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(54) BENZINE PRODUCTION

(54) PRODUCTION DE BENZINE

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SPECIFICATION

TO WHOM IT MAY CONCERN:

Be it known that we, Franz Fischer, of 1 Kaiser Wilhelm Platz, Mülheim-Ruhr, Germany, and Herbert Koch, of 68 Witthausstrasse, Mülheim-Ruhr, Germany, Chemists, having invented certain new and useful "Process for treating synthetic benzine products from hydrogen and the oxides of carbon" do hereby declare that the following is a full, clear, and exact description of the same:-

It is known that in the production of benzine by synthesis from carbon monoxide and hydrogen at normal pressure, a raw product is obtained from aliphatic hydrocarbons having highly varying boiling points, the raw product containing in addition to mono-olefines, mainly saturated hydrocarbons such as gasol, light benzine, heavy benzine, illuminating oil, heating oil and solid paraffin. It is inherent in the nature of these products that the benzines obtained satisfy present day requirements in resistance to detonation up to only a boiling point of about 100° C., even when by selecting the conditions of production, the composition of the gases, and the nature of the catalyst are so determined that there are as many mono-olefines in the benzine as possible. On the other hand it has been found (Brennstoffchemie" Vol. 15 (1934) page 229), that particularly valuable lubricating oils can be produced by condensation from the mono-olefines of the fraction between 100 and 250° C. and over. In order to convert as far as possible the whole products of the

synthesis of benzine into the particularly desirable substances, namely, anti-detonating benzine and valuable lubricating oils, it has been found particularly advantageous to proceed as follows:-

First of all light benzine which boils up to about 100° C. is removed from the raw product obtained at normal pressure by the synthesis of benzine from hydrogen and the oxides of carbon. Thereupon solid paraffin is removed from the higher-boiling benzine whether by distillation or in any other manner, for example by cooling or by solution or by thermal treatment. Lubricating oils having a low solidification point are obtained by condensation from the olefines contained in the higher boiling constituents either directly or by dilution or by an enriching operation. The production of the lubricating oils in this state is of importance, because before cracking there are no other constituents, such as aromatic hydrocarbons present in association with the lubricating oil to reduce its quality, that are subjected to the action of a condensating agent, such as aluminium chloride. Thereupon distillation is advantageously carried out under vacuum during which the lubricating oils remain behind while the transformer oils and spindle oils actually pass over. All that has not passed over into these more valuable products is subjected to a cracking process which can produce benzine that is resistant to detonation while, if necessary, soft paraffin removed before the production of the lubricating oil is added. The light benzine hereinbefore referred to and the cracked benzine produced

may then be mixed in any suitable proportions or may be used separately, according to which kinds of benzine are desired. By this method the entire raw liquid products resulting from the synthesis of benzine can be treated to produce benzine resistant to detonation and valuable lubricating oils, in addition to a small residue of oil resulting from the cracking operation. This method produces primarily a light benzine whose resistance to detonation is equal to that of Baku benzine, while furthermore cracked benzines are obtained whose octane number is over 70, and finally the combined operations described produce valuable lubricating oils having viscosity indices lying between 1.6 and 2.6, whose absolute viscosity is merely a question of concentrating by distillation.

In carrying the invention into effect according to one method 100 kg. of a raw product are taken, produced at a reaction temperature of about 200° C., from water gas at normal pressure by the use of a catalyst consisting of cobalt metal and zinc oxide. The water-clear product has a specific gravity of 0.72 at 20° C., and consists up to about 45% of olefine hydrocarbons. At first the mixture is distilled at normal pressure until the temperature of the vapour is 125° C. By this means 42 kg. of light benzine is obtained which has a specific gravity of 0.67 at 20° C., and has an olefine content of 60% by volume. The octane number determined by the C.F.R. motor method is 65. The distillation of the raw product is then continued until the temperature of the vapour is 250° C., 37 kg. of a heavy benzine

distillate being secured. The residue of distillation amounting to 31 kg., by reason of the high content of soft paraffin, solidifies to produce crude paraffin.

The heavy benzine distillate of a specific gravity of 0.74 has an olefine content of 40%, and is treated in the manner hereinafter described to produce lubricating oil.

The product is first mixed in an iron polymerisation vessel provided with a good stirrer, with 1 kg. of commercial anhydrous aluminium chloride at room temperature, whereupon the reaction temperature is raised within a period of 2 hours to 120° C. At this temperature the mixture is well stirred for a further six hours, and then allowed to cool. The reaction product is as the result separated into two layers, the lower of which consists of an addition-compound of aluminium chloride which can be used as catalyst for further conversions. To secure lubricating oil the upper layer of oil is first purified with about 1% of Fuller's earth and then is subjected to distillation. The distillation is carried out until the vapour temperature is 250° C. at normal pressure, and then is continued under vacuum at 15 mm. of mercury, until the vapour temperature is 200° C. At the same time 25 kg. of a distillate is obtained which contains practically no olefine hydrocarbons, and for conversion into benzine resistant to detonation is combined with the high-boiling residue from the first distillation. The residue from the vacuum distillation is 10.5 kg. of a lubricating oil having the following properties:- specific gravity at 20° C., 0.840; viscosity at 20° C. - 20.8° Engler, and at 50° C., 4.66° Engler;

viscosity index = 1.90; solidification point -36° C.

The residue containing soft paraffin to the amount of 21 kg., which has been obtained in the first distillation, is combined with the distillate to the amount of 25 kg., poor in olefines obtained during the production of the lubricating oil and subjected cracking, for the purpose of conversion into benzine resistant to detonation. The product is 39 kg. of cracked benzine having an octane number 75.

Thus by treating the raw product of synthetic benzine by the process according to the present invention 42% by weight of primary benzine is produced having octane number 65, 39% by weight of cracked benzine, having octane number 75, and 10.5% by weight of valuable lubricating oil with a viscosity index of 1.90.

The process of the invention is diagrammatically indicated by way of example in the accompanying drawing. As illustrated in the drawing the raw product which is obtained in the synthesis of benzine from carbon monoxide and hydrogen at normal pressure is first distilled off in the still a up to a temperature of 125° C. of the vapours passing off. These vapours provide during condensation a light benzine b which is sufficiently resistant to detonation. Thereupon the residue in the still a is further distilled until a vapour temperature of 250° C. is reached. The heavy benzines produced, after condensation pass into the polymerisation vessel c which is provided with a stirring device d. The raw product obtained during polymerisation is carried over into the still f and then distilled. A lubricating oil remains

which is drawn off at g while the distillate passes into the cracking apparatus h. Furthermore the soft paraffins remaining behind in the still a after the second distillation are passed into the cracking apparatus h. The remaining cracked benzine is drawn off at j while the uncondensed cracking gases leave at k.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

We claim:-

1. In a process of production of benzine by reacting hydrogen with carbon monoxide at elevated temperature in the presence of a catalyst, the steps of subjecting the reaction product, from which the fraction boiling below 100°C. and the paraffin capable of solidification have been separated, to polymerization in the presence of a polymerization catalyst, of thereafter distilling the polymerization product first at ordinary pressure for the recovery of a soft paraffin which is capable of yielding in a cracking treatment, a further quantity of low-boiling benzine, and of finally distilling in vacuo for the recovery of a residue adapted for use as a lubricant.

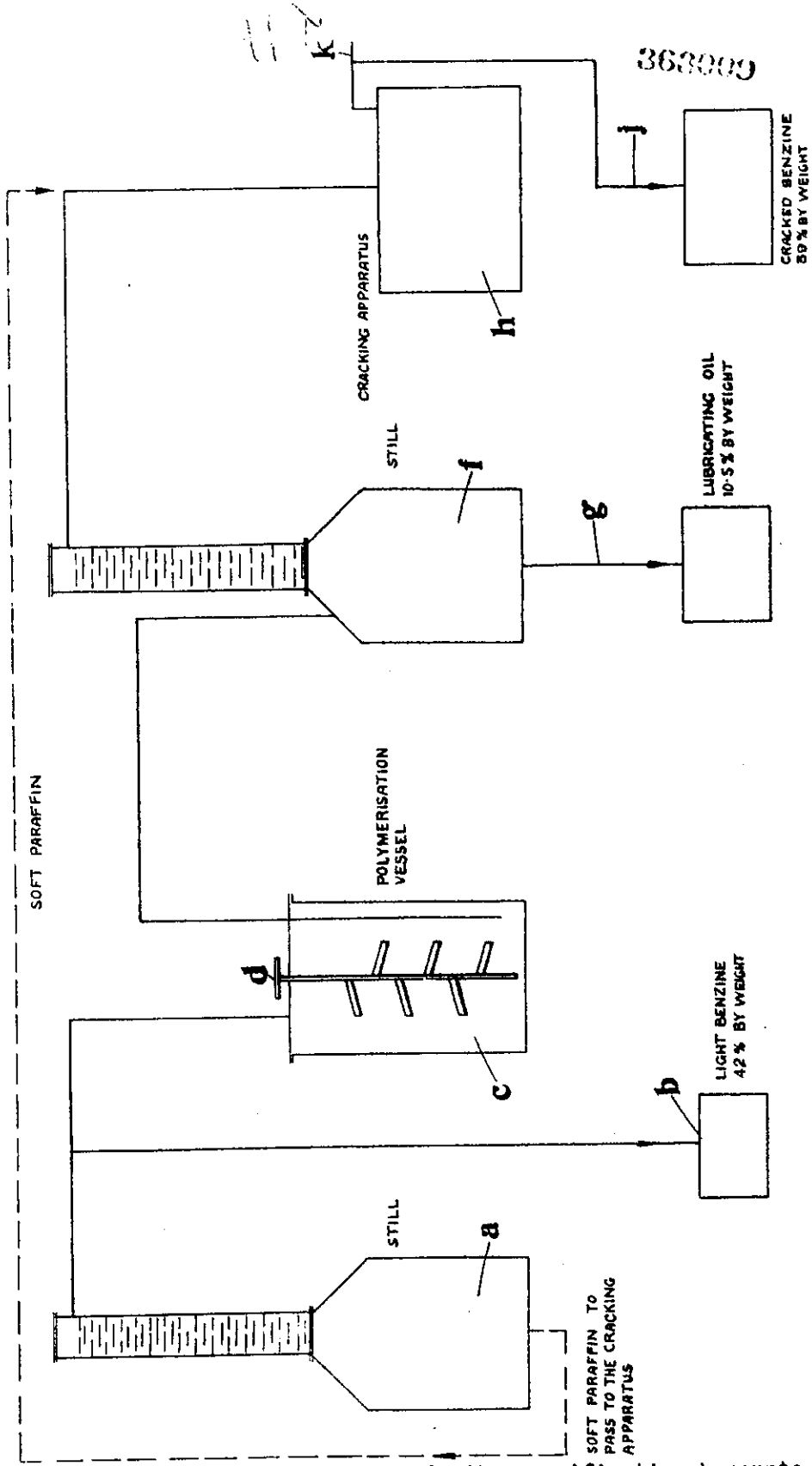
A1 2. The process of producing benzine and lubricating oil which comprises passing water gas at about 200°C. in contact with a hydrogenation catalyst, subjecting the reaction products to distillation at a temperature up to about 125°C. separating the distillate, continuing distillation up to about 250°C. heating the second distillate under stirring in the presence of a polymerization catalyst to about 120°C. purifying the oil layer, distilling same under ordinary pressure up to 250°C. cracking the distillate to recover benzine and subjecting the residue to distillation in a high vacuum at a temperature up to about 200°C. for the recovery of a residue being adapted for use as a lubricant.

(sgd) Franz Fischer

(sgd) Herbert Koch

Cologne, Germany.

27th June 1935.



Certified to be the drawings referred to in the specification hereunto annexed.
Dated at London, England, this 2nd day of July 1935

FRANZ FISCHER and HERBERT KOCH
By

Attorney