



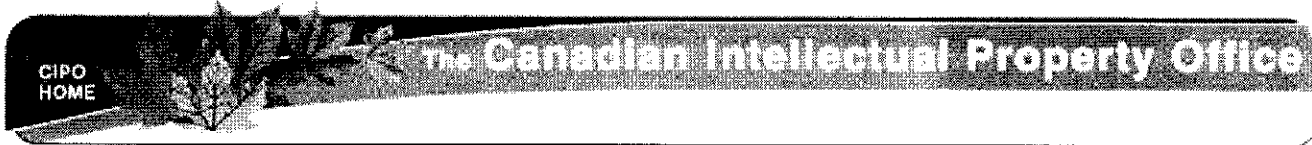
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(12) Patent:

(54) ORIENTABLE HYDROCARBON FROM CARBON MONOXIDE AND HYDROGEN

(54) HYDROCARBURE ORIENTABLE DE MONOXYDE DE CARBON ET D'HYDROGENE

(72) Inventor (Country):	ELBERT C. HERRICK (Not Available) MARK W. FARLOW (Not Available)
(73) Assignee (Country):	E.I. DU PONT DE NEMOURS AND COMPANY (United States)
(71) Applicant (Country):	
(74) Agent:	
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ABSTRACT

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CHEMICAL PRODUCTS AND PROCESS

This invention relates to polymers which are essentially hydrocarbon in nature and to methods for their preparation. More particularly this invention relates to new orientable polymers which are essentially hydrocarbon in nature and to novel catalytic methods for their preparation.

The advent of nylon and other synthetic high molecular weight polymers focused attention on such materials as sources of new films and fibers to supplement or replace films and fibers from natural sources in many applications.

10 The relative chemical inertness of the essentially saturated hydrocarbon polymers has drawn attention to such products as promising candidates for investigation. Only few hydrocarbon polymers, however, have achieved commercial importance, and of these the polystyrenes, polyisobutylenes and the normally solid polymers of ethylene are probably the best known. Although these polymers are outstanding for many industrial applications, they are deficient in one or more significant properties required for films and fibers.

J. Kleine in U.S. patent 2,351,345 has suggested the preparation of hydrocarbon polymers containing at least 600 carbon atoms in the molecule by passing a mixture of carbon monoxide and hydrogen in a ratio of 1:2.2 or 1:2.3 or less, in the liquid or vapor phase over a heated catalyst containing as an essential component an iron group metal or a metal of the platinum or vanadium groups. The only working example provided specifies a mixture of carbon monoxide and hydrogen in the ratio of 1:2.3 and the passage thereof at 11 atmospheres pressure over a cobalt-alumina-zinc oxide catalyst heated to 180°C. After 48 hours the reaction is stopped and the catalyst is fractionally extracted with boiling benzene, first at atmospheric pressure then at 6 atm. and finally at 11 atm. The product obtained in the 11 atm. extraction is said to melt at 130°C. and to amount to 10 g. per cubic meter of gas mixture. This product is said to be useful for conversion into filaments, foils and films. No data on the physical properties of these products are given.

In U.S. patent 2,352,328, J. Kleine reports the production of films and fibers melting about 130°C. which can be cold drawn to products having improved tenacity from hydrocarbon polymers obtained by hydrogenating coal or carbon monoxide under pressure over a ruthenium catalyst. The fibers from hydrocarbon polymers having molecular weights above 10,000 are said to have tenacities equaling and even surpassing those of cotton and natural silk and to be of lower specific gravity than these materials. Aside from melting point the patentee gives no specific data on the properties of his films and fibers.

It is an object of this invention to provide new polymers which are essentially hydrocarbon in nature and a novel catalytic method for their preparation. A further object is to provide orientable high molecular weight hydrocarbon polymers having relatively high inherent viscosities. A still further object is to provide orientable hydrocarbon polymers which form films having high stiffness moduli and high breaking strengths. Another object is to provide fiber-forming hydrocarbon polymers from carbon monoxide and hydrogen. Still another object is to provide a novel catalytic process for the hydrogenation of carbon monoxide to produce hydrocarbon polymers. Other objects will appear hereinafter.

The objects of this invention are accomplished by providing essentially hydrocarbon polymers which are orientable by cold-drawing and which have inherent viscosities of at least 0.74. Preferred orientable hydrocarbon polymers of this invention melt above 130°C., have inherent viscosities of at least 1.0, have stiffness moduli greater than 150,000 lbs./sq.in., and have microtensile breaking strengths above 100,000 lbs./sq.in., based on the relaxed drawn dimensions of the film.

The novel hydrocarbon polymers of this invention are the products obtained by the catalytic hydrogenation of carbon monoxide, under pressure, in the presence of a molybdate of a metal whose ions are soluble in aqueous ammonia in amount greater than that stoichiometrically required to precipitate the metal ion. Thus, these metal molybdates are molybdates of metals whose ions are not precipitated as insoluble oxides or hydroxides when solutions of their salts are treated with aqueous ammonia in amount slightly in excess of that which is

oretically required for the formation of the metal oxide or hydroxide.

The metal molybdates which are used in the process of this invention exist in two series, in the first of which the molybdenum is present in the quadrivalent state corresponding to the oxide MoO_3 and the hypothetical acid H_2MoO_4 , while in the second series the molybdenum exists in the bivalent state corresponding to the oxide MoO and the hypothetical acid H_2MoO_2 . Examples of these molybdates are copper molybdate having the formula CuMoO_4 , nickel molybdate having the formula NiMoO_4 , and cobalt molybdates having the formulas CoMoO_4 and CoMoO_3 .

In producing the essentially hydrocarbon polymers of this invention, a pressure reactor is charged with a diluent and the molybdate catalyst, the reactor is swept with oxygen-free nitrogen, cooled to 0°C ., and evacuated. The reactor is then pressured to a specific level with a carbon monoxide/hydrogen gas mixture of predetermined composition and the reaction mixture is heated to between 125°C . and 300°C . until the desired degree of reaction has been obtained. Throughout the period of reaction, the pressure within the reactor is maintained at the indicated level 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 essentially hydrocarbon polymer 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 I

A reaction mixture consisting of 97 parts of tetrahydronaphthalene, 15 parts of nickel molybdate, 5 parts of mixed dodecyl acid phosphates, and a gas mixture composed of 2 moles of hydrogen per mole of carbon monoxide was heated at 175°C. and 900 to 1000 atmospheres pressure, which was maintained over a 14-hour period by repressuring with the same gas
10 mixture. At the completion of the run, the vessel was cooled, vented, and its contents were discharged.

The polymer and catalyst were separated from the reaction medium by filtration, and washed with acetone. The filtrate was diluted with methanol, and the precipitate which formed was separated by filtration and found to amount to 0.07 part. The polymer was separated from the catalyst by two successive extractions with boiling xylene and a final extraction with boiling tetrahydronaphthalene. The first xylene extract was diluted with methanol and the precipitated polymer separated
20 by filtration, washed several times with methanol, and dried. The polymer from the first xylene extract amounted to 1.5 parts. From the second xylene extract, by a similar procedure, there was isolated 4.3 parts of essentially hydrocarbon polymer which was found to be orientable. The tetrahydronaphthalene extract, using a similar procedure, yielded 0.4 part of a polymer which was orientable. Of the total material obtained, 75% was orientable.

The orientable, essentially hydrocarbon polymer was found to have the following physical properties: polarizing

microscopic melting point, $134.7 \pm 0.5^{\circ}\text{C}$.; inherent viscosity, 1.1, measured at 0.1% concentration in tetrahydronaphthalene at 125°C .; amorphous content of a 20 mil film, annealed, 6.8%, shock cooled, 16.8%; density of the annealed film, 0.974; density of the shock cooled film, 0.952. The orientable essentially hydrocarbon polymer was found to have a stiffness modulus of 150,000 to 190,000 lbs./sq.in., measured on a film of 0.008 inch thickness. Microtensile measurements on a 1-2 mil film showed an elongation of 2400%. The microtensile breaking strength, figured on the relaxed drawn dimensions of the film, was 100,000 lb./in.². The yield point was 3,000 lb./sq.in. at an elongation of 10-30%.

Duplication of Example I using xylene as the reaction medium, instead of tetrahydronaphthalene, yielded a product which after compositing with that of other similar runs was found by analysis to have the following elementary composition: carbon, 85.50, 85.28%; hydrogen, 14.29, 14.29%; and oxygen, 0.19, 0.19%.

Infrared examination of a sample of an essentially hydrocarbon polymer similar to the above showed it to have bands characteristic of the carbonyl group, bands for terminal and internal unsaturation at 10.1 microns, 11.0 microns, and 10.4 microns, and band for branching at 11.2 microns. The infrared analysis also indicated that the material had 1.2 methyl groups per 100 carbon atoms.

EXAMPLE II

Example I was repeated, except that the catalyst charge consisted of 13 parts of nickel molybdate which had been used in two previous runs and the reaction temperature was 200°C .

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The yield of essentially hydrocarbon polymer amounted to 1.47 parts, of which 1.35 parts, or 92%, was insoluble in boiling benzene, had an inherent viscosity of 1.31, measured at 0.1% concentration in tetrahydronaphthalene at 125°C., and melted at 130°C. The benzene insoluble material was orientable. A melt pressed film which had been shock cooled in ice water had a tensile strength of 4,400 lbs./sq.in. at 80% elongation. The film was tough and orientable.

EXAMPLE III

A silver-lined pressure vessel was flushed with
10 nitrogen, charged with 5 parts of nickel molybdate, 7.5 parts of 85% phosphoric acid, and 65 parts of xylene, again flushed with nitrogen, evacuated and cold pressured to 450 atm. with a mixture of hydrogen and carbon monoxide in the molar ratio of 1:1. The vessel was agitated and maintained at 225°C. for 15 hours, during which time the pressure was maintained at 900 to 1000 atmospheres by repressuring periodically with the same gas mixture. At the completion of the run, the vessel was cooled, vented, its contents discharged, and filtered. The solid product and catalyst were washed with water, and heated
20 in xylene in order to dissolve the solid polymer. The catalyst was separated from the xylene solution of the solid polymer by filtration. After evaporation of the bulk of the xylene, methanol was added to precipitate the solid polymer, which was separated by filtration, washed several times with methanol, and dried. The yield of crude product amounted to 2.1 parts, formed fibers which could be cold drawn, and had an inherent viscosity of 0.89, measured at 0.1% concentration in tetrahydro-naphthalene at 125°C.

EXAMPLE IV

A reaction mixture comprising 87 parts of xylene, 10 parts of 85% phosphoric acid, and 15.4 parts of a nickel molybdate-cyclohexane paste containing 5 parts of nickel molybdate, and an initial gas mixture containing 3 moles of carbon monoxide per mole of hydrogen was heated at 225°C. and 900 to 1000 atmospheres pressure, which was maintained over a 15-hour period by repressuring periodically with a mixture of 2 moles of hydrogen per mole of carbon monoxide. By the procedure used in Example III there was obtained 1.3 parts of polymer melting at 129°C. The
10 crude product formed fibers which could be cold drawn.

EXAMPLE V

A reaction mixture comprising 5 parts of nickel molybdate, 1 part of mixed dodecyl acid phosphates, 17 parts of xylene, and a gas mixture of 2 moles of hydrogen per mole of carbon monoxide was heated at 175°C. and 2800 to 3000 atmospheres pressure for 3 hours. The reaction mixture was filtered to remove catalyst and polymer. The polymer was separated from the catalyst by extraction with boiling heptane, followed by extraction with boiling xylene. Addition of the xylene extract to methanol produced 0.6 part of fiber-forming
20 polymer having an inherent viscosity of 0.85, measured at 0.1% concentration in tetrahydronaphthalene at 125°C.

EXAMPLE VI

A reaction mixture comprising 50 parts of distilled water, 1.75 parts of 85% phosphoric acid, 20 parts of nickel molybdate catalyst, and a mixture of hydrogen and carbon monoxide in the molar ratio of 2:1 was heated at 175°C. and 800 to 1000 atmospheres pressure, which was maintained over a

15-hour period by repressuring periodically with the same gas mixture. The reaction mixture was filtered to remove catalyst and polymer and the latter was dried. Extraction of the dry solid with boiling benzene and addition of the hot benzene extract to methanol produced 0.92 part of solid polymer. A further extraction in the same manner with boiling xylene produced 8.0 parts of solid polymer having a relative viscosity of 1.079 and an inherent viscosity of 0.76, measured at 0.1% concentration in tetrahydronaphthalene at 125°C.

EXAMPLE VII

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A silver lined continuous contact catalytic converter containing 53 parts of 8 to 14 mesh nickel molybdate, which had been treated at room temperature with a 5% aqueous solution of phosphoric acid, was filled with decahydronaphthalene and heated to 185°C. The pressure was raised to 800 atm. by injection of decahydronaphthalene. A stream of decahydronaphthalene and a stream of mixed gas composed of 1.6 moles of hydrogen per mole of carbon monoxide were injected separately into a mixing block and fed as a single stream upward through the converter at a total pressure of 800 atm. The liquid was injected at a space velocity of 1.13 parts of liquid per part catalyst per hour and the gas was injected at a space velocity of 0.21 part of gas per part of catalyst per hour. The operating pressure was maintained at 800 atm. by regulating the rate of gas bleed-off. The reaction product, obtained by bleed-off at 4 hour intervals, was filtered and dried. The yield of essentially hydrocarbon polymer amounted to 0.44 part per hour of which 0.29 part was insoluble in boiling benzene, had an inherent viscosity of 0.90 measured at 0.1 concentration in tetrahydronaphthalene at 125°C. and a melting point of 132°C.

20

Without changing the other conditions the gas injection rate was increased to a space velocity of 0.312 part of gas per part of catalyst per hour. The yield of essentially hydrocarbon polymer under these conditions amounted to 0.60 part per hour, of which 0.38 part was insoluble in benzene, had an inherent viscosity of 0.93, measured at 0.1% concentration in tetrahydronaphthalene at 125°C., and a microscopic melting point of 131.6°C.

Without changing the other conditions the gas injection rate was again increased to a space velocity of 0.42 part of gas per part of catalyst per hour. The yield of essentially hydrocarbon polymer under these conditions amounted to 0.71 part per hour, of which 0.58 part was insoluble in boiling benzene, had an inherent viscosity of 0.93, measured at 0.1% concentration in tetrahydronaphthalene at 125°C., and a microscopic melting point of 131.8°C.

EXAMPLE VIII

A reaction mixture comprising 87 parts of xylene, 5 parts of mixed dodecyl acid phosphates, 5 parts of a chromium promoted nickel molybdate catalyst, prepared using a procedure similar to that described in Example XI for the preparation of a cadmium promoted nickel molybdate, and a gas mixture of 2 moles of hydrogen per mole of carbon monoxide was heated at 225°C. and 900 to 1000 atmospheres pressure, which was maintained over a 15-hour period by repressuring periodically with the same gas mixture. By the procedure used in Example III there was obtained 2.45 parts of polymer. The polymer, without fractionation, had an inherent viscosity of 0.75 measured at 0.1% concentration in tetrahydronaphthalene at 125°C.

EXAMPLE IX

A reaction mixture comprising 50 parts of distilled water, 5 parts of 85% phosphoric acid, 5 parts of nickel molybdate, and a mixture of hydrogen and carbon monoxide in the molar ratio of 1:1 was heated at 200°C. and 900 to 1000 atmospheres pressure, which was maintained over a 15-hour period by repressuring periodically with the same gas mixture. By the procedure described in Example III, there was obtained 2.5 parts of fiber-forming polymer which had an inherent viscosity of 0.85, measured at 0.1% concentration in tetrahydronaphthalene at 125°C.

10

EXAMPLE X

A silver-lined pressure vessel was charged with 5 parts of nickel molybdate, 87 parts of xylene, 5 parts of mixed dodecyl acid phosphates, and a gas mixture of 2 moles of hydrogen per mole of carbon monoxide, and the mixture heated at 225°C. and 450 to 550 atmospheres for 15 hours, during which time the pressure was maintained at 450 to 550 atmospheres by repressuring periodically with the same gas mixture. By the procedure used in Example III, there was obtained 0.9 part of solid polymer, which formed fibers which could be cold drawn, and which had an inherent viscosity of 0.74, measured at 0.1% concentration in tetrahydronaphthalene at 125°C.

20

A preparation of nickel molybdate, usefully employable as a catalyst in the practice of this invention is the following:

Seventeen hundred sixty-six parts of ammonium paramolybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$, equivalent to 10 moles of MoO_3 , was dissolved in 5000 parts of distilled water and neutralized

by the addition of 810 parts of 28% aqueous ammonia. The resulting solution of ammonium molybdate $[(\text{NH}_4)_2\text{MoO}_4]$ containing 1.9 moles excess ammonia was added with stirring, at room temperature, to a solution of nickel nitrate, prepared by dissolving 2908 parts of nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, equivalent to 10 moles of nickel salt, in 5000 parts of distilled water. A pale green precipitate was formed in an acid slurry having a pH of approximately 4.0. The pH of the slurry was adjusted to 7.0 (Beckmann pH meter) by the addition of 450 parts of 28% aqueous ammonia. The precipitate was then washed, filtered, dried, and calcined at 400°C. for 18 hours. The calcined product, by analysis, was found to contain 23.2% nickel and 46.4% molybdenum.

The calcined product, prepared as described above, was reduced in hydrogen at gradually increasing temperatures from room temperature up to 550°C. for a total of 25 hours, of which period 18 hours was at 550°C. The reduced product was highly pyrophoric and glowed on exposure to air. Analysis of the reduced material showed it to contain 26.66% nickel and 53.1% molybdenum corresponding to $\text{NiMoO}_2/0.2\text{MoO}_3$.

Another preparation which gives nickel molybdate in a very active catalytic form is the following:

Eight hundred eighty-three parts of ammonium paramolybdate and 2500 parts of water were stirred together at room temperature and converted to a clear solution containing 5 moles (26% solution) of normal ammonium molybdate $[(\text{NH}_4)_2\text{MoO}_4]$ at pH 8.0 by adding 379 parts of 28% aqueous ammonia. In another solution, 1454 parts of nickel nitrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, equivalent to 5 moles of nickel, was dissolved in 2500 parts of water and adjusted to a pH of 6.5 by adding 271 parts of 28% aqueous ammonia. The nickel nitrate solution was then added to the ammonium molybdate

solution at room temperature (27-28°C.) with stirring, at the
 rate of approximately 1500 parts/hour. A yellow-green precipitate
 was thus formed in an aqueous medium at pH 7.9 to 6.9. The
 precipitate so formed was filtered and dried without washing
 at 110°C. to 120°C. for 18-20 hours and connected to 8/14 mesh
 granules by pelleting, crushing the pellets, and screening
 the crushed pellets to size. The granular product so obtained
 was found to contain by analysis, 19.8% Ni; 35.7% Mo; and
 7.9% of NH_3 , corresponding to a mole ratio of 1.0 Ni/1.1 Mo/
 10 1.4 NH_3 , and had a surface area of 4 M^2/g .

One hundred eighty parts (200 cc.) of the granular
 (8/14 mesh) product was reduced in hydrogen at a space velocity
 of 1000/hr. at ⁻¹ gradually increasing temperatures from room
 temperature to 400°C. for a total of 26 hours, of which period
 22 hours was at 400°C. The reduced product was then cooled to
 room temperature in hydrogen, flushed at room temperature with
 oxygen-free nitrogen, and discharged under nitrogen to a receiver
 and sealed under nitrogen.

The catalyst so prepared was highly pyrophoric and
 20 glowed on exposure to air. Analysis of the reduced catalyst
 showed it to contain 29.22% nickel and 53.50% molybdenum,
 corresponding to a nickel/molybdenum ratio of 1.0/1.12.

EXAMPLE XI

A reaction mixture comprising 87 parts of xylene,
 5 parts of 85% phosphoric acid, 5 parts of a cadmium promoted
 nickel molybdate catalyst containing 90 mole percent of nickel
 molybdate and 10 mole percent of cadmium molybdate, prepared
 as described below, and a gas mixture of 2 moles of hydrogen
 per mole of carbon monoxide was heated at 225°C. and 900 to
 1000 atmospheres pressure, which was maintained over a 15-hour
 30 period by repressuring periodically with the same gas mixture.

By the procedure used in Example III, there was obtained 1.5 parts of solid polymer which formed fibers which could be cold drawn.

The cadmium modified nickel molybdate catalyst, used in the above example, was prepared as follows:

Eight hundred eighty-three parts of ammonium paramolybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$, equivalent to 5 moles of MoO_3 was dissolved in 2500 parts of distilled water and neutralized by the addition of 405 parts of 28% aqueous ammonia. The resulting solution of ammonium molybdate $[(\text{NH}_4)_2\text{MoO}_4]$, containing 0.95 mole excess ammonia, was added with stirring at room temperature to a solution prepared by dissolving 1310 parts of nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}]$, equivalent to 4.5 moles of nickel, and 155 parts of cadmium nitrate tetrahydrate $[\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}]$, equivalent to 0.5 mole of cadmium, in 2500 parts of water. A pale blue-green precipitate was formed in an acid slurry having a pH of approximately 6.4. The pH of the slurry was adjusted to 7.0 (Beckmann pH meter) by the addition of 189 parts of 28% aqueous ammonia. The precipitate was then washed, filtered, dried and calcined at 400°C . for 24 hours. The calcined product by analysis was found to contain 20.15% nickel, 5.94% cadmium, and 42.8% molybdenum.

The calcined product, prepared as described above, was reduced in a 3:1 mixture of nitrogen and hydrogen at gradually increasing temperatures from room temperature up to 450°C . for a total of 28 hours, of which period 23.5 hours was at 450°C . During reduction at 450°C . cadmium metal was formed and volatilized out of the reduction zone and deposited as a metallic mirror in the cold exit end of the reduction tube. The reduced catalyst was then cooled to room temperature in nitrogen, discharged,

and sealed under nitrogen. The reduced product was pyrophoric and glowed on exposure to air. Analysis of the reduced material showed it to contain 25.4% nickel, 3.6% cadmium, and 53.3% molybdenum.

EXAMPLE XII

A mixture of 20 parts of nickel molybdate, 50 parts of 85% phosphoric acid, and 370 parts of water was heated for one hour under reflux. The resulting mixture was washed thoroughly with water and used, wet, in the following hydrogenation.

10 A reaction mixture containing 85 parts of xylene and the nickel molybdate catalyst treated as described above was heated at 175°C. for a 15-hour period at 900 to 1000 atm. pressure of hydrogen and carbon monoxide in the mole ratio of 2:1, as described in Example I. There was isolated from the reaction mixture 8 parts of essentially hydrocarbon polymer, of which 6 parts had an inherent viscosity of 0.74, measured at 0.10% concentration in tetrahydronaphthalene at 125°C.

EXAMPLE XIII

20 Example I was repeated, except that the reaction mixture consisted of 10 parts of nickel molybdate catalyst and 90 parts of cyclohexane, together with hydrogen and carbon monoxide. The yield of essentially hydrocarbon polymer amounted to 3 parts, of which 2 parts were insoluble in boiling benzene and had an inherent viscosity of 0.86, measured at 0.1% concentration in tetrahydronaphthalene at 125°C.

EXAMPLE XIV

Example XIII was repeated, except that the catalyst consisted of 20 parts of cobalt molybdate and the reaction temperature was 225°C. The yield of the essentially hydrocarbon

polymer was 4 parts, of which 3 parts were insoluble in boiling benzene and was orientable.

The examples have illustrated certain conditions of temperature, pressure, catalyst concentration, carbon monoxide/hydrogen mixed gas composition, etc. It is to be understood that these are interdependent variables and that variation in one requires compensating adjustments in the others.

The process by which the essentially hydrocarbon polymers of this invention are obtained can be operated as a batch, or as a semi-continuous or continuous 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:

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

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 from 3:1 to 1:2 are used because gas mixtures in this range of compositions give optimum results from the standpoint of yield of desired high molecular weight hydrocarbons.

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 essentially hydrocarbon polymers are obtained in the range 150° to 250°C., this range embraces the preferred operating temperature conditions.

The process is generally operated under a total pressure of at least 200 atmospheres. Because better yields of desired high molecular weight essentially hydrocarbon polymers, with maximum utilization of the carbon monoxide and hydrogen, are achieved using pressures in excess of 500 atmospheres, the use of such pressures is economical and embraces a preferred
10 aspect of operation. The upper limit of pressure is not critical and the maximum is determined by the mechanical restrictions of the equipment used. Since the use of pressures in excess of 5000 atmospheres does not lead to any compensating advantages from the standpoint of yield of desired high molecular weight, essentially hydrocarbon polymers, or economy of operation, it represents the practical upper limit of pressure.

Because the reaction is highly exothermic, it is preferred to operate in the presence of a reaction medium, which besides aiding in the dissipation of the heat of reaction also
20 functions to bring about better catalyst contact and hence improves the efficiency of the process. Suitable media are water, aromatic and aliphatic hydrocarbons, alcohols and the like. When the hydrogenation is carried out in an aqueous medium, it is advantageous, but not necessary, from the standpoint of molecular weight of essentially hydrocarbon polymer obtained, to operate in the presence of an acid, such as sulfuric acid or other mineral acid. When the hydrogenation is carried out in the presence of organic media such as toluene, xylene, etc., satisfactory results are obtained in the presence or
30 absence of added acids or alkyl acid phosphates, such as mono-

and didodecyl acid phosphates, etc. Instead of adding acid to the reaction medium, the catalysts can be pretreated with an acid before use in the hydrogenation reaction.

The process can also be carried out in the presence of basic materials, such as the alkali metal hydroxides and carbonates, etc.

The reaction medium can occupy up to 60% or as little as 5% of the reactor volume. Generally, however, in batch operation 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 essentially hydrocarbon polymers as being of suitable quality for superior films and fibers. Melting point can be reduced by the presence of small amounts of low molecular weight material without seriously affecting other properties, which render it highly useful for film and fiber uses, provided the inherent viscosity is sufficiently high. Thus, if the inherent viscosity of the polymer is at least 0.74, then the melting point can fall below 130°C. without sacrifice in the usefulness of the polymers for high quality films and fibers. The preferred essentially hydrocarbon polymers, because of their outstanding usefulness for superior films and fibers, are those having inherent viscosities of at least 1.0 and melting above 130°C.

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

[By "orientable" as this expression is used herein is meant that orientation is observed when a fiber or film

prepared from the polymer is subjected to cold-drawing.

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 suitable reaction periods are from 5 to 20 hours.

10 [The metal molybdates used in the process of this invention can contain promoters or modifiers such as cadmium barium, chromium, thorium, cobalt, zinc, copper, etc., if desired. Preferred molybdates, because of their high degree of activity and selectivity, are the molybdates of nickel, cobalt, and copper. These molybdates can be employed in the form of pellets or as finely divided powders, and they can be used as such or extended on inert supports such as charcoal, alumina, silica, etc. The particular physical form of the catalyst for maximum activity depends upon the condition under which the hydrogenation reaction is to be effected. Thus, for continuous operation, it is best to have the catalyst in the form of pellets, thus minimizing mechanical losses. If the process is to be operated as a batch operation, the physical form of the catalyst is less important, and either granular or
20 finely divided catalysts are suitable.

The amount of catalyst used depends upon such interdependent variables as temperature, pressure, general method of operation, catalyst activity, etc. As a rule, in batch operation the amount of catalyst employed will be between 1.5% and 30% and preferably between 2.5% and 20% by weight of the reaction medium employed.

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 usually at least ten times the catalyst weight.

When the activity of the catalyst decreases or disappears through prolonged use, it may be restored by oxidizing the spent molybdate in air or oxygen at temperatures up to 500°C. and then reducing the resulting molybdate back to molybdate.

10 The surface of the reactor in contact with the reactants appears to be an important factor in determining the molecular weight and yield of essentially hydrocarbon polymer obtained. Satisfactory results are obtained using silver-lined, copper-lined, or stainless steel equipment.

20 The process of this invention, for the first time, makes it possible to convert carbon monoxide into products which are essentially all high molecular weight. These products, without purification, have molecular weights of at least 12,000, inherent viscosities greater than 0.74 and are convertible into fibers and films having strength and tenacity characteristics unobserved in any hitherto available synthetic hydrocarbon polymer films and fibers.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

CLAIMS:

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The orientable hydrocarbon polymer which is the reaction product of carbon monoxide and hydrogen, said hydrocarbon polymer having an inherent viscosity of at least 0.74, measured at 0.1% concentration in tetrahydronaphthalene at 125°C., and being capable of forming films which show orientation when cold drawn.
2. The orientable hydrocarbon polymer which is the reaction product of carbon monoxide and hydrogen, said hydrocarbon polymer having an inherent viscosity of at least 0.74, measured at 0.1% concentration in tetrahydronaphthalene at 125°C., melting above 130°C., and being capable of forming films which show orientation when cold drawn.
3. The orientable hydrocarbon polymer which is the reaction product of carbon monoxide and hydrogen, said hydrocarbon polymer having an inherent viscosity of at least 1.0, measured at 0.1% concentration in tetrahydronaphthalene at 125°C., melting above 130°C., and being capable of forming films having a stiffness modulus greater than 150,000 lb./sq.in. and a microtensile breaking strength above 100,000 lb./sq.in., based on the relaxed drawn dimensions of the film.
4. A process for preparing hydrocarbon polymers which comprises reacting carbon monoxide with hydrogen under pressure in the presence of a molybdate of a metal whose ions are soluble in aqueous ammonia in amount greater than that stoichiometrically required to precipitate the metal ion, said metal molybdate being a metal salt of an acid having one of the formulas corresponding to H_2MoO_3 and H_2MoO_4 .

5. A process for preparing orientable hydrocarbon polymers which comprises reacting carbon monoxide with hydrogen at a temperature of 150° to 250°C. under a pressure in excess of 500 atmospheres, and in the presence of a molybdate of a metal whose ions are soluble in aqueous ammonia in amount greater than that stoichiometrically required to precipitate the metal ion, said metal molybdate being a metal salt of an acid having one of the formulas corresponding to H_2MoO_3 and H_2MoO_2 .

6. A process for preparing orientable hydrocarbon polymers which comprises reacting carbon monoxide with hydrogen under pressure in the presence of a nickel molybdate having the formula $NiMoO_2$.

7. A process for preparing orientable hydrocarbon polymers which comprises reacting carbon monoxide with hydrogen at a temperature of 150° to 250°C. under a pressure in excess of 500 atmospheres, and in the presence of a nickel molybdate having the formula $NiMoO_2$.

8. A process for preparing orientable hydrocarbon polymers which comprises reacting carbon monoxide with hydrogen under pressure in the presence of a cobalt molybdate having the formula $CoMoO_3$.

9. A process for preparing orientable hydrocarbon polymers which comprises reacting carbon monoxide with hydrogen at a temperature of 150° to 250°C. under a pressure in excess of 500 atmospheres, and in the presence of a cobalt molybdate having the formula $CoMoO_3$.