oxide of the metallic element, as a catalytic material, the metallic element and the metal oxide being chosen from the group of metals and their oxides with commonly known lower and higher oxides and consisting of copper, iron, nickel, cobalt, silver, tin, bismuth, antimony, cadmium, chromium, manganese, lead, mercury, bolybdenum, tungsten and vanadium and their oxides, and finally the step of heating for establishment of reaction the unsaturated, dehydrogenated petroleum hydrocarbons with glycerol, colophony resin, linseed and soya bean oils condensed with colophony resin, in the presence of copper hydrogen phosphate which had been heated with infusorial earth.

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