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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Purification and Reactivation of Contaminated Solid Catalytic Material

(A communication from Standard Oil Development Company, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America.)

I, John Conrad Arnold, a British Subject, of 29, Southampton Buildings, London, W.C.2, 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:—

This invention relates to a method for the purification and reactivation of a Fischer-Tropsch synthesis catalyst which contains an active hydrogenating constituent and is contaminated with waxy and oily deposits.

In the synthesis of normally liquid hydrocarbons from CO and hydrogen, there is unavoidably formed on the catalyst a quantity of oily and waxy material which impairs the activity of the catalyst, and therefore, requires periodic treatment of the catalyst to remove said waxy and oily deposits.

Methods are known for the reactivation of wax-contaminated catalysts in which the contaminated catalyst is first treated with a suitable solvent and subsequently subjected to hydrogenation.

According to the present invention, Fischer-Tropsch synthesis catalysts contaminated with waxy and oily deposits and which contain an active hydrogenating constituent are subjected first to destructive hydrogenation and then to treatment with a wash solvent. The destructive hydrogenation improves the efficiency of the subsequent solvent treatment for the following reasons:—

(1) The pores within the catalyst particles are partially freed of wax by destructive hydrogenation, thus making access of solvent into the pores more easily accomplished.

(2) The lowered viscosity or melting point of the wax due to prior destructive hydrogenation favours a more rapid solution of the wax in the solvent.

The destructive hydrogenation of the contaminants may be readily effected due to the presence of the active hydrogenating constituent in a Fischer-Tropsch synthesis catalyst. For example the metals of the iron group which constitute a part of the hydrocarbon synthesis catalyst are also very effective for the hydrogenation of hydrocarbons.

In the accompanying drawing, a flow plan has been shown which illustrates a preferred method of carrying the improvements into practical effect.

Referring in detail to the drawing, a hindered settler reactor 2 has been shown containing a body of "fluidized" catalyst, that is to say, a mass of powdered catalyst suspended in the reaction gases or vapors. This type of reactor is known in the catalytic cracking art, and the method of its operation need not be fully explained herein, for it does not go to the heart of the invention. It will be sufficient merely to point out that the synthesis gases, consisting of CO and hydrogen properly proportioned, are charged by line 1 to reactor 2 where they contact the catalyst C (which may be cobalt activated by thoria and carried on kieselguhr, or alternatively, it may be an iron catalyst), under proper conditions of temperature and pressure and for a sufficient period of time to effect the desired conversion. Whereupon, a product for recovery is taken off overhead through line 6 and recovered and treated in a known manner. It is indicated during the reaction, that oily and waxy materials form on the catalyst, and the powdered catalyst is withdrawn through a bottom drawoff pipe 3 carrying a flow control valve 5. Of course, it will be understood that an equal quantity of catalyst must be fed to the reactor to replace that withdrawn, and this catalyst may be added with the synthesis gas entering through line 1. Referring again to drawoff pipe 3, the same is provided in a known manner with a plurality of taps 4 through which a small quantity of gaseous material such as inert hydrocarbon, portion of the synthesis gas, or the like, may be forced into the downflow stream of catalyst to increase the fluid flow thereof, and to prevent bridging or plugging of the catalyst in the pipe. The catalyst discharges into a stream of hydrogen or hydrogen-containing gas, the latter being introduced through pipe 9, heated in the fired coil 11, and thence pumped by pump 14 through line 15 into line 3 and thence into a hydrogenation reactor 16 wherein it forms a dense suspension of catalyst in the hydrogen-containing gas similar to that in reactor 2. This fluid condition may be achieved, as is known, by regulating the linear velocity of the gasiform material controlled within the limits of $\frac{1}{4}$ to 10 feet per second, preferably however, from $\frac{1}{2}$ to 3 feet per second. The conditions of temperature and pressure will be set forth hereinafter, but for the present it will simply be stated that the waxy material contained on the catalyst is subjected to known conditions of temperature and pressure for a sufficient period of time to effect a substantial amount of destructive hydrogenation to form certain volatile products which are withdrawn overhead through line 17 and to lower the molecular weight and/or viscosities of the oily material and wax remaining on the catalyst, and also to make it more pervious or porous, so that it will be more adaptable for effective treatment with the wax solvent to remove it from the catalyst. The volatile material in line 17 is forced through a condensing coil 18, and thence discharged into a separation drum 19, from which the hydrogen-containing gas is withdrawn overhead through line 22. Since this gas will be associated normally with hydrocarbon gases, it is advisable to scrub the said gas with a light naphtha or other scrubbing oil in S, for the purpose of dissolving out substantial quantities of the said hydrocarbons, and thus, purifying the hydrogen stream, whereupon the major part of the hydrogen stream is then recycled to line 9 for further use in the process. A minor amount of the gas in line 22 is rejected from the system, by means of line 22a.

Meanwhile, the catalyst is withdrawn from hydrogenator 16 through a drawoff pipe 20 carrying a flow control valve 22b, and also gas introducing leads 21 performing the same function as taps 4 in line 3, and the thus withdrawn catalyst is discharged into a mixer 30 where it is mixed with a solvent for the wax such as, for example, a naphtha fraction, the mixer being provided with a suitably driven mixing means 32 to provide agitation, and therefore, good contact between the liquid solvent and the catalyst. The solvent is introduced through line 35; however, another portion of solvent is introduced into the bottom of an extraction tower 40 through line 39 and passes upwardly against the catalyst which flows downwardly from mixer 30 to a sump or well 42. Thus, the catalyst is subjected to a countercurrent solvent wash. In order to provide more intimate contact between the catalyst and the liquid solvent, the extraction tower 40 is provided with a plurality of baffles 41, which cause the catalyst to follow a tortuous path in passing from the mixer 30 to sump 42. A slurry of catalyst and solvent is withdrawn from well 42 through line 50, and after heating in 52 is discharged into a separation drum 53 from which the solvent is taken off overhead as a vapor, thence condensed in the coil 54 and returned to solvent storage 60. However, the catalyst may be returned to the reactor 2 in the form of a slurry, in which case, of course, the slurry would not be heated to flash off the solvent to recover a dry catalyst.

The solvent, as indicated, passes up through tower 41 and is withdrawn through line 70, thence passed into a heater 72 and thereafter discharged into a fractional distillation column 73 from which the solvent, substantially free of wax and oily material originally on the catalyst, is recovered overhead through line 75 and cooled in the condenser 78 and returned to solvent storage 60 for further use in the process. The oily and waxy bottoms are rejected from the system through line 80.

Referring again to the separation drum 19, the hydrocarbon bottoms withdrawn through line 23 may be processed to recover valuable hydrocarbons.

In the foregoing description, there has been set forth the essentials of an operation in which a powdered catalyst employed in a fluid solid type of operation was purified. Of course, the improvements extend also in their broadest aspect to successive destructive hydrogenation and solvent treatment of any fouled catalyst contaminated with waxy and oil deposits and containing an active hydrogenating constituent, regardless of the physical form of the catalyst or the type of operation in which it is employed. Thus, if reactor 2 were a stationary bed type of reactor where the catalyst in the form of pills, pellets, granules, etc., is supported on a foraminous support of some sort, the catalyst may be purified by periodically discontinuing the productive phase of the process, and thereafter treating the catalyst phase with hydrogen to destructively hydrogenate the deposits on the catalyst, and after that, the catalyst may be treated with a suitable wash solvent to complete the substantial removal of oily and waxy material from the said catalyst.

As to operating conditions during the destructive hydrogenation step, they are those for normal destructive hydrogenation and depend upon the activity of the catalyst. It is preferred to operate as follows:—

Temp. in °F. for reactivating a cobalt type catalyst	360° to 500°
Press. in lbs./sq. in. (gauge)	0 to 300
Temp. in °F. for reactivating an iron type catalyst	450° to 750°
Press. in lbs./sq. in. (gauge)	25 to 750
Preferred	25 to 350

As to the solvent, any cheap hydrocarbon solvent is satisfactory such as naphtha, gasoline, and liquefied normally gaseous hydrocarbons.

After the catalyst is freed of wax, it may be returned to the reactor in the dry powdered state or it may be returned as a slurry or in any other form that is convenient.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. The method of purifying a solid Fischer-Tropsch synthesis catalyst which contains an active hydrogenating constituent and is contaminated with waxy and oily deposits, which comprises first subjecting catalyst to the influence of hydrogen-containing gas under conditions adapted to cause destructive hydrogenation of at least part of the said oily and waxy materials, and thereafter treating the catalyst with a solvent for the so treated oily and waxy materials.

2. The method set forth in claim 1 in which the solvent treated catalyst is returned to the reactor in the form of a slurry.

3. The method set forth in claim 1 in which the catalyst is returned to the reactor in a dry state.

Dated this 5th day of March, 1946.

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Agents for the Applicant.

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615,647 COMPLETE SPECIFICATION 1 SHEET

[This Drawing is a reproduction of the Original on a reduced scale.]