

# PATENT SPECIFICATION

703,739



Date of Application and filing Complete Specification Jan. 15, 1952.

No. 1188/52.

Application made in United States of America on Jan. 30, 1951.

Complete Specification Published Feb. 10, 1954.

Index at acceptance:—Classes 1(1), F3B1; 1(3), DX, DX—G22; 2(3), B1C; and 2(5), P11(A: D6), P11P1(B: C), P11P(2X: 3), P11P6(B: F), P11T1B.

## COMPLETE SPECIFICATION

### Process for Preparing High Molecular Weight Hydrocarbons

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of 10th and Market Streets, Wilmington 98, Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a catalytic process for preparing high molecular weight hydrocarbons. More particularly it relates to a process for synthesizing high molecular weight polymethylenes from carbon monoxide and hydrogen.

It is well known that in the presence of specific catalysts and under certain conditions of temperature and pressure carbon monoxide and hydrogen react to give methanol and branched chain higher alcohols. It is also known that under other reaction conditions involving the use of certain cobalt-containing or ruthenium-containing catalysts the reaction between carbon monoxide and hydrogen leads to the formation of paraffin waxes. High molecular weight straight chain alcohols and other oxygen-containing organic compounds also have been obtained by hydrogenation of carbon monoxide in the presence of metals of the eighth group suspended in paraffin hydrocarbons. In general, the waxes previously obtained were produced simultaneously with compounds of relatively low molecular weight (Fischer and Pichler, Brennstoff-Chemie 20,247—50(1939)), the average molecular weight of the reaction products being generally less than 1000. These previously known waxy reaction products contained ingredients which could be distilled at high temperatures and low pressures (200° C./2 mm.). A very recent development in this art is the discovery that the course of the CO—H<sub>2</sub> reaction in the presence of water and a

ruthenium catalyst is determined by the pH of the medium; strongly alkaline media cause the formation of C<sub>2</sub> to C<sub>10</sub> alcohols rather than hydrocarbon waxes which are formed when the pH is on the acid side. Another important recent development in this art is the discovery that macromolecular polymethylenes can be prepared from carbon monoxide and hydrogen in the presence of metal molybdate catalysts.

An object of this invention is to provide a process employing novel catalysts for the preparation of macromolecular hydrocarbon compositions of improved quality from carbon monoxide and hydrogen. Another object is to prepare relatively high melting polymethylenes in high yield. Other objects of the invention appear hereinafter.

In accordance with this invention, macromolecular essentially hydrocarbon compositions of improved quality are prepared by introducing hydrogen and carbon monoxide into a reaction vessel, and heating the reactants in the presence of a catalyst containing a metal tungstate at a pressure of at least 200 atmospheres, preferably 500 to 5000 atmospheres, and at a temperature within the range of 125° to 300° C., preferably 150° to 250° C. The catalysts employed are preferably nickel and/or cobalt tungstate.

This invention provides radically new macromolecular hydrocarbon polymers, i.e. polymers which are essentially hydrocarbon in nature, which are characterized by having an inherent viscosity greater than 1.3, measured as a 0.1% solution in tetrahydronaphthalene at 125° C., which melt above 130° C., which show orientation along the fiber axis when subjected to cold drawing, and which yields films which are superior to films from previously known hydrocarbon polymers in their stiffness and breaking strength characteristics.

In one manner of producing the hydro-

carbon polymers of this invention a pressure reactor is charged with a diluent and the tungstite catalyst, the reactor is swept with oxygen-free nitrogen, cooled to 0° C., and evacuated. The reactor is then pressurized with a carbon monoxide/hydrogen gas mixture and the reaction mixture is heated to between 125° and 300° C. Throughout the period of reaction the pressure within the reactor is maintained above 200 atmospheres, preferably 500 to 5000 atmospheres, by repressuring with carbon monoxide/hydrogen gas mixture of the same or of different composition from that initially used. After reaction is complete, the reactor is permitted to cool, opened, and the contents discharged and filtered. The solid polymeric product is separated from the catalyst by extraction or by other means known to those skilled in the art.

The examples which follow are submitted to illustrate and not to limit this invention. Unless otherwise stated, parts are by weight.

#### EXAMPLE 1

A reaction mixture comprising 87 parts of xylene, 5 parts of mixed dodecyl acid phosphates, 20 parts of nickel tungstite and a gas mixture of 2 mols of hydrogen per mol of carbon monoxide was heated at 225° C. and 900 to 1000 atmospheres pressure, which was maintained over a 15-hour period by repressuring with the same gas mixture. At the completion of the run, the vessel was cooled, vented, its contents discharged and filtered. Extraction of the solid obtained with boiling heptane and addition of the hot heptane extract to methanol produced 0.80 part of solid polymer. A further extraction in the same manner with boiling xylene produced 1.85 parts of solid polymer having a microscopic melting point of 133° C., and an inherent viscosity of 1.89 measured at 0.1% concentration in tetrahydronaphthalene at 125° C.

#### EXAMPLE 2

A reaction mixture consisting of 90 parts of xylene and 20 parts of granular nickel tungstite, and a gas mixture composed of 2 mols of hydrogen per mol of carbon monoxide was heated at 225° C. and 900 to 1000 atmospheres pressure, which was maintained over a 15-hour period by repressuring with the same gas mixture. At the completion of the run the vessel was cooled, vented and its contents discharged. The polymer and catalyst were separated from the reaction medium by centrifuging, and washed with acetone. The polymer was separated from the catalyst by extraction first with boiling benzene

then with boiling xylene. The benzene extract was diluted with methanol and the precipitated polymer, separated by filtration, washing with acetone and drying, amounted to 0.8 part. From the xylene extracts, by a similar procedure, there was isolated 3 parts of essentially hydrocarbon polymer which was found to be orientable and to have an inherent viscosity of 1.33, measured at 0.1% concentration in tetrahydronaphthalene at 125° C.

#### EXAMPLE 3

A reaction mixture consisting of 80 parts of cyclohexane and 20 parts of a cobalt tungstite catalyst was heated under a pressure of hydrogen and carbon monoxide as in Example 2. There was isolated 2.15 parts of essentially hydrocarbon polymer which was found to be orientable by cold drawing.

#### EXAMPLE 4

A reaction mixture consisting of 90 parts of xylene, 20 parts of a mixed nickel-tungstite-molybdate and 5 parts of mixed dodecyl acid phosphates was heated at 200° C. in the presence of hydrogen and carbon monoxide as in Example 2. The yield of essentially hydrocarbon polymer was 3.85 parts, of which 2.63 parts had an inherent viscosity of 1.44, measured at 0.1% concentration in tetrahydronaphthalene at 125° C.

#### EXAMPLE 5

A silver lined continuous catalytic converter containing 40 parts of 8-11 mesh nickel tungstite mixed with 80 parts of copper pellets, having approximately the particle size of the catalyst, was pressured with mixed gas composed of 1.6 moles of hydrogen per mole of carbon monoxide and heated to 225° C. The pressure inside the converter was adjusted to the operating level of 800 atmospheres. A stream of decahydronaphthalene and a stream of mixed gas were injected separately into a mixing block and fed into the top of the converter at a total pressure of 800 atmospheres. The mixed gas was injected at a space velocity of 0.51 part per part of catalyst per hour and the liquid was injected at a space velocity of 0.53 part per part of catalyst per hour. The operating pressure was maintained at 800 atmospheres by regulating the rate of gas bleed-off. The reaction product, obtained by bleed-off at 6-hour intervals, was filtered, washed with acetone, and dried. The yield of essentially hydrocarbon polymer amounted to 0.2 part per hour. The polymer was orientable by drawing and has a microscopic melting point of 130.4° C.

## EXAMPLE 6

Example 5 was repeated except that the converter was charged with 66.5 parts of cobalt tungstite mixed with 100 parts of copper pellets. The yield of essentially hydrocarbon polymer amounted to 0.56 part per part of catalyst per hour.

## EXAMPLE 7

A reaction mixture consisting of 80 parts of cyclohexane and 20 parts of an iron tungstite catalyst was heated at 250° C. under pressure of hydrogen and carbon monoxide as in Example 2. There was isolated 0.6 part of solid polymethylene. In similar tests, zinc tungstite and copper tungstite were employed in place of iron tungstite and were found to be active for production of solid polymethylene.

The nickel tungstite catalyst used in Examples 1 and 2 was prepared as follows:—

Four moles of ammonium tungstate in a 10% aqueous solution, prepared by dissolving 1080 grams of ammonium paratungstate in 7000 cc. of water and 310 cc. of 28% aqueous ammonia at 85° C. was added to 4 moles of nickel nitrate in a 16% solution, prepared by dissolving 1163 grams of nickel nitrate in 6000 cc. of water at 85° C. A pale green precipitate was formed in a slurry having a pH of approximately 6. The pH of the slurry was adjusted to 7 at 75° C. by addition of 404 cc. of 28% aqueous ammonia. The resulting precipitate was washed, filtered, dried, and calcined at 400° C. The product thus obtained was charged into a furnace and heat treated at 400° C. in a stream of nitrogen at a space velocity of 390 l./hr. for 12 hours, cooled to room temperature in nitrogen and the product then reduced for 24 to 27 hours at 450° to 480° C. in hydrogen at a space velocity of 600 to 1000 l./hr. The reduced product corresponded by analysis to nickel tungstite ( $\text{NiWO}_3$ ) containing a slight excess of  $\text{W}_2\text{O}_3$ . The product was not spontaneously pyrophoric when exposed to air at room temperature. On warming slightly over a Bunsen flame, however, the product ignited with a bright glow and oxidized to yellow nickel tungstate.

The mixed tungstite-molybdate catalyst employed in Example 4 was prepared as follows:—

A solution prepared by dissolving at 80–85° C. 176.6 g. of ammonium paramolybdate tetrahydrate and 270 g. of ammonium paratungstate hexahydrate in 3000 ml. of water and 170 ml. of 28% ammonium hydroxide, was added with stirring to a solution of 581.6 g. of nickel nitrate hexahydrate in 2000 ml. of water

at 80–85° C. A yellow-green precipitate formed in a slurry. The pH of the slurry was adjusted to 7 by addition of 86 ml. of 28% ammonium hydroxide at 80–85° C. The neutralized slurry was pale green, and it was stirred for one hour after neutralization. The precipitate was washed four times by decantation using 6 liters of water in each washing. The washed precipitate was filtered by suction and dried overnight at 105° C. The dry weight was 477 g. and analyzed 19.7, 19.77% nickel, 13.28, 13.41% molybdenum, and 34.95, 34.98% tungsten. The dry cake was calcined at 400° C. for 20 hours and then reduced in hydrogen at a space velocity of 1000 volumes of gas per volume of catalyst per hour at 450° C. for 22 hours. The reduced product was cooled in hydrogen, flushed with nitrogen and stored under nitrogen. The product was a black, slightly pyrophoric material.

The process can be operated as a batch or semi-continuous operation, or as a continuous down or up-flow operation. Whether, for batch, semi-continuous, or continuous operation, the desired mixtures of carbon monoxide and hydrogen are readily made up on the basis of pressures, calculated by successive substitutions into the following equation:—

$$P \text{ (of CO)} = \frac{(C \text{ initial CO}) (P \text{ final})}{(C \text{ final CO}) + N(C \text{ final H}_2)}$$

where P stands for pressure, C stands for the compressibility of the carbon monoxide and of the hydrogen at the indicated pressure, and N is the desired carbon monoxide/hydrogen mole ratio in the mixture.

The mole ratio of carbon monoxide to hydrogen in the gas mixture may vary from 10:1 to 1:5. Usually mole ratios of 3:1 to 1:2 are used because gas mixtures in this range of composition give optimum results from the standpoint of yield of desired high molecular weight hydrocarbon polymer.

The temperature at which the hydrogenation of the carbon monoxide is effected lies in the range of 125° to 300° C. Because good reaction rates with best yields of desired high molecular weight hydrocarbons are obtained in the range of 150° to 250° C., this range embraces the preferred operating temperature conditions.

The process is generally carried out under a total pressure of at least 200 atmospheres. Because maximum rates of production of desired high molecular weight products are achieved using pressures in

excess of 500 atmospheres, the use of such pressures is economical and embraces a preferred aspect of operation. The upper limit of pressure is not critical, and the maximum is determined by the mechanical restrictions of the equipment employed. Since the use of pressures in excess of 500 atmospheres does not lead to any compensating advantages from the standpoint of yield of desired high molecular weight essentially hydrocarbon polymer or economy of operation, it represents the practical upper limit of pressure.

Since the reaction is highly exothermic, it is desirable to operate in the presence of a reaction medium, which in addition to aiding in the dissipation of the heat of reaction also functions to bring about better catalyst contact and hence improve the efficiency of the process. Suitable media are water, aromatic and aliphatic hydrocarbons, and alcohols.

If desired, there may be incorporated into the reaction medium an acid material such as a mineral acid, for example, phosphoric acid; or an alkyl acid phosphate, for example, didodecyl acid phosphate, etc. The process can also be operated in the presence of alkaline materials such as the alkali metal carbonates or hydroxides.

The reaction media can occupy up to 80% (or more) or as little as 5% (or even less) of the reactor volume when operating as a batch process. Generally, however, the reaction medium occupies between 30 and 50% of the reactor volume.

Although melting point is an important physical property, in itself it is not sufficient to characterize the hydrocarbon polymers as being suitable for conversion to superior films and fibers. Melting point can be reduced by the presence of small amounts of low molecular weight material without affecting other properties, which are determinants in the utility of the products for film and fiber applications. Thus polymers melting below 130° C. are useful for conversion to such films and fibers if their inherent viscosity is at least 1.3, measured at 0.10% concentration in tetrahydronaphthalene at 125° C.

The melting points specified in the example represent the temperature at which complete disappearance of the crystalline structure is observed under a polarizing microscope.

The time of reaction depends upon such interdependent variables as temperature, pressure, and amount and type of catalyst employed. Under the preferred conditions for batch operation the desired degree of reaction is reached in from 5 to 20 hours.

The catalysts used in the preparation of the hydrocarbon polymers of this invention are tungstites. Preferred catalysts because of their high degree of activity and selectivity are the tungstites of nickel and cobalt. These tungstites may contain modifiers or promoters such as barium, cadmium, chromium, thorium, cobalt and copper, as desired, and they may be employed in the form of pellets or as finely divided powders. They may also be used as such or blended with molybdates as illustrated in Example 4. These tungstites may be extended on inert supports such as charcoal, alumina, silica, etc., or they may be unsupported. The particular form of catalyst for maximum activity depends upon the conditions under which the hydrogenation is to be effected. Thus, for vapor or liquid phase operation it is best to have the catalysts in the form of pellets, thus minimizing mechanical losses. If the process is to be operated as a batch operation, it is best that the catalyst be in finely divided form because in this way maximum catalyst activity is realized.

Example 5 illustrates the use of nickel tungstite mixed with copper pellets as the catalyst. The copper pellets function as a heat transfer medium and permit better temperature control of the reaction. In place of copper other metals in pellet form may be used, such as aluminium, and iron.

The amount of catalyst employed depends upon such interdependent variables as temperature, pressure, desired mode of operation, desired duration of contact time if in continuous operation, etc. As a rule, in batch operation the amount of catalyst will be between 1.5 and 30% and preferably between 2.5% and 20% by weight of the reaction medium.

In continuous operation the weight of product in the reactor at any time is ordinarily less than the weight of the catalyst, but the total weight of material processed during the active life of the catalyst is a least 10 times the catalyst weight.

The surface of the reactor in contact with the reactants appears to be an important factor in determining the molecular weight and yield of hydrocarbon polymer obtained. Silver, copper, or stainless steel surfaces are satisfactory.

The process of this invention makes it possible to convert carbon monoxide into solid products which are virtually all of high molecular weight. These solid products, without further purification, have molecular weights of at least 25,000, and inherent viscosities of at least 1.3. They

are convertible into fibers and films having strength and tenacity characteristics exceeding those of hitherto available synthetic hydrocarbon polymer films and  
5 fibers.

What we claim is:—

1. A process for preparing macromolecular essentially hydrocarbon compositions, which comprises heating carbon  
10 monoxide with hydrogen at a temperature of from 125°—300° C. under a pressure of at least 200 atmospheres in the presence of a metal tungstite catalyst.

2. A process according to Claim 1 in  
15 which the catalyst employed comprises nickel and/or cobalt tungstite.

3. A process according to Claim 2 in which the catalyst employed is a mixed nickel tungstite-molybdate catalyst.

20 4. A process according to any of the preceding claims in which the reaction is carried out in the presence of an inert organic liquid medium, such as a hydrocarbon such as xylene.

25 5. A process according to any of the preceding claims in which the reaction is effected under a pressure of from 500 to

5000 atmospheres and preferably at a temperature of from 150° to 250° C.

6. A process according to any of the  
30 preceding claims in which the initial mole proportion of carbon monoxide and hydrogen is 1:2.

7. A process according to claim 6 in which the carbon monoxide and hydro-  
35 gen are heated at 225° C. under 900 to 1000 atmospheres pressure in the presence of xylene and a nickel tungstite catalyst, to obtain a macromolecular hydrocarbon composition having an inherent viscosity  
40 of 1.38, measured at 125° C. in a 0.1% solution in tetrahydronaphthalene, and thereafter separating the macromolecular hydrocarbon composition from the result-  
45 ing reaction mixture.

8. The process for preparing macromolecular, essentially hydrocarbon, compositions substantially as hereinbefore described.

PAGE, WHITE & FARREN,  
Chartered Patent Agents,  
27, Chancery Lane, London, W.C.2,  
Agents for the Applicant.