FILM STUDY GROUP

REPORT ON MICROFILM REEL NO. 17

Prepared by

THE ATLANTIC REFINING COMPANY

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SCANNING OF REEL #17

U. S. Government Technical Oil Mission

(Orig. Ident. Reel 17A)

Bag 3041 - Target 30/4.02

21. REMOVAL OF H_2S BY AMMONIUM SULPHITE SOLUTION

A report from the Leuna Laboratories, Oct. 24, 1936. Frames 405 - 417.

The equation: $2(NH_4)_2SO_3 + 2\ NH_4SO_3H + 2\ H_2S \longrightarrow 3(NH_4)_2S_2O_3 + 3\ H_2O$ illustrates the process.

Reviewer's comment: This process depends upon conjunction of a number of favorable conditions to make it acceptable over well established methods for the recovery of H_2S, followed by regeneration of the absorbing solution. So far there has been no mention of this process.

22. REPORT FOR 1941 ON WATER GAS PURIFICATION AT OPPAU

Frames 418 - 441, Mar. 5, 1942.

The report is not explicit on the commercial operations outlined, presuming a knowledge of processing and equipment not described.

23. ELECTRICAL APPARATUS FOR DETERMINING ORGANIC SULPHUR IN GASES - An I.G. Report, Ludwigshafen

Frames 442 - 452, Mar. 31, 1937.

The method consists in burning the sulfur-containing material in the presence of oxygen, conducting the combustion gases over platinum contact mass, precipitation of the SO_3 water vapor fog into hydrogen peroxide solution and determination of the sulphuric acid thereby formed as barium sulphate. The method had been used in the Oppau #2 Gas Plant and had given satisfaction. It was claimed that the time for combustion had been reduced from five hours to two hours. The apparatus is readily transportable; the SO_3-fog precipitator operated on a 4-volt battery.

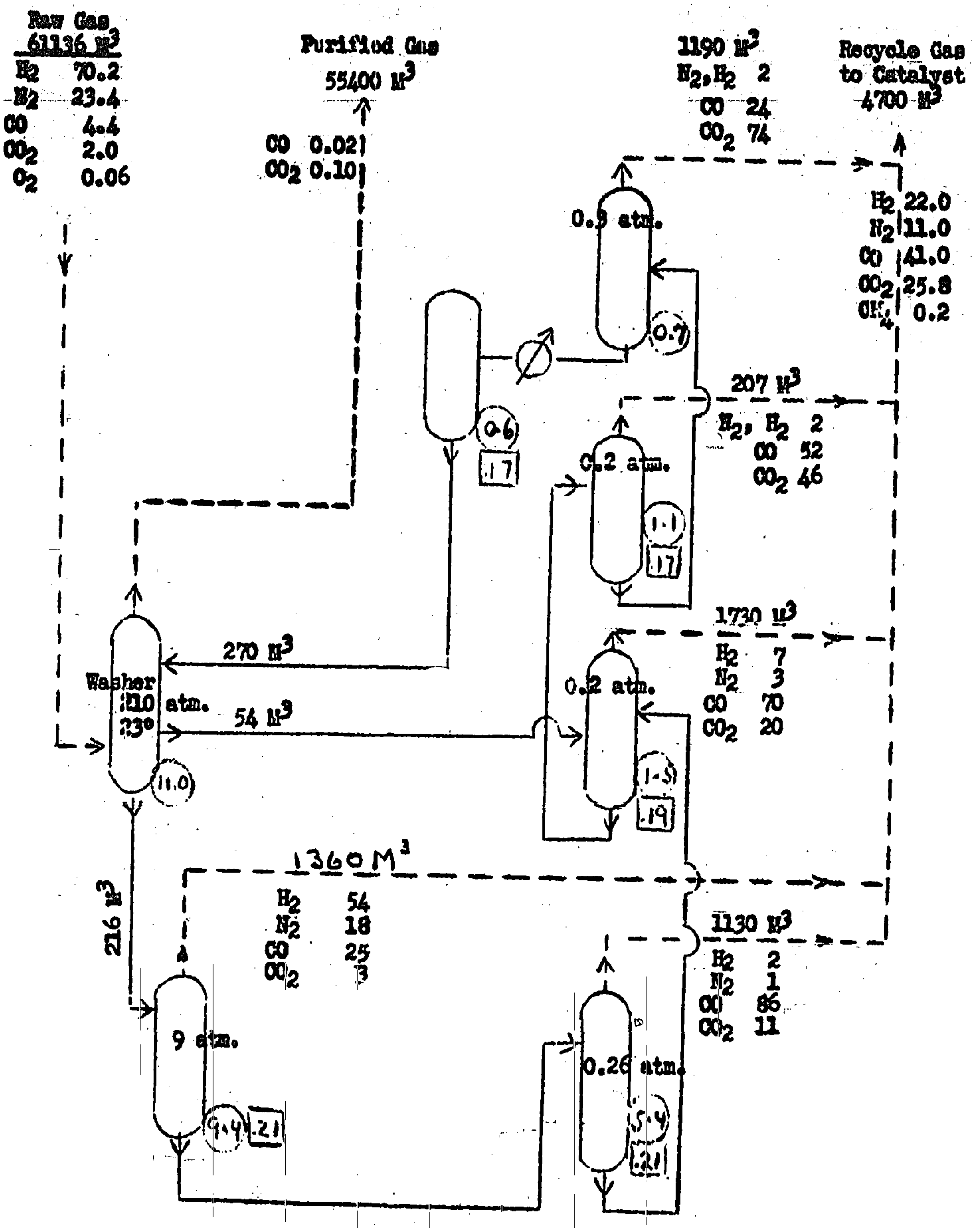
24. SEPARATION OF CO_2 FROM SYNTHESIS GAS BY COOLING

Frames 453 - 476. An Oppau report, Mar. 31, 1939.

The separation of carbon dioxide from gas mixtures at high pressure (150 to 325 atmospheres) by deep chilling to recover the carbon dioxide in liquid form was desired. The solubility of hydrogen, nitrogen, CO and methane in liquid carbon dioxide was investigated. It was shown, what was already known for ammonia operation, that carbon dioxide in gas mixtures has a higher vapor pressure than pure carbon dioxide. A method was sought which would be simpler, cheaper and freer from losses than water washing at high pressure. The writer of the report did not sound optimistic that the process would compete with the relatively cheap, high-pressure water washing process. Graphs accompanying this report are not entirely legible, but do show some of the PVT relationships discussed.

REEL 17, SECTION 25, FRAME 558

Numbers in circle = cc CO/cc solution.
Numbers in square = g atom Cu "/liter solution.



25. REMOVAL OF CO FROM AMMONIA SYNTHESIS CHARGE GAS BY COPPER SOLUTION

Frames 477 - 560. Oppau, Oct. 11, 1937.

Ammoniacal copper salt solution had been used in Leuna for the removal of carbon monoxide and carbon dioxide from ammonia synthesis gas. The present report describes work to increase the effectiveness of the process. The findings were as follows:

(a) To increase the copper content of the solution, it was first necessary to increase its ammonia content. No other means of increasing solubility in a suitable manner appeared available.

(b) Carbon monoxide analysis was so improved that it became a reliable control.

(c) Removal of CO by the solution depends primarily on pressure and temperature, less so on the copper, ammonia and carbon dioxide content.

(d) Measurements with formate solution showed that at low CO pressure much more CO will be removed than with carbonate solution.

It was found that 25°C. is a favorable solution temperature; lower temperatures are disadvantageous. The speed with which different solutions remove CO, CO_2, O_2, N_2, and H_2 were measured.

Slow evolution of gas from the CO-laden, quiescent solution takes place. Small scale continuous degassing showed that the volume of released gas approaches closely the calculated amount absorbed.

The composition of the solution is given in gram atoms or mols per liter:

1.61 atom copper, 5.95 mols ammonia, and 2.99 mols carbon dioxide. From .18 to .20 atoms per liter of the copper should be in the bivalent form. The principal features of equipment and operation are shown in sketch on the facing page. The description of the research work is made in such detail that practical duplication of this process should be possible.

26. PLANT AND COSTS FOR CO REMOVAL FROM WATER GAS

Frames 560 577. A report from Leuna, July 13, 1942.

Calculations of investment and operating costs have been made for plants to effect the removal of carbon monoxide from 50,000 cubic meters gas per hour. The discussion revolves around the question as to whether processing shall be done at 325 atmospheres or 28 atmospheres pressure, assumptions being made in both cases as to the means of effecting energy recovery from the compressed gas streams. The discussion is of a speculative nature, and because the conditions apply to specific plants the choice on paper is of minor importance.

The reviewer has not found correspondence as yet which indicates which application was made.

27. DECOMPOSITION OF METHANE WITH STEAM AND CARBON DIOXIDE

Frames 579 - 589. A report from the Oppau Laboratory, Aug. 12, 1938.

The equilibrium constant of the reaction:

$3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2$ was calculated for 650 to 1,000°C. The constants were also calculated by Nernst's approximation and by the Einstein-Eucken equation. The agreement between the values of Einstein-Eucken equation and the experimental values is good, while the approximation gives satisfactory results. From the experimentally determined constants, the degree of conversion for different conditions of an excess of water and carbon dioxide were determined for 1 and 10 atmospheres. The information can be applied also to the reaction of methane with oxygen.

28. PATENT APPLICATIONS - GASIFICATION AND GAS PURIFICATION

Frames 590 - 658.

A series of about 10 patent applications relating to gasification and gas purification. No correspondence appears in this section to denote the progress through the patent office. Unless otherwise noted, the material is from Ludwigshafen.

(a) Regulating Device for Cyclic Operation in Water Gas Production
No. 13022, Oct. 1, 1941, Frame 591.

The valve-changing operations are so interlocked and actuated as to reduce the dead time encountered in conventional design.

(b) Production of Gases with a High Concentration of Carbon Monoxide
No. 13147, Dec. 8, 1941, Frame 598.

In continuous operation of equipment for the gasification of brown-coal coke with oxygen and carbon dioxide in the blast gas, and employing mechanism for fuel bed stirring and withdrawal of clinker, it was shown that the preferred mixture of oxygen and carbon dioxide introduced under the grate was in the range of 28 to 33%. An example is given in which a producer fitted with a Brassert grate employed a blast mixture of oxygen and carbon dioxide in which the oxygen content was 30%. The producer gas analyzed:

CO_2 - 23.1%
CO - 68.0%
H_2 - 8.2%
CH_4 - 0.2%
N_2 - 0.5%

(c) A Rectangular Vertical Oven for Retorting of Non-caking Bituminous Fuels by Washed Gas
No. 13338, Mar. 25, 1942, Frame 601.

Burners and gas mixing devices are employed for heating the washed gas in a long wall of the oven, passing the washed gas over the fuel to be coked, withdrawing gases from an opening at the opposite end of the oven, and separating the tar vapor and the retort gases mixed with wash gas. Variation of the flow and arrangement of oven construction is given.

(d) Production of Water Gas from Bituminous, Non-caking or Poorly Caking Fuel
No. 13422, May 6, 1942, Frame 610.

A water gas practically free of hydrocarbons could be made in gasification equipment with the simultaneous recovery of tar, to operate periodically and without employment of recycle gas if the retorting was done exclusively with blast gas. The blast is introduced into the lower part of the retort. In the water gas production part of the cycle, superheated steam is introduced about midheight of the column and is allowed to pass downward through the already retorted material in the lower part of the retort.

(e) Production of Hydrogen-free Gas Mixtures from Hydrocarbons
No. 13718, Oct. 12, 1942, addition to 167962 V/24e, Frame 618.

The decomposition of hydrocarbons or gases containing these, by means of oxygen and steam to form hydrogen-carbon monoxide mixtures, is described. The temperature of the hot gases produced in the operation is controlled by slag, by spraying with water, or the introduction of cold gas.

(f) Gas Producer
No. 13758, Oct. 31, 1942, Frame 620.

The foundation is in one piece, but raised somewhat so that the whole is cooled slightly on all sides. The shell, which is water cooled, extends down to the base. To care for leakage which may take place through the bottom of the producer, a collecting space or shell is provided with a gas withdrawal line.

(g) Separation of Carbon Monoxide from Gases
No. 13919, Jan. 14, 1943, Frame 625.

1. In the process for the separation of carbon monoxide from gases which were made from brown coal, and using a cuprous oxide solution under pressure, there is added to the solution small amounts of synthetic alcohol with more than 12 carbon atoms in the molecule or mixtures containing these alcohols.

2. Operating according to claim 1 with alcohols which were the result of reaction of carbon monoxide and hydrogen on olefins, followed by hydrogenation of that product, or made through reduction of carbon monoxide with hydrogen at medium pressure, in the presence of catalyst of the iron group at a temperature below 250°C.

3. Use of the alcohol in the form of an aqueous emulsion, or if necessary by the addition of an emulsion-producing material.

4. As an emulsion-producing material, the introduction of ethylene oxide into the alcohol-producing compound.

Discussion of the process states that hitherto the use of copper oxide salt solutions had been accompanied by much foaming in the equipment, resulting in reduced capacity, loss of solution and less effective gas purification.

(h) Process for the Practically Complete Gasification of Fuel

No. 14078, Mar. 17, 1943, Frame 630.

With complete gasification of solid fuels in a gas producer where the gasifying medium is introduced at two different levels into the fuel bed, (1) the upper part of the column makes power gas, particularly water gas, in the usual manner by hot blow and cold blow. During the cold blow period in the upper part of the column, oxygen together with other gasification media is admitted to the lower section, (2) the gasifying medium introduced into the lower part of the column and passing through the heated mass is itself preheated, (3) operating according to claims 1 and 2, the introduction of oxygen in the lower part of the column only during a part of the cold blow time of the upper section, or in each gas making period.

(i) Method for the Production of Nitrogen-free Synthesis Gas of Uniform Composition in Metallurgical Ovens

No. 14093, Mar. 22, 1943, Frame 636

Processes in which oxygen or other gasifying media are used distinguished in that (1) oxygen and usual gasifying media are heated in a common heat reservoir from 700 to 1400°C. at the expense of the heat reservoir (2) is concerned with regulation of the mass of oxygen by-passing the heat reservoir.

(j) Process for Utilization of the Deoiled Residues of Coal Liquefaction

No. 14610, Feb. 23, 1944, Frame 640.

In the utilization of deoiled residue of coal liquefaction (by pressure hydrogenation) in which the carbon content of the residue either through processing or through the resultant admixture of carbonaceous material is increased to at least 40%. The residue is briquetted without further binder material and is employed in producers using oxygen and steam to make water gas.

(k) Utilization of Gases Containing Hydrogen Sulphide

No. 14693, Apr. 4, 1944, Frame 643.

Decomposition by oxidation of the hydrogen sulphide to sulphur with the theoretical amount of air or oxygen, (1) in such a manner that the oxidised gas is brought into contact with molten sulphur, the remaining gases are decomposed to sulphur dioxide with air or oxygen, and are employed in making sulphuric acid, (2) a part of the heat of reaction is used for steam generation.

(l) Purification of Gas-washing Liquids

No. 14991, Oct. 24, 1944, Frame 647.

Purification by alkali salts of amino acids as liquid media for the removal of sulphur dioxide or carbon dioxide gases at low temperature, and which give up these gases when heated: (1) the wash liquids in acid or neutral solutions are treated with reducing substances, (2) treatment with reducing substances in the presence of aldehydes, (3) the gas washing liquid before treatment with reducing substances, particularly aldehyde, is purified according to patent 680675.

(m) Process for the Separation of Foreign Gas Substances from Gas Mixtures Under Pressure
Unnumbered, Frame 652.

(1) In which the gas mixture is washed with some medium, in which the purified gas has a high degree of solubility, is characterised by flashing of the wash solution and partial return of the evolved gas to the lower section of the column. The washing medium is regenerated. The so-treated solution is again contacted with the synthetic gas mixture in different places. (2) The regeneration of the wash material is accomplished by flashing and/or heating whereby the released gas mixture is compressed at the pressure of the process step.

29. REPORTS AND PATENT APPLICATIONS - ALKYLATION

Catalytic Refining, Production of Aromatics, Alkylation.

Part I. Evaluation of Zinc Sulphide Catalyst for the Vapor Phase Refining of Oils Derived from Coal.

A report, Feb. 13, 1939, believed to have its origin in the Ludwigshafen Research Laboratories. Frames 660 - 672.

Two catalysts, one a natural zinc blende and the other zinc sulphide on Terrana, were examined. The natural zinc blende was completely inactive. Zinc sulphide on Terrana gave a naphtha having octane number of 100. Catalyst was suitable only on phenol free or middle oil. Gas production was about 18%. The stability of the catalyst extended throughout the 100 day research period. Other catalyst with highly extended surface had lesser life but gave naphthas of similar quality.

The synthetic zinc sulphide catalyst (K42) was said to be made as follows: a mixture composed of 80% Terrana which has been leached with hydrofluoric acid and 20% of $ZnCl_2$ was treated with H_2S at 400°. The catalyst is formed into relatively soft pellets 4 mm. in diameter by 2 to 4 mm. thick hardened in a hydrogen stream at 450°.

The charge stock was a Welheim Diesel oil with an inspection as follows:

Density - .991
Aniline point - 20°
Sour oil - 3.2%

Boiling Point Analysis

Temperature	Percent
220°	0.6
250°	42.0
280°	78.4
300°	95.4
307°	98.8

Production of Aromatic Hydrocarbon
No. 12454, Nov. 25, 1940, Frame 673.

In the catalytic alkylation of aromatic hydrocarbon with methanol, dimethylether or olefin-producing substances at elevated temperature and pressure, (1) by a catalyst made of a mixture of 5 to 40% kieselguhr, 5 to 30% zinc oxide, and 55 to 90% phosphoric acid, drying the resultant mixture at 130 to 500°C, (2) processing of benzol as the aromatic hydrocarbon and using methanol or dimethylether as alkylation agents, (3) operating in conformance with claims 1 and 2 and changing the direction of flow to the catalyst.

Production of Valuable Hydrocarbons
No. 12733, Apr. 26, 1941. Addition to patent I.61766 IVd/12$_o$. Frame 680.

In the reaction of volatile olefins in the presence of phosphoric acid on asbestos or slag wool, the patent stipulates temperatures between 140° and 400°C. and preferably between 200 and 300°C. for the conversion of volatile iso-olefins.

Production of Valuable Fuels
No. 12864, July 1, 1941, Frame 685.

The alkylation of iso-paraffins with olefins, especially of isobutane with normal butene, separation of the olefins from their mixture with normal paraffins, by means of heavy metal solutions which combine with olefins.

Process for the Production of Valuable Fuels
No. 12882, July 9, 1941, Frame 693.

In the alkylation of lower molecular weight olefins with lower molecular weight isoparaffins by means of 80% to 90% and preferably 86 to 88% sulphuric acid, the acid esters are recovered and/or converted.

Production of Aromatic Hydrocarbons
No. 12988, Sept. 15, 1941. Addition to I.68284 IVd/12$_o$. Frame 705.

In the alkylation of aromatic hydrocarbons with methanol, diethylether or olefins or olefin-producing substances, according to patent (I.68284 IVd/12$_o$) at elevated temperature and pressure in the presence of catalyst, made of a mixture of 5 to 40% kieselguhr, 5 to 30% zinc oxide, and 55 to 90% phosphoric acid (the mixture is dried at 130 to 500°C.), the catalyst has added to it natural or synthetic hydrosilicates.

THE PRODUCTION OF HIGH OCTANE GASOLINE BY ALKYLATION OF ISOBUTANE WITH BUTYLENE-1 IN SEMIWORKS UNIT

A report from the Oppau Laboratory Jan. 20, 1942. Frames 710 - 725.

This report discusses the alkylation of isobutane with butene-1 in a continuous unit processing 350 to 400 kilograms per day. The reaction is in liquid phase at 0°C. and a throughput of 12 to 14 liters olefin per hour to 30 liters of sulphuric acid. Proportions of isobutane to olefin are about 15 to 1. Satisfactory emulsion formation was attained by intensive stirring. The acid utilisation (without reconcentrating) was equivalent to 6.5 weight percent of the recovered alkylate. The alkylate consisted of saturated hydrocarbons, of which about 90% was in the gasoline boiling range and consisted principally of 2,2,4-, 2,3,4-, and 2,3,3-trimethyl pentanes, showing a motor octane number of 93 to 94.5 and exhibiting high lead susceptibility.

Reviewer's notes: The fraction boiling up to 185° which was said to have an octane number between 93 and 94.5, when leaded with 100 tetraethyl lead per liter showed an increase in the motor octane number from 93.5 to 108.5. The lead susceptibility is said to be between 14 and 15. It is likely that they were using a susceptibility chart similar to that of Hebl, Rendel and Garton. Further reference to the alkylation of individual olefins will be found in the scanning of reel #30.

Production of Valuable Hydrocarbons

No. 13349, Mar. 28, 1942, Frame 726.

Alkylation of isoparaffins with olefins, especially isobutane with normal or isobutylene in the liquid phase and in the presence of catalyst, especially strong sulphuric acid, subsequent vaporisation of a portion of the hydrocarbon (1) lessening the fluidity in the reaction vessel and maintaining motion in the reaction mixture with a stirrer (2) processing according to claim 1 where the proportion of height of liquid to the diameter of the reaction vessel is one or less.

Production of High Octane, Isoparaffinic Motor Fuels by Alkylation of Aliphatic Hydrocarbons

A report from Leuna, Jan. 6, 1943, Frames 730 - 765.

A patent and literature survey on alkylation was made. Reaction conditions and their influences on alkylate quality and acid consumption were derived. Material balances of 98% were attained; the yield of alkylate on butylene was 210 to 220%. The yield of alkylate on H_2SO_4 was one ton alkylate to 11.8 - 15.7 kilograms 100% H_2SO_4 calculated upon the use of 98% fresh acid discarded at 90%. It was recognised that to make the most substantial use of alkylation, means for isomerising nC_4H_{10} must be employed. A complete alkylation plant designated as AT-244 was planned. This report is of the nature of a historical and speculative nature in which we need be concerned only with a summary of principal results.

Temperature

Alkylation was carried out in the range -10° to +20°C. Although yield, quality and reaction speed were to a minor extent dependent upon temperature, the general observation was made that above 5°, acid consumption rose; below 0°, there is some crystallization of acid.

Pressure

Sufficient to maintain the reacting substances in a liquid condition.

Isobutane Concentration

The concentration of iC_4H_{10} is an important factor in acid consumption, yield and quality of the resultant alkylate. The greater the tendency of olefins to polymerise in the presence of concentrated H_2SO_4, the more desirable it is to have a high concentration of iC_4H_{10}. The lower limit with reference to acid consumption, yield and quality of the alkylate when alkylating butylene-1 and -2, is in the neighborhood of 40 to 45 volume percent, while with iC_4H_8, a concentration of 70% is desirable. Higher iC_4H_{10} concentrations favor in each instance the alkylation reaction, while lower concentrations increase the acid consumption, gave lower yield on olefin and a somewhat inferior product.

Effect of Normal Butane and Propane Concentration

These two hydrocarbons are inert as far as the alkylation reaction is concerned, but should be held at as low a level as possible in the reactor charge because they diminish the concentration of isobutane.

Acid Concentration

In continuous operation, a concentration of 91 to 92% appeared favorable and was maintained by the addition of fresh 98% acid. One speaks of apparent acid concentration, because through titration of the sulphuric acid esters and sulphonic acid, which are formed as intermediate and side reaction products of the alkylation reaction, the true acid concentration will not be found. At an apparent acid concentration of 91 to 92% the alkylation acid will contain 2-1/2 to 3-1/2% of hydrocarbon. The above deterioration of acid is attributed to increase in butylsulphate esters favored by the polymerisation reaction. As the apparent acid concentration drops, there is a pronounced dropping off of octane number.

The Emulsion

Several arrangements and devices were employed to create the emulsion of acid and hydrocarbon, including stirrers, baffle plates and nozzles. It was possible to attain emulsions which persisted for several days. Since there was no product improvement with such intensive emulsification, the investigators adopted the least energy input which would give satisfactory alkylate. The emulsifying conditions which were believed favorable, used a container 1.65 meters diameter, height of liquid 1.75 meters, diameter of stirrer 0.5 meters, height of stirrer 0.2 meters; speed of stirrer 100 to 200 r.p.m. At 0°C., an energy input of 2 to 3 kilowatts was necessary. With such a reactor a daily production of 7 to 8 tons of alkylate of uniform quality was obtained.

Olefin Introduction

Since high olefin concentration in the presence of concentrated acid favors polymerisation, it is advantageous to mix the olefin with as much isobutane as possible before introducing the mixture into the reactor.

Removal of Heat of Reaction

The heat of reaction is taken as 250 kg. cal./kg. alkylate. This heat of reaction is absorbed in vaporizing hydrocarbon which, after compression and cooling, is again liquefied and returned to the alkylation process. Only as reactor temperature influences product quality, is the removal of heat of reaction considered important. It was observed that the equipment with greatest depth, as contrasted to shallow reactors, tended to give product boiling above and below octane, and was accompanied by higher acid consumption. It appears that the favorable dimensions of width to height were one to one.

Residence Time

It was felt that with alkylate concentration of 15%, a residence time of 30 to 60 minutes was suitable. Higher residence time had little influence on the alkylation reaction, while lesser time was unfavorable. With higher alkylate concentration, a longer time is required; with lesser concentration, shorter time is necessary.

Acid-hydrocarbon Proportions in the Reactor

The most favorable proportion of acid to hydrocarbon was one to one. Acid content above 65 volume percent and lower than 35 volume percent favors side reactions which yield less-desirable, complex products.

Effect of Reaction Conditions

The following law may be deduced: failure to attain any one favorable operating condition or conversely an improvement in this operating condition, brings about a corresponding deterioration or improvement, as reflected by octane number, boiling range, bromine number, acid consumption and alkylate yield.

Super-charge Characteristics

Throughout this report, reference is made to curves and graphs which would illustrate certain significant features of the data; none of the figures appear in the reels.

The reviewer has translated the term "Uberladbarkeit" as meaning characteristics when rated in a super-charged engine, but because of lack of a reference diagram, cannot be certain of this translation.

The alkylates derived from the present study were compared with other fuels, essentially iso-octane, and no significant difference was observed.

Effect of Water

The dilution of the sulphuric acid by water brought in with the charged stock or synthesized, was recognized to have an adverse effect both on product quality and acid consumption. Preparation of feed stocks, taking propane overhead, eliminates much of the water from this system. The formation of a propane-water azeotrope was postulated. Charge containing 0.4 weight percent water was dried to a moisture content of 0.015 to 0.02% water.

Alkylation of Propylene

Early work on the alkylation of iC_4H_{10} with C_3H_6 gave complex products with relatively low octane number (88 to 90). High acid consumption and low alkylate yield limited the use of C_3H_6. The alkylation of C_3H_6 with iC_5H_{12} in the presence of concentrated H_2SO_4 was carried out in Leuna. These latter results confirmed the conclusion previously reached that the H_2SO_4 alkylation of iC_4H_{10} or iC_5H_{12} with C_3H_6 as compared to C_4H_8, had no present advantage. It was shown that a C_3H_6 content of 5 to 10% in a butylene-propylene mixture, can be tolerated without great depreciation in quality. The differences in octane number and rich rating of such alkylate from pure butylene alkylate lie within the experimental error, as are similar differences in vapor pressure, boiling point and other analytical features. The acid consumption increased about 10%; that is from 10 to 11%, calculated upon the alkylate production.

The utility of a butane isomerization plant to obtain the maximum yield of alkylate was recognised.

Alkylation of Hydrocarbons
No. 257-1944, June 13, 1944, Frame 766.

Reviewer's note: An inscription in English appears at the bottom of the page "official patent application is missing".

In a vertical chamber, heated on the exterior, activated clay containing chromium oxide moves downward to dehydrogenate normal butane. The catalyst is separated from hydrocarbon rich material and restored to activity by drying. The advantage of moisture control apparently lay in the fact that with preferred conditions, the product butylene contained very little butadiene, and the alkylation of olefin with H_2SO_4 showed 18% acid consumption, compared to 50% made with moist catalyst in the dehydro step. If this is the correct interpretation, it is interesting to note that the experience with butadiene parallels that of American investigators.

Frame 768 refers to the same patent application. Frame 768A appears to have been misplaced from an application dated October 27, 1941 and probably refers to polymerisation rather than alkylation.

30. PATENT APPLICATIONS PERTAINING TO POLYMERIZATION AND CONDENSATION

Production of Useful Hydrocarbons
No. 12147, May 16, 1940, Frame 774.

In production of valuable hydrocarbons (1) by-passing aromatic hydrocarbons together with higher boiling products of methanol synthesis at elevated pressure and temperature in the vapor phase over a suitable condensing catalyst, (2) use of oxygen-containing phosphorous compound deposited on silicate carriers, (3) employing silicate carriers of a fibrous structure, (4) the product of the process according to the first three claims is subjected to a hydrogenation step.

Discussion of the patent application. Motor fuels of high octane number are produced from aromatic hydrocarbons and higher boiling aliphatic alcohols (five or more carbon atoms). The present process does not depend solely upon splitting out of water to yield olefins which combine with the aromatic hydrocarbons, but entails a splitting of the aliphatic hydrocarbons into fragments yielding the aromatic aliphatic compound of a shorter side chain than the length of the chain in the alcohol employed.

The motor fuel has an octane number of 115, and because of its relatively high initial point is advantageously used in safety fuels. Compounds of phosphorus, such as o, m and p-phosphoric acids, or their salts, anhydrides and their derivatives and esters or mixtures of these compounds, on silicate carriers such as fuller's earth or kieselguhr are suitable. An example is the mixing of one part of asbestos with two parts of ortho phosphoric acid to form a stiff paste, processed into pellets and dried at a temperature not to exceed 150°, if possible in vacuo, until the catalyst is hard and contains 70 to 80% free phosphoric acid.

The condensation itself is carried out most advantageously between 300 and 400° and preferably at 20 to 100 atmospheres. The mild hydrogenation of the product has for its purpose conversion of olefin to paraffin, thereby improving the anti-knock properties.

Recovery of Lubricating Oil
No. 12444, Nov. 18, 1940, Frame 780.

In production of lubricating oil by treating volatile olefins having 2 to 4 carbon atoms with aluminum chloride or its double compounds with olefin and in any case together with small amounts of other catalysts for the Friedel-Crafts' reaction (1) that in the presence of paraffin hydrocarbons with 3 to 4 carbon atoms, taking care that the hydrocarbon is completely free of oxygen and sulphur compounds, (2) the use of aluminum chloride having not more than 5% and preferably not more than 2.5% residue, (3) employment of reaction vessels of which at least that part in contact with the reactants is made of nickel, chromium or their steel alloys, (4) for each molecule of paraffin hydrocarbon at least one molecule of olefin is employed.

Production of Valuable Hydrocarbon
No. 12733, April 26, 1941, Frame 791.

The reviewer believes this is the same subject matter as was discussed on frame 680+.

Recovery of Valuable Lubricating Oil
No. 13984, Feb. 8, 1943, Frame 796. - Extension of patent 718130.

The claim allows temperatures to rise to 150 - 200° and preferably 160 - 200°; then allows temperature to fall to about 100 - 150° in accordance with the patent, continuing the reaction at this temperature. The example states that in an N6 steel reactor, 1200 parts oil and 125 parts of aluminum chloride are pressured with ethylene to 20 atmospheres. Exterior heat is applied until the temperature increases to 165°. The reactor is cooled to 15° and at this temperature ethylene is continuously admitted until the autoclave is filled.

From the raw polymer product one gets a lube oil with properties:

Sp. Gr. - 0.852
Vis @ 38° - 91.7°E
" @ 99° - 6.33°E
V.I. - 114
Flash - 225°
Flowpoint - -38°

<u>Polymerisation of Diolefins</u>
No. 14001, Feb. 18, 1943, Frame 798+.

The patent claims polymerisation of diolefins having nonconjugated double bonds by means of Friedel-Crafts' catalysts at -10°C. The example cites the use of a reactor to which is admitted liquid propane and 2,5-dimethyl hexadiene-1,5 in proportions of 200 to 110. After cooling the mixture to about 75°, boronfluoride is admitted so that after about 5 to 10 minutes 2,000 to 3,000 cc. of gaseous boronfluoride has been added.

<u>Production of Condensation Products</u>
No. 14404, Sept. 20, 1943, Frame 801.

From olefinic compounds and formaldehyde by condensation in the presence of solid acids, preferably of resin origin. An example cites the use of 200 parts styrol, 320 parts paraformaldehyde, 800 parts of water, and 500 parts preferably of an omega-sulphonic acid group containing exchange compounds such as are used in water purification, heated for 6 to 8 hours at their boiling point and with reflux, meanwhile stirring. The catalyst is separated from the reaction mixture and the oily liquid is distilled in vacuo giving a yield of 79.5%. The principal fraction is 4-phenyl-1,3-dioxan.

<u>Polymerisation of Olefins</u>
No. 14568, Jan. 20, 1944, Frame 804.

Polymerisation of lower molecular weight olefins employs as catalyst solid acids on a resin basis (hydrogen ion exchange material). In the example liquid isobutylene is treated with solid acids derived from phenol, formaldehyde and sodium sulphite for six hours at 100° and 20 atmospheres. From this is obtained iso-octane.

<u>Technically Useful Material</u>

Note: This material does not bear an application number but is dated March 2, 1945. Frames 806 - 811.

Useful condensation products whereby benzine, diesel oil, heavy oil fractions whose aliphatic and cyclic portions were obtained by thermo-chemical treatment from solid bituminous substances by means of condensation in the presence of halogens or mineral acids and their derivatives but causing little or no attendant substitution. The example cites the fraction 185 to 225° of a retorting product from brown coal is freed of organic base with 10% sulphuric acid and freed of acid substances (phenol, cresol) with 10% sodium hydroxide and distilled.

The distillate is treated with 500 parts by weight of boronfluoride (106 parts) -phosphoric acid (134 parts 85% acid). After cooling 10 to 20°, the refined product is held at 50 to 60° for 5 hours. After separation of the boronfluoride-phosphoric acid, it is washed with sodium chloride solution until acid free, and is subjected to vacuum distillation. The fraction boiling above 240°C. amounting to 26% is a clear, light brown, highly viscous oil which appears suitable for inclusion in lubricants.

31. REPORTS AND PATENT APPLICATIONS - ISOMERIZATION

Hydrocarbon Rearrangement
No. 13653, Sept. 8, 1942, Frame 813, I.67816 IVd/12o.

Extension of a patent application where catalytic rearrangement of low-boiling aliphatic, straight chain hydrocarbon with four or more, and preferably four to seven, carbon atoms in the molecule by heating in the presence of hydrogen halides and aluminum halides as catalyst in which the aluminum halides in the outflowing stream flow over packing, the spent catalyst is withdrawn, in which a catalyst-free space is provided above the catalyst layer in which gaseous or volatile substances are maintained.

The essence of this improvement to the original patent appears to be the use of a free space or a packing between the reactor exit line and the body of the catalyst itself.

Hydrocarbon Rearrangement
No. 12349, Sept. 11, 1940, Frame 816.

In isomerization of low-boiling aliphatic straight chained hydrocarbon with four or more, and preferably four to seven, carbon atoms in the molecule by heating in the presence of halogen acids and aluminum halides as catalyst, characterised by the aluminum halide in the reactor products flowing over packing, withdrawing the used catalyst from the liquid reaction product.

Shifting of the Double Bond in Olefin Hydrocarbons
No. 13662 Sept. 11, 1942, Frame 820.

Olefinic hydrocarbons with at least four carbon atoms in the straight chain are subjected to metal carbonyls. The example cites a pressure vessel in which 2% of carbonyls is reacted with normal dodecylene-1 for an hour at 150° while exerting a pressure of 100 atmospheres with carbon monoxide. The product consists of 8.1 dodecylene-1, 27% dodecylene-2, 23% dodecylene-3, 18.1 dodecylene-4, 13.3 dodecylene-5, and 10.3% dodecylene-6.

Isomerisation of Normal Butane with Aluminum Chloride
Leuna report Feb. 22, 1943, Frames 825 - 842.

The development work upon isomerisation of normal butane appears to have been done in the period 1939-1940. The reviewer believes this report was made for the purpose of clarifying patent applications, and because there is only generalised data given, no strict comparison with American practice is possible.

In view of the numerous foreign patents and literature references, the writer did not believe that basic German patents could be obtained. However, the work differed fundamentally from previous disclosures by the use of aluminum chloride on packing and lessening of decomposition or deposition of catalyst in the lines by provision of a large free space above the contact mass.

Scanning of the material did not disclose substantial improvement in operations as reported by the A.G.A.C. Isomerisation Sub-Committee, but the reviewer believes that this report will be of interest to U. S. refiners employing isomerisation by means of aluminum chloride.

Highly Branched Hydrocarbon from Naphthenic Hydrocarbon
No. 14808, June 17, 1944, Frame 843.

At a temperature below 130° and preferably 50 to 100°C. in the presence of hydrogen and hydrogen chloride at pressure above 10 atmospheres and preferably between 30 and 200 atmospheres, employing aluminum halide as catalyst.

32. PATENT APPLICATIONS - SYNOL- and OXO- PROCESSES

Reaction of Carbon Monoxide with Hydrogen
No. 11499, April 28, 1939, Frame 848.

(1) Formation of hydrocarbons, employing heat exchangers with a vaporised liquid, in which the cooling medium from the reaction vessel forms steam in a closed system is condensed and the condensate again returned to the exchanger. (2) Decomposition in plural reactors in the cooling system of these ovens; the vapors formed are cooled and in various closed systems again returned to the heat recovery system. (3) and (4) cover variations of the above arrangement.

The description of the patent claims might perhaps be summarised as recovery of the heat of reaction by means of heat exchange systems employing vaporisation and condensation of a volatile fluid.

Decomposition of Carbon Monoxide with Hydrogen
No. 13005, Sept. 23, 1941, Frame 855.

Catalytic decomposition of carbon monoxide with hydrogen to liquid, stable oxygen-containing organic compounds whereby there is accomplished in one step the thruput of only as much gas to produce not more than 20 and preferably not more than 15% CO_2. Alcohols are an important part of the liquid product.

Production of Aldehydes and Ketones
No. 13059, Oct. 24, 1941, Frame 866.

(1) Processing of compounds having olefinic double bonds with CO and H_2 at elevated temperature and pressure in the presence of catalyst containing metals of group 8, particularly cobalt and in the presence of materials which suppress the hydrogenation tendencies of the catalyst. (2) Cites the presence of metalloids of groups 5 and 6, particularly of sulphur or its com-

pounds, in which the metalloid atoms are not directly bound to oxygen.

Example cites use of 60 parts catalyst (34% cobalt, 2.2% thorium, 1.4% magnesium oxide and 62% kieselguhr) is reacted with 800 parts of an olefinic mixture having a boiling range 250 - 260° and two parts of carbon disulphide. The catalyst was made by precipitation of the metals as carbonate in the presence of kieselguhr and subsequent reduction with hydrogen at 400°. The charge and catalyst is stirred at 140° with a mixture of equal parts of CO and H_2 at a pressure of 200 atmospheres until no more is taken up. Residual CO is displaced with H_2, the vessel is heated for 15 minutes at 180° at 200 atmospheres. The product consists of aldehyde and paraffin with a carbonyl number of 110 and a hydroxyl number of 0.0.

Decomposition of Carbon Monoxide with Hydrogen
No. 13281, Feb. 27, 1942, Frame 872.

Production of liquid and solid oxygen derivatives of hydrocarbons at elevated temperature and under such conditions that the oxygen-containing product, other than desired compounds, is chiefly CO_2, characterised by maintaining a low reaction temperature, the rate of decomposition is so low that at most 70%, and preferably less than 50%, of the heat of reaction is produced; decomposition to several hydrocarbons without undue CH_4 formation.

Decomposition of Carbon Monoxide with Hydrogen
No. 13346, Mar. 27, 1942, Frame 881.

Conversion of CO and H_2 to several hydrocarbons, if necessary with considerable amounts of liquid and solid oxygen derivatives, in the presence of iron catalysts, (1) at pressures preferably between 35 and 55 atmospheres, moistening the catalyst with liquid and quickly removing the heat of reaction, employing steam generation vessel for this purpose, (2) the process can be carried out in several steps.

The example cites the use of a precipitated iron catalyst in a tubular device surrounded by boiling water as control, into which a gas consisting of CO and H_2 in the proportion 1 to 0.8 is passed at 40 atmospheres and 198°, at a space velocity of 360 vol/vol catalyst/hr.

Oils boiling about 200° are withdrawn, gases are separated, passed through a separator of 120° and then through a separator at 35°. The recovered condensate after separation of the greater part of the oxygen-containing portion is recirculated to the reactor. The alcohol content of the fraction boiling from 230 to 350° was 47%.

Regeneration of Catalyst
No. 13565, July 21, 1942, Frame 890.

The patent specifies treating the used iron catalyst mass after separation of the attendant reaction product by treating with a solvent or with hydrogen at high temperature, and with a small amount of oxygen or a weakly oxidising gas until it is no longer heated in air, and then fusing it in a stream of oxygen.

Foam Suppressing Materials
No. 13638, Aug. 31, 1942, Frame 894.

Employment of alcohol derived from the catalytic reduction of carbonmonoxide with hydrogen, especially at medium pressure and with catalyst of the iron group.

The example cites that where ammoniacal copper salt solutions are employed in carbon monoxide washing equipment, foaming loss may be reduced by addition to the wash liquor of 0.05% of a fraction boiling between 220 and 240°, derived as follows: Purified water gas is contacted with a precipitated iron catalyst at 200° and 25 atmospheres, in a unit provided with steam generation jacket for removal of heat of reaction. The product is separated by distillation. The recovered fraction (220 to 240°) contains 40% alcohol, 5% acids and esters, 34% olefins and 21% paraffin hydrocarbons.

Carrying Out Chemical Decompositions
No. 13717, Oct. 13, 1942, Frame 898.

Control of chemical decomposition where means for adding or removing heat are provided to hold within a given temperature limit by heat exchange equipment, in horizontal or slightly inclined tubes for removal or addition of heat of reaction from material lying between the tubes which may be filled with a catalyst.

Reviewer's comment: The essence of this invention appears to be the suggestion that the catalyst lying between the tubes, i.e. in the shell, may be more readily removed from the outside of the tubes than from within the tubes.

Manufacture of Oxygen-containing Compound
No. 13835, Dec. 10, 1942, Frame 906.

The claim provides for the addition of CO and H_2 with compounds having an olefinic double bond. In the liquid phase, the presence of group 8 metals and treatment of the oxy compounds with hydrogen at elevated pressure and temperature, the reactor may have a free space of 0.5 - 0.1 meter for separation of the gas and liquid. The example cites the treatment of 97 parts of a mixture of olefinic hydrocarbons boiling from 200 to 250° with three parts of a slurry of cobalt precipitated on kieselguhr and activated with thorium oxide and magnesium oxide at 150° and 220 atmospheres. It is reacted with water gas. The slurry coming out of the reactor contains 0.2% cobalt in the form of dissolved cobalt carbonyl. The provision of a free space in the upper part of the reactor resulted in exit gases containing no cobalt carbonyl.

Note: The liquid charge is introduced in the upper part of the retort and liquid product is withdrawn at the base. Hydrogen is introduced at the base.

Production of Ethers
No. 13969, Feb. 1, 1943, Frame 912.

Compounds of organic hydroxyl derivatives and metals whose hydroxides with water do not form alkaline solutions are decomposed by organic hydroxyl compounds.

The example cites an aluminum alcoholate made by reaction of 5,5-dimethyl, 3 methylhexanol-1 with aluminum, is combined with similar alcohol. To 1000 parts of the alcoholate, 950 parts of pure alcohol is added. The liquid alcoholate is miscible with the alcohol. The fluid mixture is heated in a pressure vessel at 320° for 12 hours. After cooling, the mixture is treated with dilute hydrochloric acid, the oily layer is washed with water, dried and distilled at reduced pressure. There was obtained 870 parts of ether. The ether boiled between 290 and 300°. The oxygen content is 5.5%.

From the ether is attained 410 parts olefin with 9 carbon atoms and 90 parts olefin with 18 carbon atoms. The remainder, 450 parts, consists of unaltered alcohol which can be recycled.

Organic Oxygen Compounds
No. 13983, Feb. 8, 1943, Frame 916.

By the catalytic reduction of CO with H_2, using as catalyst metals of the iron group at medium pressure and below 250°, if necessary by addition of compounds with hydroxyl or aldehyde groups. Under mild conditions, a dissociation with water is possible. An example cites the use of 850 parts of a material derived by synthesis from H_2 and CO_2 at 25 atmospheres and about 190° produced in the presence of small amounts of iron catalyst containing potassium and aluminum; the material boiling between 140 and 155° has 55% of oxygen-containing material and is mixed with 310 parts of an aldehyde which has an average number of 12 carbon atoms, is heated for two hours with dry HCl and allowed to stand for 15 hours. The synthesised water is distilled off; hydrocarbon separated from the water which was distilled off is returned to the vessel. There is recovered 650 parts of material boiling up to 200° which is useful for softeners in plastics.

Condensation Products
No. 14046, Mar. 3, 1943, Frame 920.

One of the examples cites treatment of equal parts of H_2 and CO with iron catalyst at 25 atmospheres and at 188 - 193° in a manner to produce equal amounts of alcohol and hydrocarbon. The alcohol fraction is separated from the neutral oils by esterification with boric acid; the portion boiling between 285 and 320° is dissociated over aluminum hydroxide at 270° with water, and the recovered olefin mixture is treated as follows: 200 parts (calculated as pure olefin) is reacted with 200 parts of pure phenol and 100 parts of water-free zinc chloride. The mixture is stirred and refluxed for 12 hours at 180°. The condensation product is washed with water, and when the oily layer is distilled at 15 mm. pressure, the greater part is taken over between 190 and 240° as a pale yellow oil.

The oil is mixed at 30° with 1-1/2 times its weight of sulphuric acid monohydrate and then for some time warmed at 70 to 75°. When tests show that a sample is completely soluble in water, the mixture is diluted with twice its volume of water and neutralised with caustic. After extraction with ethyl alcohol and vaporisation of the alcohol and water, there is obtained a salt-free, bright mass with exceptional emulsifying properties.

Production of Oxygen-containing Organic Compounds
No. 14718, Frame 928.

With catalyst containing iron at medium pressure and temperatures below 250°, which is below that favorable for hydrocarbon formation with such catalyst, the catalyst contains potassium in amounts preferably from 0.1 to 0.7%, or an equivalent amount of other alkali metal.

A blend of 96.5 parts of pure iron and 3.5 parts of aluminum oxide is mixed with different amounts of potassium nitrate and fused in oxygen. The cooled fused mass is broken up and reduced with hydrogen, placed in a reactor to serve as a catalyst for decomposition of equal parts of H_2 and CO at a thruput of 350 parts of gas per volume of catalyst per hour, temperature of 190° and pressure of 25 atmospheres. The fraction boiling between 200 and 400° contains alcohol varying with the amount of potassium in the catalyst. At the preferred conditions there is 62% alcohol fraction boiling between 200 and 300°C. and 53% in the fraction boiling between 300 and 400°

33. PATENT APPLICATION - PREPARATION OF PURE ORGANIC COMPOUNDS

Production of Halogen Olefin Dimers
No. 12033, Feb. 24, 1940, Frame 933.

An example is cited where a solution of 35 parts benzoyl peroxide in 700 parts isobutenyl chloride (1-chlor-2-methylpropene-2) is refluxed. The boiling point rises in less than 15 minutes from 68 to 88° and remains unchanged. One now distills 281 parts of unreacted isobutenyl chloride, at atmospheric pressure. By distillation at 2 mm., there is recovered 383 parts of di-isobutenyl chloride (b.b. at 2 mm. is 66 to 68°; b.b. at 760 mm. is 203°). There remains 90 parts of residue. By heating this residue to 150 - 200°, it is decomposed into benzoic acid and chlor isobutenyl benzoate.

If one treats isobutenyl chloride under the same conditions, with 12% dioxyheptyl peroxide, the temperature rises in the course of 20 hours from 70 to 78°. The yield of di-isobutenyl chloride is 30%.

Production of Brominated Hydrocarbons
No. 12984, Sept. 11, 1941, Frame 937.

By bromination of saturated hydrocarbons or halogen hydrocarbons, characterized by catalytic treatment of the charge with bromine in the presence of chlorine or under the influence of actinic rays.

The example cites a mixture of 170 parts dodecane with 40 parts of bromine agitated and exposed to the light of a mercury vapor lamp for 1 to 1-1/2 hours, admitting 18 parts of chlorine vapor. The temperature rises from 20 to 50°. The end of the reaction can be recognised because the reacting materials become colorless. The dissolved HCl is expelled by warming gently at reduced pressure, and there is obtained 208 parts of bromdodecane containing 18.7% bromine. The chlorine content is only 0.7.

Production of Organic Sulphur Compound
No. 13562, July 22, 1942, Frame 941.

Reaction of non-aromatic oxygen-containing substances with SO_2 and Cl_2, and the saponification of the sulphochloride, to which one adds reducing substances during or after the saponification.

The example cites the use of 100 parts of an aliphatic alcohol with 15 carbon atoms in the molecule treated for 4-1/2 hours with 116 parts of Cl_2 and 75 parts SO_2 per hour at 50° in the presence of actinic rays from a mercury lamp. The product contains 9.5% sulphur combined with chlorine and 15.8% total chlorine. The product is saponified with 10% Na_2CO_3, with the addition of 5% formaldehyde sulphoxylate, and the solution is evaporated. There is obtained a bright yellow sulphonate which on long exposure to the air does not change appearance.

Production of Higher Molecular Alcohol
No. 14417, Sept. 29, 1943, Frame 944.

In processing to make higher molecular weight alcohol from lower molecular weight alcohol in the presence of alcoholates, there is used less than one mol of alcoholate to two mols of alcohol, and in the presence of a water-retaining material at temperatures below 260°.

One of the examples cites the use of 542 parts of normal butyl alcohol, two parts of sodium and 96 parts of about 80% pulverized calcium carbide, vigorously stirred in a pressure vessel. The gases so formed, principally hydrogen and lesser amounts of the acetylene are separated. The temperature is increased to 250°. The mixture is heated for 24 hours longer at this temperature, and from it is obtained 215 parts of a dimer alcohol, 10.3 parts of butyric acid and 13.4 parts of dimer acid.

Recovery of Acetone
No. 13712, Oct. 10, 1942, Frame 947.

Claims recovery of pure acetone from aqueous mixtures containing hydrocarbons by the use of a distillation column, and at a point several plates below the top of the column withdraws liquid acetone, and also stipulates that material taken overhead is diluted with water for separation of hydrocarbons, and the aqueous layer is returned to the distillation.

Recovery of Pure Methylethyl Ketone
No. 13739, Oct. 21, 1942, Frame 949.

In the separation of methylethyl ketone from mixtures produced by thermal decomposition of carbonaceous materials, it is specified that this mixture is distilled with the addition of low boiling hydrocarbons or halogen hydrocarbons to impart fluidity. The oily layer of the first azeotrope is completely returned to the distillation and distillate taken only from the aqueous layer. Also that azeotropic distillation with carbon tetrachloride of the upper aqueous layer is returned to distillation and distillate is taken only from the lower boiling layer until this is consumed, and then by further distillation of the lower aqueous layer a part of the distillate is recovered as water free methylethyl ketone.

This may be summarised as embodying variations of azeotropic distillations and employs dehydrogenation for separation of minor components.

Production of Brominated Hydrocarbon
No. 14030, March 1, 1943, Frame 957.

The brominated hydrocarbon is separated from the unreacted hydrocarbon with the help of selective solvents. Acetonitrile, methanol or liquid sulphur dioxide or mixtures are used.

Recovery of Trimethylolethane
No. 14160, May 8, 1943, Frame 963.

(1) Process for recovery of trimethylolethane from solutions resulting from the reaction of formaldehyde on propionaldehyde with addition of alkaline substances characterised by the reaction solution is extracted with solvents which are slightly or not at all soluble in water and separates the trimethylolethane from the extract. (2) Processing as in (1) characterized by use of ketone, alcohols and esters as solvents.

Recovery of Pure Meta-Xylol
No. 14487, Nov. 30, 1943, Frame 967.

In the processing of meta-xylol through sulfonation and the hydrolysis of xylolsulphonic acid, it is claimed that by passing steam through the sulfonation mixture without separation of the unreacted sulphuric acid, that only the meta-xylol sulphonic acid is hydrolised.

Production of Aliphatic and Cycloaliphatic Nitro-Hydrocarbons
No. 14924, Aug. 21, 1944, Frame 971.

Aliphatic or cyclo-aliphatic hydrocarbons are treated at elevated temperature and pressure with nitrogen tetroxide without addition of water. The conditions are such that the reaction takes place in a homogeneous liquid phase.

One of the examples cites a mixture of 200 parts by weight dodecane and 60 parts nitrogen tetroxide when pressured with nitrogen or carbon dioxide at 25 atmospheres and a rate equivalent to a residence time of 3.75 minutes, is heated at 155° in a V2A tube.

The reaction product is cooled, diluted with half its volume of methanol and stirred with a solution of 60 parts by weight of potassium hydroxide in 150 parts of water for about 1-1/2 hours. It is then further diluted with 300 parts of water, slowly separates into layers, and the unreacted hydrocarbon is withdrawn. The dark red alkaline layer is shaken with pentane and saturated with carbon dioxide. The nitro product which separates out is separated and distilled at reduced pressure. The alkali-carbonate solution is acidified with mineral acid to yield fatty acids. The processing yields 84 parts by weight of mononitrodecane, 28 parts dinitrodecane and 2 parts fatty acid (acid no. 255).

Production of Valuable Alcohol
No. 14633, March 1, 1944, Frame 975.

Aldol or 1,3 ketol which by reduction can be changed over to glycol with a primary or a secondary hydroxyl group, at ordinary or elevated pressure, in the presence of hydrogenation catalyst with a hydrogenation inducing metal or metal oxide such as oxygen compounds of the element group 4 or 6.

Separation of Pure Nitrile from Mixtures
No. 14670, March 23, 1944, Frame 978.

1 - Azeotropic distillation for the separation of the higher homologues of acetonitrile obtained from ketone oils and the like by the thermal decomposition of carbonaceous material, wherein there is employed for the separation of the desired fractions, aliphatic or cycloparaffinic hydrocarbons, or halogen hydrocarbons.

2 - Water is carried through the azeotropic distillation so that the greater part of the nitrile distills overhead with the water and the oily layer of the distillate is returned to the column.

3 - Provides for the elimination of alcohol from the charge to the azeotropic step.

4 - Similarly provides for elimination of pyridine.

Production of methylcyclopentane and its Homologues
No. 14968, Oct. 2, 1944, Frame 983.

Claims that cyclohexane or benzol or their homologues are passed over wolfram sulphide catalyst at temperatures of at least 350° but below 400°, at pressures of at least 50 atmospheres. The catalysis is performed in the vapor state and in the presence of hydrogen.

Production of Improved Phenols
No. 15000, Oct. 31, 1944, Frame 986.

Production of singly valent phenol from multi-valent phenols or their mixtures, whereby the charge and hydrogen is passed over the catalyst, the unvaporized portion of the charge is separated from the lower part of the vaporizer in batchwise or continuous fashion. The conditions are chosen so that only a portion of the multi-valent phenols are decomposed to uni-valent phenols.

The example cites that the charge is passed into a trickle tower at 240° and flows counter current to a stream of hydrogen at a pressure of 25 atmospheres. The amount of hydrogen is such that 5/6 of the charge is vaporised. The hydrogen-vapor mixture is passed over a zinc chromium oxide catalyst at the rate of 0.21 kilograms multi-valent phenol per liter of catalyst per hour. At a catalyst temperature of 420°, 82% of the phenol is decomposed to a product which is 97% uni-valent phenol and 3% hydrocarbon.

34. PATENT APPLICATIONS - PREPARATION OF LUBE AND TRANSFORMER OILS BY ESTERIFICATION

Production of Valuable Oils
No. 11761, Sept. 6, 1939, Frame 992.

1 - Aliphatic hydrocarbons with at least 3 carbon atoms and which contain 2 or more primary alcohol groups are esterified with fatty acids having at least 6 carbon atoms.

2 - In accordance with claim 1 the esterification is done with fatty acids having straight chains and fatty acids with branched chains.

3 - The use of esters from fatty acids of at least 6 carbon atoms and aliphatic hydrocarbons with at least 3 carbon atoms, which have two or more primary alcohol groups, alone or in mixture with other lubricating substances, particularly natural or synthetic hydrocarbons as lubricating oil.

Production of Olefins. Addition to Patent I.55196 IV/d12.
No. 11480, Apr. 12, 1939, Frame 1003.

One of the examples shows that passing 125 volumes of isobutane per volume of catalyst per hour over this catalyst which is composed of 48% zinc oxide, 50% chromium oxide and 2% barium chloride at 575° and ordinary pressure, 35% of the isobutane is decomposed to isobutylene of 88% purity. After 900 hours the necessary temperature was 620°, decomposition 25% and the isobutylene yield 70%.

Employing a chromium oxide catalyst free of zinc oxide, but which is activated with 5% barium chloride, at the same rate and temperature and pressure, when operating for 130 hours the temperature rises to 620°, a decomposition of 25% is obtained and the yield of isobutylene is only 60%.

Process for the Production of Diolefin
No. 14254, June 21, 1943, Frame 1008.

Production of diolefins from 1,3 dioxans which may be dialkyl substituted in 4, 5 or 6 position, or in several of these positions, in the vapor phase by means of catalyst composed of phosphoric acid in a mixture with silicic acid, especially kieselguhr.

Production of Unsaturated Compounds
No. 14547, Jan. 6, 1944, Frame 1012.

Heating of compounds containing hydroxyl groups in the presence of substances which will split out water, provide for the use of solid acid from synthetic resins, particularly the so-called Wofatite.

Recovery of Paraffin
No. 13344, Mar. 27, 1942, Frame 1016.

To oils containing paraffin is added solvent followed by cooling, wherein oils are dewaxed, there is careful aging of the polymer and without which the asphalt content is remarkably increased or separates.

An example is cited - a fraction boiling between 345 and 450° is dewaxed with propane at -40°, the mixture of paraffin, oil and propane is filtered, the paraffin mixture is washed several times with propane and filtered at -40°. After distilling off the propane, the wax has a melting point of 48° and still contains 15% oil. It is unsuitable for making fatty acids.

The same paraffin containing oil fraction is treated with 0.3% of a condensation product of chlorinated paraffin and naphthalene as a filter aid, and the oil separated from the paraffin by twice treating with propane in the above-described fashion. The wax recovered has a melting point of 49.5° and contains 4.7% oil. Before using in manufacture of fatty acids, the filter aid must be recovered by distillation, taking the hydrocarbon overhead and leaving the filter aid as a residue.

If the fraction is carefully aged before dewaxing by storing in a heated vessel for one week, in the absence of air, a similar twofold treatment with propane gives a wax with melting point 49.4° and an oil content of 4.2%. The paraffin wax can be used directly in production of fatty acids without distillation.

Dewaxing of Hydrocarbon Oils
No. 14425, Oct. 9, 1943, Frame 1020.

Patent claims are (1) dewaxing by addition of selective solvents, separation at low temperatures, by filtration of the crystallised wax, it is specified that screen is used as the filter material, (2) further adds that the filtrate is given a subsequent filtration with filter cloth or a substitute, (3) in accordance with claims 1 and 2, stepwise and counter-currently washes the material retained on the filters and yet containing some oil, with a solvent material.

Dewaxing of Oils
No. 14554, Jan. 10, 1944, Frame 1029.

Cooling in the presence of solvent, it is specified that tetrahydrofuran is used with such solvents which promote crystalline formation, but which themselves can be readily washed out of the product.

One of the examples cites the use of 5 kg. of lube oil containing 15% paraffin with 3 times its weight of a mixture of 85% tetrahydrofuran and 15% acetonitrile dissolved at 60° and cooled within 2 hours to -20°. The crystallised paraffin is separated by filtration at 100 mm. vacuum. Through the wax deposit is passed an additional equal weight of cooled solvent; by distillation of the solvent from the washed paraffin, a product is obtained with a freezing point of 56°. From the first filtrate after distillation of the solvent, there is obtained an oil with a flow point of -22°.

Dewaxing of Oils. Addition to Patent I 76558 IVd/23b
No. 14705, Apr. 6, 1944, Frame 1035.

The addition to the above-mentioned patent specifies that the oil after treating with a selective solvent and treating the raffinate without separation of the solvent after addition of tetrahydrofuran and if necessary further amount of selected solvent is subjected to dewaxing.

Refining of Waxy Oils
No. 14820, June 22, 1944, Frame 1038.

1 - In dewaxing by dilution with solvents and by cooling, it is found that stratification of the solution of dewaxed oils takes place.

2 - Stratification by cooling to essentially as low temperatures as employed in dewaxing.

3 - Operating according to claim 1, a sufficient quantity of material causing precipitation of the oil is added.

4 - The solution rich layer after separation of the oil separating material is wholly or partly returned to the raw oil treating step.

5 - Characterized in that the separated wax slurry is counter-currently washed with the solvent material, by which the solvent rich layer of the separated filtrate, if necessary after separation of the oil-precipitating agent, is brought back in this counter-current washing, desirably in the first step.

Separation of Mixtures of Alcohol and Hydrocarbon
No. 13570, July 22, 1942, Frame 1050.

The patent claims separation in which the mixture dissolved in liquid media is allowed to flow over substances which retain only the alcohol, and from which the alcohol may be dissolved with suitable material.

The example cites dissolving of alcohol-containing mixture in a large amount of pentane and passing the solution over silica gel. After the separation of the major part of the pentane stream, the silica gel is leached with methanol and this resulting solution distilled. The silica gel is heated for 4 hours at 100° and at reduced pressure to reactivate it.

Separation of Mixtures of Alcohol and Hydrocarbon. Addition to Patent I 72811 IVd/12.

No. 13831, Dec. 8, 1942, Frame 1054.

Expansion of the means of recovery of alcohol fraction from the absorbing silica gel.

Safety Fuels

Leuna, Dec. 7, 1938, Frame 1059, application unnumbered.

Alkyl benzines or their derivatives or homologues having side chains with more than two carbon atoms. Mixtures of the above-described alkyl benzine with other hydrocarbons, alcohol, ethers, ketones. Addition of anti-knock agents such as tetraethyl lead, iron carbonyl, etc.

The application is rewritten May 3, 1939, the principal changes being in latitude of composition of the aromatic material.

Production of High Octane Stable Gasoline

No. 12069, Mar. 19, 1940, Frame 1070.

Process for improving unstable gasolines, particularly those made by cracking of hydrocarbon or by the catalytic hydrogenation of CO, by treating with H_2 and CO containing mixtures at elevated temperature and pressure in the presence of catalyst is characterized by the decomposition of hydrocarbon mixtures at such temperature and pressure in the presence of catalyst, so that the CO and H_2 produce stable hydrocarbon.

Production of High Octane Gasoline

No. 12513, Dec. 21, 1940, Frame 1077.

Processing by cracking hydrocarbon oils and transforming the low octane or heavy naphtha into high octane hydrocarbons by treating the charge in several steps with inter-heaters in the presence of catalyst and hydrogen, it is provided that the charge to each step has added to it hydrocarbons of the methane series with five or less carbon atoms which are introduced to the reaction zone in a heated state.

The second claim operates as above, but employs catalyst of increasing activity in each of the succeeding individual steps.

Production of Aromatic High Octane Gasoline from Aromatic Refractory Middle Oils

No. 14426, Oct. 11, 1945, Frame 1081.

Two pages are missing from this write-up but it is deduced that the catalyst employed may be aluminum oxide, kieselguhr, etc., at temperatures of 480 to 550°, pressures of 100 to 700 atmospheres, at a hydrogen partial pressure of above 50 atmospheres, whereby the oxygen, sulphur, nitrogen and unsaturated components of the aromatic charge are hydrogenated, the resulting naphtha is separated and the portion boiling above naphtha range is subjected to strong cracking induced by magnesium or aluminum silicate with minor amounts of oxide or sulphide of metals of the second to eighth groups. At temperatures of 350 to 500° and pressures of 40 to 300 atmospheres, this produces an aromatic naphtha.

Production of Clay-containing Catalyst
No. 11583, June 9, 1939, Frame 1087.

Catalysts of high activity and mechanical strength are prepared by making a paste of technical aluminum hydroxide and aqueous colloidal solutions of basic aluminum nitrate, if necessary with the addition of acid, which is then mixed with water and the resulting self hardening mass is solidified in the desired form by heating to a temperature of about 400°. Claim No. 2 specifies that kaolin or clay may be added to the material, while claim 3 covers the addition of other catalytic substances, particularly heavy metal compounds.

High Octane Hydrocarbon
No. 12240, July 9, 1940, Frame 1094.

When making high octane hydrocarbons by cracking or hydrocracking of hydrocarbons in the presence of aluminum oxide or one or more heavy metal oxides as catalyst, specifies the use of aluminum oxide made by the action of dilute acetic acid on activated metallic aluminum and heating the recovered aluminum compound to about 600 to 700°.

Recovery of Alumina
No. 13253, Feb. 9, 1942, Frame 1098.

In the production of alumina by acid treating of natural or synthetic clays containing iron and the separation of the alumina from the reacted solution, it is specified (1) that before the separation of the alumina, the treating liquor is freed of iron by reaction with dithiocarbamin or soluble salt of these acids, (2) deals with hydrolysis of the liquor, (3) states that in cases where materials deficient in silicic acid are employed, the hydrolysis of the reactor liquor is done in the presence of added colloidal silicic acid, (4) further adds to the preceding claim, the stepwise addition of dithiocarbamin acid or its salt solution.

Catalyst Regeneration with Oxidizing Gases
No. 13255, Feb. 11, 1942, Frame 1103.

When reactivating spent catalyst by means of oxygen-containing gases in a vertical oven, through which the spent catalyst is passed, it is specified that the several zones be provided, in which the regenerating gas is successively higher in oxygen content. Supplementary claims deal with the division and recycling of portions of the oxidising gas.

Regeneration of Catalyst
No. 13723, Oct. 15, 1942, Frame 1109.

In regeneration of catalyst in which there is a combustible coke-like deposit by heating in the presence of oxygen containing gases, it is specified that at the beginning of the regeneration the temperature of the catalyst is lower, the temperature of the oxygen containing gas higher than the combustion temperature of the carbonaceous deposit. Supplementary claims are concerned with variations in the circulating gas streams.

Production of Surface Active Catalytic Substances
No. 14345, July 28, 1943, Frame 1118.

In the production of especially reactive catalytic substances by precipitation from solutions, it is specified that (1) the liquids are quickly mixed to lessen the growth of crystalline forms or colloidal substances in the separated precipitated product, (2) specifies that when operating as in claim 1, the necessary energy input is brought about by the kinetic energy of mixing nozzles.

Highly Porous Silicic Acids and Aluminum Oxide or Magnesium Oxide, or Mixtures of the Two
No. 14428, Oct. 11, 1943, Frame 1122.

This extension to Patent I 70028 IVb/12_1 specifies all the ingredients are ground so that at least 90% passes a screen having 100 meshes/sq.cm. but is retained on a screen having 10,000 meshes/sq.cm.

Production of Highly Porous Silicic Acid and Aluminum Oxide or Magnesium Oxide Containing Masses
No. 14429, Oct. 14, 1943, Frame 1125.

Extension of I 70028 IVb/12_1, which specifies that the mixture of aluminum hydroxide and magnesium hydroxide with silica gel is done without previous peptization with acids.

Catalyst Containing Phosphoric Acids
No. 12413, Oct. 22, 1940, Frame 1128.

In making solid phosphoric acid catalysts, it is specified that they are dried on corrosion resistant material in the presence of added reducing metals such as metallic Zn, Cd, Al, etc., that mixed oxide be added in such amount that the phosphoric acid is in excess of that necessary for formation of secondary zinc phosphates, and dried to a water content of 5 to 8%. A fourth claim specifies that the mixture which contains 5 to 40% kieselguhr with 5 to 30% zinc oxide and 55 to 90% phosphoric acid is dried at temperatures between 130 and 500°.

Development of Hydrogenation Reaction
No. 13912, Jan. 11, 1943, Frame 1133.

In the carrying out of catalytic hydrogenation reaction, it is specified that catalysts are employed which were derived by reduction of metal compounds of the iron group at 300 to 500°, treating the cooled reaction product with weakly oxidising gas until no more oxygen is taken up, and reducing the material at the temperature employed in the first step.

Production of Activated Fuller's Earth
No. 14296, July 8, 1943, Frame 1141.

It is specified that substances containing silicic acid and clay, especially water insoluble natural or synthetic silicate, is reacted with acids, the solution neutralised and the product precipitate converted in the presence of water or aqueous solutions is heated under pressure and can be given an after treatment with acids. Pressure heating between 250 and 350° and preferably between 280 and 320° is specified. The third claim specifies that in accordance with claims 1 and 2, the pressure heating is done in the presence of alkalic or alkaline earth metal, or magnesium oxide or hydroxide in amounts of about 0.1 mol Na_2O or about one mol MgO per mol of Al_2O_3 in the precipitate.

Dehydrogenation of Volatile Hydrocarbons
No. 14450, Nov. 2, 1943, Frame 1145.

In catalytic dehydrogenation of saturated hydrocarbons with 3 or 4 carbon atoms, by means of difficultly reducible metal oxide as catalyst, it is specified that the hydrocarbon is passed through catalyst at 450 to 600°. The catalyst is in tubes heated on the exterior and when the activity drops off the catalyst can be regenerated with oxidising gases; the dehydrogenation is always done in a brief interval of time, so the catalyst only becomes inactive to the extent it may be regenerated by a temperature equal to or not higher than that employed in the dehydrogenation part of the cycle. The catalyst temperature increases in the direction of the gas passage, as may the activity of the catalyst itself. Claim 4 states that operating as specified in claims 1 to 3, the reactivation of the catalyst is done only to the extent that a part of the carbonaceous matter is burned off; the fifth claim recapitulates the others and specifies catalyst as free as possible from water.

Production of Iron-free Silicic Acid from Ferrous Slags
No. 14611, Feb. 23, 1944, Frame 1150.

In the preparation of iron-free silicic acid from ferrous slags by treating with nitric acid, it is specified that one employ at moderately high temperatures an excess of aqueous nitric acid which contains less than 200 grams HNO_3 per liter.

Dehydrogenation or Cracking of Hydrocarbons
No. 14807, June 16, 1944, Frame 1152.

In dehydrogenation or cracking of hydrocarbons by heating in the presence of catalysts which are periodically reactivated, it is specified that the catalysts are dried during or after the reactivation.

Heating of Gaseous or Volatile Hydrocarbons
No. 12094, Apr. 6, 1940, Frame 1156.

When heating gaseous hydrocarbons. it is specified that the hydrocarbons are passed at high velocity through the heating zone and by such control of the heater and pump pressure that the pressure is least in the part of the heater in which there is danger of carbon separation at ordinary pressure. It is also specified that a heater be employed whose cross section decreases with increasing temperature.

Means for Increasing the Inflammability of Combustible Gases
No. 13491, June 13, 1942, Frame 1160.

In the combustion of gases with low burning velocity, it is specified that hot combustion gases be admixed with the gas-air mixture before combustion of the latter. Other claims are concerned with modifications of the first.

Filter Device
No. 13527, June 30, 1942, Frame 1164.

The device is specified as a continuous filter cloth passing over rollers, and the suction face, i.e. the filter cloth, moves across the opening into the vacuum vessel, and after passing across this opening is exposed to a device for removing solids from the cloth.

Automatically Maintaining Constant Light Intensity
No. 13607, Aug. 18, 1942, Frame 1167.

May be summarized as employing photo cells and galvanometer circuits for regulation of light sources to attain constant intensity illumination.

Degassing of Liquids
No. 13651, Sept. 8, 1942, Frame 1172.

In the operation of piston engines which serve for recovery of the energy in pressure degassing of liquid it is specified that the energy of the evolved gas or the flashed liquid, exerting pressure on the piston is employed to raise the pressure upon fluids to be processed at higher pressure. There are six claims dealing with the arrangement of equipment and the utilization or routing of streams at different energy levels.

Separation of Low-boiling Gas Mixtures
No. 13857, Dec. 17, 1942, Frame 1186.

The process for separating low boiling mixtures, especially air, in reversing operation whereby the cold reservoir is alternately swept through by charge gas and purified separation product, the disclosure specifies return to the separating device of gas to be recovered mixed either with the washing-out gas or the cold-reservoir gas.

Drying of Gases
No. 13953, Jan. 25, 1943, Frame 1189.

The patent describes construction and heating arrangements to bring well-dried catalyst into contact with the gases to be dried and at temperatures to prevent condensation of moisture on the drying material.

Separation of Catalyst from Liquids and Remixing with Fresh Charge

No. 13955, Jan. 26, 1943, Frame 1193.

(1) Separation by centrifuging and (2) operating as in claim 1, employing a centrifuge in which two fluid layers are formed, the innermost of which is withdrawn free or practically free of catalyst, while the outer catalyst-containing layer is mixed with fresh charge in the centrifuge.

Catalytic Decomposition of Fluid Substances

No. 13965, Jan. 29, 1943, Frame 1197.

Decomposition of liquids in the presence of solid catalyst with return of the separated catalyst from the reaction product, it is claimed that from the fluid reaction product there is continuously or periodically taken a portion of the finest catalyst, returning only the coarser portion to the reaction vessel.

Operation of Rectifying Column

No. 14375, Aug. 24, 1943, Frame 1201.

Improved operation of rectifying columns is claimed in which the heat input to the reboiler is in proportion to the amount of material vaporized in the reboiler, thereby constituting control.

Reviewer's note: Meter in the vapor line from reboiler to column actuates valve admitting heating medium to reboiler tubes.

Packing for High Pressure Pumps

No. 14794, June 10, 1944, Frame 1204.

Packing for plungers and pistons, in which the individual packing elements consist of two rings to turn in conical surfaces, uses as material of construction for the rings wood or material of similar porosity which lubricates and cools, (2) specifies acacia, maple or elm, (3) operating in accordance with the first two claims, the wood rings are pretreated with liquid at ordinary or elevated temperature and in any case under pressure or under vacuum, or both.

Decomposition of Hydrocarbons

No. 14810, June 17. 1944, Frame 1208.

In cracking of hydrocarbons, conversion of low octane gasoline or heavy naphtha into high octane hydrocarbons and dehydrogenation of lower molecular weight hydrocarbons by passage of the charge over solid catalyst, it is claimed that catalysts of different granule size are so arranged in the reactor space that the charge is first contacted with the coarsest and then with the more finely divided catalyst.

Catalytic Decomposition
No. 14831, June 28, 1944, Frame 1211.

Decomposition by means of catalyst, in which the catalysts are alternately passed through the reaction zone and through a regenerator, whereby the spent portion of the catalyst is regenerated, it is claimed that the velocity, the stability and the chemical properties of the catalyst are so controlled that when the catalyst has wholly or to a defined degree has lost its effectiveness and is reduced to small size by mechanical attrition, is separated and removed from the system.

Recovery of Liquid Oxygen by Separation of Air
No. 14840, July 1, 1944, Frame 1214.

Processing for the simultaneous recovery of liquid oxygen with other gases from air, the patent specifies supplementary cooling and process flow, which was said to be effective.

Continuous Extraction or Refining of Liquid or Residues
No. 14341, July 24, 1943, Frame 1220.

Processing for the continuous extraction or refining of liquids or of residues in which the extraction or refining medium and the materials to be extracted or refined are carried in several successive steps; in each step first mixed and then separated, characterised, in that the two liquid phases within individual mixing and separating steps are done in parallel flow. Four other claims deal with process flow and arrangement.

Treating of Gases or Vapors with Granular Catalyst
Unnumbered - Nov. 24, 1944, Frame 1228.

Catalytic decomposition, in which the catalyst is passed through a reaction zone, in which the great area of surface exposed gives good exchange of heat between reacting and heating materials; as for example tubular ovens with a circular reactor space, characterised by (1) through suitable devices or parts of the reactor are loaded with catalyst having fairly equal proportions of fine and coarse materials, (2) operating in accordance with claim 1 and characterised by devices whereby the distribution of the catalyst to individual places in the reactor is done by means of funnel-shaped distribution cones, on whose uppermost point the catalyst to be distributed is delivered.

35. PATENT APPLICATIONS - SOAPS, BLEACHING, ACID RESISTANT STEEL

Formed Washing and Cleaning Material
No. 13561, July 20, 1942, Frame 1234.

Such material obtained by alkaline saponification of the reaction product of sulphur dioxide and chlorine upon higher molecular weight aliphatic hydrocarbons, or chlorhydrocarbons producing alkali sulfonate and polymeric alkyl oxide.

Treating of Bleaching Clays
No. 14009, Feb. 22, 1943, Frame 1237.

Processing or treatment of bleaching earth with basic materials characterized in that one uses the basic material in a non-aqueous solution or suspension to act upon the bleaching clay.

The example cites treating clay with twice its weight of a methyl alcohol caustic solution (100 grams methyl alcohol and 4 grams caustic soda) stirred for about 15 minutes at 40°, separation of the liquid, washing twice with equal volumes of methyl alcohol, and drying at 110°. It was claimed that when aqueous solutions were used, 8 times as much clay was needed in decolorizing an oil.

Production of Material with High Surface Tension
No. 14780, June 5, 1944, Frame 1240.

Reacting higher molecular primary or secondary aliphatic, cyclo aliphatic or aryl aliphatic amines with aliphatic dicarbon acid anhydrides.

Steel which is stable against Inter-crystalline Corrosion
Unnumbered - Dec. 27, 1944, Frame 1242.

Such steels are characterized by chromium content between 3 and 12%.

36. LUBRICATING OIL

Recovery of Lubricating Oil from the Hydrogenated Product of Pressure Thermal Cracking and Polymerisation of the Cracked Product
Leuna Laboratories, Jan. 27, 1940, Frame 1245 - 1276.

Summary: (1) It was shown that the pressure thermal cracking of hydrogenated material followed by the recovery of olefinic cracked distillate could be accomplished. (2) This cracked distillate when polymerised with aluminum chloride or similar substances, yielded useful and suitable engine lubricants. (3) In their properties they are in every case equally good to the product of non-pressure cracking; with a mixed base starting material they are superior to the oils derived from non-pressure cracking. (4) The lower yield of lubricating oil resulting from the lesser olefin content is compensated by the higher cracked distillate yield when cracking at elevated pressure. (5) The hydrogenating after-treatment of the highly unsaturated oils produced by polymerisation makes lubricating oils of equal and sometimes of superior quality directly from the process. Items 6, 7 and 8. Attempts to use only the paraffinic "raffinate" from the extraction of paraffinic-naphthenic oils for cracking and lube oil recovery were unfruitful because of the imperfect separation of such oils. In contrast, predominantly paraffinic portions of these oils could be selectively cracked in a certain range. These cracked distillates, by polymerisation, gave better lubricants than by more severe and therefore less selective cracking.

Examination of the text showed the following high lights of this investigation.

(1) Recovery of Olefins

a - Chlorination and dechlorination.

The two steps (chlorine substitution and splitting out of hydrochloric acid) gave inferior quality lubricant; abandoned in favor of thermal pressure cracking.

b - Thermal cracking under pressure.

Cracking was done in small scale equipment, using a lead bath. In some instances the cracked distillate was separated into several fractions, the individual working up of such fractions has many advantages. The upper limit is determined by the flow point of the oil, and it is not feasible to go above a boiling point of 330°. An example of cracking conditions is given, in which the temperature varied from 500 to 550°; the pressure was 40 atmospheres inlet and 30 atmospheres outlet. The thruput was 155 liters per hour; the crack per pass varied from 1.2 up to 11.2%. Choosing the cracking temperature of 550° with a crack per pass of 11.2%, the reaction products were as follows:

Distillate - 74.8%
Iodine number - 162
Distillation
  I.B.P. - 44°
  50% -153°
  E.P. -202°

The yield of cracked gas was 24.8% containing 40% olefin. Tar amounted to 0.4%. The charge stock was TTH residue boiling above 300°.

(2) Polymerisation of Olefinic Substances to Lube Oil

The polymerization of the olefinic cracked distillate was performed in the presence of 3 to 10 weight percent of aluminum chloride, which was demonstrated to be superior to sulphuric acid, phosphoric acid and boron fluoride. The polymerization was done in the temperature range of 90 to 180°, chiefly at 120° in the presence of diluting material (at most 40% of the cracked product) and with vigorous stirring but without need of exterior heating. Aluminum chloride is added in small portions in the course of an hour. The oily layer is freed of aluminum chloride and hydrochloric acid by washing with water and caustic and distilled in vacuum (0.5-2.0 mm.) until the residue shows a viscosity of about 10° Engler at 50°.

The text is supported by numerous data tables which appeared to be condensations of more elaborate original data.

Synthetic Lube Oils from Pure Hydrocarbons

A report by Drs. Haag and Zorn, Oppau, Oct. 3, 1938, Frames 1278 - 1306.

Summary:

The quality of lube oils fractions boiling above 150° at 1 mm. Hg. and derived by the polymerization of pure aliphatic olefins with aluminum chloride under the research conditions, was found to be highly dependent on the constitution of the charged olefins. In the definition of quality, the temperature-viscosity relation (VI) of the oils, and their accelerated change (Sligh-oxidation test) were taken as the criteria. It could be shown that:

(1) The best VI values were obtained from olefins with terminal $CH=CH_2$. Again those olefins with long unbranched chains gave the highest VI values; short chains and branching resulted in lowering of the VI.

(2) Olefins with double bonds not at the end of the compound gave poorer VI values than olefins with a terminal double bond.

(3) The more highly branched the olefin, the poorer the VI.

(4) Altogether the olefinic polymers are very resistant to change and yield low asphalt in the Sligh test.

(5) The specific gravities of all the oils were about 0.85. It can be concluded that no aromatic or hydroaromatic rings are being formed.

The olefins produced by cracking of paraffins consist for the greater part of straight chained aliphatic olefins with terminal double bond. The result of research with the specified pure olefins could also be applied to the individual fractions as to the total olefins of cracking.

By co-polymerization of pure aliphatic olefins with aromatic or hydroaromatic hydrocarbons, as well as by the condensation of the latter with those made with halogen acids, the product has a favorable temperature-viscosity relationship.

The specific gravity of these oils is notably higher on account of the aromatic content than the oil from pure olefins; namely, over 0.9. Furthermore, the oxidation characteristic is commonly poorer than for pure olefinic oils. It is dependent on the number of side chains introduced; therefore, on the proportion of olefin to naphthalene or tetralin.

The result of polymerising aromatic and hydroaromatic hydrocarbons with pure olefin is equally applicable to the copolymerisation with olefins derived by cracking. Here too, the best VI values were obtained when using higher fractions which contained long chain olefins. By using the total cracked product, the short chain olefins can be changed over into longer chained material by pre-polymerisation which is done by stirring with naphthalene. This pre-polymerization of the olefin molecule results in ring closure so that at the cost of lower VI, an insufficient number of side chains are introduced into the tetralin molecule, resulting in poor oxidation characteristics.

The experimental results of this system - cracking olefins - tetralin (hydrogenation) can be applied directly to the system - cracking olefins - coal hydrogenation oil. Here too, the improvement of VI by pre-polymerisation and improvement of the oxidation characteristics can be attained through after-polymerisation with fresh cracking olefins.

(This ends reel #17)

U. S. TECHNICAL OIL MISSION
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