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PATENT SPECIFICATION

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3666

COMPLETE SPECIFICATION.

Process for Treating the Products of the Synthesis of Benzine from Hydrogen and the Oxides of Carbon.

We, STUDIEN- UND VERWERTUNGS-GESELLSCHAFT MIT BESCHRANKTER HAFTUNG, of Mülheim-Ruhr, Germany, a body corporate organised and existing according to the Laws of the German State, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is known that in the production of benzine by synthesis from carbon monoxide and hydrogen at normal pressure, gaseous and liquid aliphatic hydrocarbons are obtained having highly varying boiling points, and containing in addition to mono-olefines, mainly saturated hydrocarbons, such as gasol, that is to say, a mixture of gaseous saturated and unsaturated aliphatic hydrocarbons, and more particularly a mixture of ethane and ethylene with their higher gaseous homologues. There are also obtained light benzine, heavy benzine, illuminating oil, heating oil and solid paraffin. It is inherent in the nature of these products that from the benzines obtained only the benzine having a boiling point up to about 100° C., satisfies present day requirements in resistance to detonation, 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 160 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 liquid raw products 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 fractional distillation. Lubricating oils having a low solidification point are obtained by condensation from the olefines contained in the higher boiling constituents either directly or after dilution or after an enriching operation.

The diluting of the olefines before polymerisation is effected, for example, by the addition of saturated liquid paraffin hydrocarbons, advantageously with hydrocarbons that boil at a low temperature, for the purpose of preventing the temperature from rising too high during the polymerisation reaction. The enriching of the olefinic hydrocarbons before polymerisation may be carried out by extracting the olefines from their mixture with the paraffin hydrocarbons by the use of liquid sulphur dioxide and by subjecting the olefines in an enriched condition to polymerisation after the sulphur dioxide has been vapourised.

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 this way by reason of the absence of aromatic hydrocarbons lubricating oils are obtained, the viscosity of which is dependent in smaller measure upon the temperature. Thereupon distillation is advantageously carried out under vacuum during which the lubricating oils remain behind. The distillate 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

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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. The mixture is first 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 21 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 additional-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% 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. This produces 25 kg. of a distillate, and as residue 10.5 kg. of a lubricating oil having the following properties:

Specific gravity at 20° C. 0.840; viscosity 20.8° Engler at 20° C. and 4.66 Engler at 50° C.; viscosity index 1.90; solidification points — 36° C. The distillate contains practically no olefine hydrocarbons, and is cracked for conversion into anti-knock benzine together with soft paraffin which is left in distilling the raw product which serves as raw material for the process.

The residue which contains soft paraffin to the extent of 21 kg. and the distillate poor in olefines originating from the manufacture of lubricating oil to the extent of 25 kg. produce during combined cracking 39 kg. of a cracked benzine whose octane number is 75.

By the process 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.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for treating the products of the synthesis of benzine from hydrogen and the oxides of carbon to produce benzine resistant to detonation and valuable lubricating oils, characterised by first removing the light benzine boiling up to 100° C. or a little over, then removing the paraffins from the higher boiling fractions, condensing the olefines in the higher boiling fractions to produce lubricating oils, removing the non-condensed hydrocarbons from the lubricating oils thus produced and cracking the aforesaid hydrocarbons, if desired, together with the paraffins removed from the higher boiling fractions of the initial material.

2. A process for treating the products of the synthesis of benzine from hydrogen and the oxides of carbon to produce benzine resistant to detonation and valuable lubricating oil substantially as hereinbefore described.

Dated this 19th day of July, 1935.

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Agents for the Applicants.

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