NOTE.—*The application for a Patent has become void.*
This print shows the Specification as it became open to public inspection.

407

PATENT SPECIFICATION

Convention Date (France): July 27, 1925. **255,828**

Application Date (in United Kingdom): May 27, 1926. No. 13,484/26.

Complete not Accepted.

COMPLETE SPECIFICATION.

Improved Process for the Treatment of Gases obtained from the Distillation of Coal.

We, SOCIÉTÉ ANONYME: COMPAGNIE DE BETHUNE, a company duly organised according to the French laws, of Bully-les-Mines (Pas-de-Calais), France, 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 the gases arising from the distillation of coal form a complex mixture of various gases amongst which particularly predominate hydrogen, methane, carbon monoxide, ethylène.

Taken separately, each of these gases is a product having a certain value, as in a pure condition, or at least in a very concentrated condition, it becomes a raw material, interesting for various chemical syntheses; but mixed together, as they are in the gas arising from distillation of coal, their value is from this fact very diminished.

However among these gases, carbon monoxide has been the most refractory to all chemical syntheses and its transformation into methyl alcohol for instance has been possible only from the day high pressures have become realizable in practice. In fact, it is known since a long time that the increase of pressure has a useful effect every time the reaction corresponds to a diminution of the number of molecules; however, as the reaction $CO+2H_2=CH_4O$ is not the only one capable of taking place, it was necessary to find, moreover, for its realisation, a suitable medium and specially a suitable catalyser. It is known that when several reactions are possible, they can be sometimes directed either in a direction, or in the other by means of a catalyser of different chemical nature, all the other conditions remaining the same. Thus, at the same temperature of 300° C., the isobutyl alcohol divides into aldehyde and hydrogen in presence of copper; into isobutylene and water in presence of alumina; in presence of uranous oxide, the action is intermediate and at the same time aldehyde and ethylenic carbide are obtained. Likewise, chlorine reacts on acetylene either by giving carbon and hydrochloric acid with an important evolution of heat whilst, in certain conditions and with a suitable catalyser tetrachlorethane is produced. All the organic chemistry shows the action of selection capable of being exerted by catalysers.

The Badische Anilin und Soda Fabrik who were the first to be familiarized with high pressures by their synthesis of ammonia were the first to obtain synthetic methyl alcohol to the expense of carbon monoxide (French Patent 468,427 of the 13th February 1914—German Patents 249,787 of the 8th March 1913, No. 295,202 of the 31st May 1914—No. 295,203 of the 23rd June 1914); but, at that time, as their catalyser was not yet sufficiently selected, they obtained, besides, a complex liquid constituted by a mixture of aldehydes, ketones, ethyl alcohol, of complex hydrocarbons the

[*Price* 1/-]

formation of which is easily explained by the fact that besides methyl alcohol, methane was also produced arising from the reactions:

$$CO + 3H_2 = CH + H_2O$$
$$2CO + 2H_2 = CO_2 + CH_4$$

the methane reacting in its turn and under the effect of the pressure, on the constituent gases CO and H_2 and also on CO_2 for producing aldehydes, acids, ethyl alcohol, etc. At the same time this Company practically carried out the various following equations.

$CO + CH_4 = C_2H_4O$ acetic aldehyde
$CO + CH_4 + H_2 = C_2H_6O$ ethyl alcohol
$2CO + 2H_2 = C_2H_4O_2$ acetic acid
$CO_2 + CH_4 = C_2H_4O_2$ acetic acid
$CO + H_2 = CH_2O$ formic aldehyde.
etc.

Later on only this Company by rigorously selecting the various catalysers succeeded, by completely suppressing the use of iron, in avoiding the formation of methane and in commercially manufacturing methyl alcohol with suitable outputs.

It is moreover by the same processes that Mr. Claude incidentally realized the synthesis of methyl alcohol at the same time as that of ammonia and, since his process works, in the water issuing from the purifying tube (which is adapted to destroy the carbon monoxide contained in the mixture $N + H_2$) are found notable proportions of methyl alcohol and upper alcohols; but here again the catalyser is not sufficiently selected, as a great portion of the carbon monoxide transforms into methane.

In the same order of ideas, can be again cited the works of Fisher who, with a catalyser constituted by iron impregnated with carbonate of potash, transforms a mixture of $CO + H_2$ into a very complex liquid constituted by alcohols, ketones, acids, aldehydes, oils, etc.; the patents to G. Patard; the works of the Société Nationale de Recherches.

To sum up, the trials of hydrogenation of carbon monoxide under pressure have shown that a mixture of carbon monoxide, hydrogen and also of highly compressed methane, by passing over a suitable catalyser and at a predetermined temperature, was capable of giving liquid products constituted by methyl alcohol, ethyl alcohol, upper alcohols, aldehydes, hydrocarbons, etc.; the respective proportions of these various products being more or less high according to the nature of the catalyser, the initial proportions of the gases entering in reaction; in a word, according to the conditions of experience.

It is these conditions of experience which form the characteristic feature of the numerous patents taken up to this day on a question of such importance.

The present process has for object the preparation of organic liquid products from gases arising from the distillation of coal, either of normal composition, or even after dehydrogenation more or less partial; in a word, of gases constituted by methane, hydrogen, carbon monoxide in any proportions whatever; such a mixture constituting an abundant raw material. The process is characterised by the fact that the gases, after being subjected to a cracking under pressure over a first catalyser at a more or less high temperature, are, after cooling and elimination of the products formed, sent on a second catalyser; having a chemical nature different from the first one and playing the part of polymerization or condensation agent.

In fact, it has been noted that if a gaseous mixture having the composition previously indicated, is caused to pass, under any pressure (400 atmospheres for instance) and at a temperature comprised between 400 and 600° C., over iron oxide Fe_3O_4 contained in a tube 1 an alcoholic aqueous liquid more or less acid first separates after cooling, in the separator 2; as the condensation of the aqueous products has been made under pressure, all the more or less volatile products carburetting the residual gas have been deposited nearly in totality; however the gas thus cracked has been subjected to such a modification that if it is subsequently caused to pass over another catalyser, of different nature (condensation agent for instance contained in a second tube 3) it separates again in the separator from important quantities of organic liquid products non nuisible with water, boiling for the greater part before 100° C., the passage of the residual gases, after the first cracking under pressure, can be effected on the second catalyser, either under pressure, or at the atmospheric pressure.

Actually the mechanism of the reactions giving rise to carbides of hydrogen which have been formed by contact with the second catalyser is not yet explained; the fact that they settled in the separator 4 indicates their formation in the tube 3 to the expense of a preliminary transformation of the gasous constituents by contact with the first catalyser.

The initial composition of the gases can vary in very wide limits; the temperature at which the initial cracking takes place is comprised between 300 and 600° C.; that of the second catalysis between 100 and 400° C.; however, these figures do not constitute a limitation.

The present process can be carried out in any manner whatever, whether the two catalysers are separated in two tubes or even contained in a single tube, whether the gases react successively or at the same time on the two catalysis and condensation agents, whether the two groups of aqueous and oily products which are formed are then sucessively or separately collected and this according to the temperatures of the two agents of the reaction.

The cracking agent indicated is mainly constituted by a metallic oxide such as Fe_3O_4, the condensation agent by activated coal, but other catalysers can also be found without departing thereby from the principle of the invention.

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:—

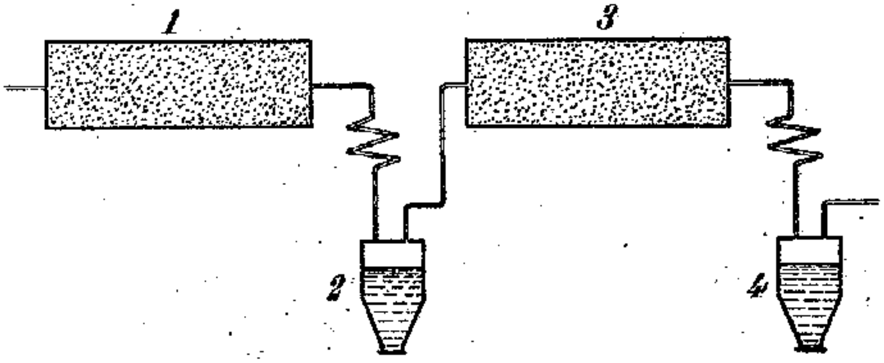
1. Process for the treatment of gases arising from the distillation of coal or of gases constituted by a mixture of hydrogen, methane and carbon monoxide in any proportions, in view of obtaining alcohols and liquid carbides of hydrogen, which consists in successively subjecting these gases to the action of two different catalysers under pressure and at a temperature comprised between 100 and 600° C., the first catalyser being constituted by a metallic oxide and the second one by a polymerization or condensation agent.

2. Process for the treatment of gases arising from the distillation of coal, substantially as hereinbefore described with reference to the accompanying drawing.

Dated this 26th day of May, 1926.

SOCIETE ANONYME: COMPAGNIE DE BETHUNE,
Per: Boult, Wade & Tennant,
111/112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.—1927.



Charles & Read Ltd. Photo Litho.