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OIL-SOLUBLE HIGH-MOLECULAR WEIGHT
COMPOUNDS AND PROCESS FOR THEIR
PREPARATION

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This invention relates to valuable high-molecular weight polar organic compounds which are soluble in hydrocarbon mixtures such as the mineral oils, and it also relates to a practical and economical process for the production of such high-molecular weight oil-soluble organic compounds which comprises condensing an olefine with a substituted polyolefinic compound of polar character.

An object of the invention is to provide a process for the production of synthetic polar organic compounds of high-molecular weight, which are characterized by being soluble in the higher hydrocarbons and mixtures of the higher hydrocarbons, from unsaturated hydrocarbons and substituted unsaturated hydrocarbons derived from petroleum, petroleum products and other carbonaceous materials.

The products obtained in accordance with the process of the invention are adapted to many commercial uses. They are stable polar organic compounds, which, in general, have a molecular weight greater than about 1500, and which are soluble in hydrocarbon oils. They are particularly useful as agents which may be added to the higher hydrocarbon mixtures, such as the mineral lubricating oils, to improve the general quality and particular characteristics of such oils. For example, the products when added to lubricating oils in effective amount increase the viscosity and the viscosity index of said oils. Many of the products, particularly those which possess one or more carboxy groups in their molecules, increase the lubricating qualities of lubricating oils and greases by increasing their oiliness. In general, the high-molecular weight compounds prepared by the process of the invention increase the stability of lubricating oils and greases to which they are added. Thus, many of them, particularly those containing halogen atoms, sulphur atoms, selenium atoms, tellurium atoms and the like, when added to lubricating oils and greases render them more suitable for use as lubricants under extreme conditions of temperature and pressure. Many of the compounds act as antioxidants and inhibit the auto-oxidation of hydrocarbon mixtures to which they are added. Other uses of the high-molecular weight organic compounds of the invention will be apparent to those skilled in the art.

In executing the process of the invention, any olefine or mixture of olefines may be condensed with one or a plurality of species of polyolefinic hydrocarbons, one or more hydrogen atoms of which have been replaced by a polar group of

either electropositive or electronegative character. The condensation reaction, which is one which does not involve to any substantial extent the polar group or groups of the polyolefinic compound, but which involves linkage of carbon atoms of the olefine with carbon atoms of the substituted polyolefine to form products containing long hydrocarbon chains and containing the original polar groups of the substituted polyolefines involved, is preferably effected in the presence of a condensation or polymerization agent or catalyst at a temperature and pressure at which the condensation reaction proceeds at a practical rate.

The following are representative olefines: ethylene, propylene, alpha-butylene, beta-butylene, isobutylene, the secondary base and tertiary base amylenes, the hexylenes, the heptylenes, the octylenes, the nonylenes and the like and their higher homologues and suitable substitution products, which compounds are hydrocarbons of the general formula C_nH_{2n} . Thus it is seen that the olefine co-polymers as dipropylene, di-beta butylene, diisobutylene, trisobutylene, the diamylenes, the dihexylenes and the like, as well as the olefine inter-polymerization products obtainable by polymerization of an olefine with a dissimilar olefine, are within the scope of the invention. In general, the lower olefines, especially those containing an unsaturated tertiary carbon atom, are more reactive than the higher olefines of secondary character and are preferably employed in the execution of the process of the invention. The tertiary base olefines as isobutylene, the tertiary amylenes, the tertiary hexylenes, the tertiary heptylenes and the tertiary octylenes are members of this preferred subgroup of olefines.

Olefines from any convenient source may be used. Relatively pure olefines or mixtures comprising a plurality of olefines may be employed. Hydrocarbon mixtures containing saturated and/or aromatic hydrocarbons and one or a plurality of olefines, as well as small amounts of other unsaturated hydrocarbons, are useful starting materials. Such hydrocarbon mixtures are obtainable by the pyrogenesis or cracking of petroleum oils, shale oils, petroleum products, etc., and by the destructive distillation of coal, peat, pitches, waxes, asphalts, animal oils, vegetable oils and the like carbonaceous material. Cracked petroleum distillates, or special fractions of cracked petroleum distillates, are particularly suitable for our purpose. Certain fractions of petroleum and other hydrocarbon distillates may

be used per se or mixed in varying proportions depending upon their composition and the desired composition of the mixture to be treated, or varying proportions of relatively pure olefines may be mixed with such hydrocarbon fractions to provide starting materials of the desired composition.

The olefine-containing hydrocarbon mixtures may, prior to their use, be fractionated into fractions which contain, for the most part, hydrocarbons containing the same number of carbon atoms to the molecule. Typical fractions of this sort are the ethane-ethylene fraction, the propane-propylene fraction, the butane-butylene fraction and the like. If desired, the olefines or a particular olefine may be previously recovered from such a fraction by fractionation, extraction and the like means.

In accordance with the invention, the olefine or mixture of olefines is reacted with one or a plurality of polyolefinic compounds of polar character. The polyolefinic compounds are characterized by the possession in their structure of at least two olefinic linkages, each olefinic linkage being between two carbon atoms of aliphatic character, and by the possession of at least one polar radical or polar group linked to a carbon atom of the compound. The olefine linkages in the polyolefinic compound may be conjugated, or they may be separated by one or more directly linked saturated carbon atoms. The olefinic linkages as well as the polar radical or radicals may be embraced in a straight or branched chain which may or may not be linked to a cyclic radical, or the polyolefinic substituted hydrocarbon chain may comprise a cyclic compound of aliphatic character.

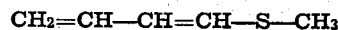
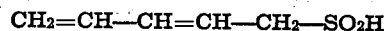
The polyolefinic polar compounds may for convenience be regarded as polyolefinic hydrocarbons, one or more hydrogen atoms of which have been replaced by either an electropositive or electronegative monovalent or polyvalent radical of inorganic or organic character. The following are representative electronegative and electropositive polar radicals, one or more of which is present in a suitable polyolefinic compound: the radicals of the metals as the alkali metals, the alkaline earth metals, copper, silver, zinc, cadmium, mercury, tin, thallium, lead, arsenic, etc., the nitrogen-containing radicals as —NH_4 , —NH_2 , —NH— , —NO_2 , —CN , —SCN and the like, the halogen radicals as —F , —Cl , —Br and —I , the sulphur-containing radicals as —S— , —SH , —SO_2 , —SO_3 , $\text{—SO}_3\text{H}$, —SO_4 , $\text{—SO}_2\text{H}$, —S_2 , —SC— , —OS— and the like, the oxygen-containing radicals as —OH , —COOH , —COO— , —CO— , —CHO , —O— , $\text{CH}_3\text{O—}$, and the like, and the radicals as —Se— , —SeH , —Te— , —NP— , =PO_3 , $\text{—PO}_3\text{H}_2$, $\text{—PO}_4\text{H}_2$, —SeO_2 , $\text{—SeO}_3\text{H}$, —BO— , =BO_3 , $\text{—BO}_3\text{H}_2$, —BaO_7 , —SiH_3 , —SnH_3 , —As_2 and the like. A preferred group of substituted polyolefinic hydrocarbons comprises those containing at least one of the polar radicals: —F , —Cl , —Br , —I , —NH_2 , —S— , —NO_2 , —COOH and —OH .

Suitable representative polyolefinic compounds containing one or more halogen atoms are: chloro-1-butadiene-(1,3), chloro-2-butadiene-(1,3), dichloro-1,4-butadiene-(1,3), bromo-1-butadiene-(1,3), bromo-2-butadiene-(1,3), methyl-2, chloro-1-butadiene-(1,3), chloromethyl-2-butadiene-(1,3), dichloromethyl-2-butadiene-(1,3), bromomethyl-2-butadiene-(1,3), chloromethyl-1-butadiene-(1,3), methyl-1, chloro-1-

butadiene-(1,3), methyl-1, chloro-2-butadiene-(1,3), chloroethyl-1, chloro-2-butadiene-(1,3), and the mono- and poly-chlorinated and -brominated derivatives of the straight chain, branched chain and cyclic pentadienes, hexadienes, heptadienes and the like and their homologues and substitution products. Monohalogenated and polyhalogenated polyolefinic compounds wherein the double bonds are not conjugated are also suitable. Such compounds are the halogenated pentadiene-(1,4), diallyl, allylpropenyl, dipropenyl, heptadiene-(1,6), di-crotyl, diisobutenyl and the like and their homologues, analogues and substitution products.

Suitable representative polyolefinic compounds containing a polar radical comprising a nitrogen atom are the following: amino-4-butadiene-(1,3), 2-methyl, amino-4-butadiene-(1,3), amino-5-pentadiene-(1,3), amino-3-hexadiene-(1,5), methylamino-5-pentadiene-(1,3), diamino-3,4-dimethyl-2,5-hexadiene-(1,5), nitro-4-butadiene-(1,3), nitro-5-pentadiene-(1,3) nitrile-1-hexadiene-(2,4), sorbic acid amide, and the like and their homologues, analogues and substitution products.

Suitable representative polyolefinic compounds containing the radical —S— or a polar radical comprising a sulphur atom are the following:



and the like and their homologues, analogues and substitution products.

Suitable representative polyolefinic compounds containing an —O— , —OH or —COOH radical are the following: diallyl carbinol, the alkyl ethers of diallyl carbinol, methyl diallyl carbinol, diallyl ethyl alcohol, ethyl diallyl carbinol, 2,6-dimethyl-heptadiene-(1,6)-ol-4, geraniol, methyl geranyl ether, nerol, linalool, methyl linalyl ether, alpha-methyl geraniol, alpha-ethyl geraniol, beta-vinylacrylic acid, 4-carboxy-pentadiene-(1,3), carboxy-1-hexadiene-(2,4), carboxy-1, chloro-4-hexadiene-(2,4), alpha-methyl sorbic acid, alpha-ethyl sorbic acid, diallyl acetic acid, dimethyl sorbic acid, the acids from Chinese wood oil and the like and their homologues, analogues and substitution products.

The process of the invention is preferably executed in the presence of a condensation or polymerization catalyst or agent. Any condensation agent capable of accelerating the condensation reaction may be used. A wide variety of such catalysts or agents are known to the art. The particular condensation catalyst to be employed will depend upon the particular unsaturated compounds condensed, upon the conditions under which the condensation is to be effected, upon the cost and availability of the particular catalyst, and, to a certain extent upon the choice of the operator.

Acid-acting condensation catalysts are preferably employed. The acid-acting catalysts are those which give an acid reaction in the presence of water. This subgroup of catalysts includes the mineral acids, particularly the strong polybasic mineral oxy-acids, the mineral-acting acids, the acid salts as zinc sulphate, cadmium sulphate,

lead sulphate, bismuth oxy-chloride, copper phosphate, the acid-acting metal halides and the like.

A particularly suitable group of acid-acting condensation catalysts comprises the acid-acting halides of the class consisting of the acid-acting metal halides and the boron halides. A catalyst of this group may consist of or comprise an acid-acting halide of the elements as aluminum, boron, iron, tin, antimony, arsenic, bismuth, molybdenum, tungsten, vanadium, zinc, titanium, thorium, cerium, zirconium and the like. The acid-acting halide catalysts may be used severally or in admixture. Catalysts comprising an acid-acting metal or boron halide in combination as a complex compound with an organic or inorganic compound possessing a dipole moment are advantageously used in the execution of the invention. For example, the acid-acting metal or boron halide may be in combination, to form a complex catalyst, with a hydrogen halide; with a neutral-acting metal halide such as a halide of an alkali metal, alkaline earth metal, silver, nickel, cobalt and the like; or with an organic oxy-compound possessing a dipole moment such as the nitro-paraffins, the nitro-aralkyl compounds, the nitro-alicyclic compounds, the ketones of aliphatic, aralkyl, aromatic or mixed character, the aliphatic, aralkyl and aromatic acid halides, the organic sulphones and other organic compounds which possess a dipole moment and are capable of combining with an acid-acting metal or boron halide to form a complex catalyst.

A preferred subgroup of acid-acting condensation catalysts containing an aluminum halide embraces the following: AlF_3 , AlCl_3 , AlBr_3 , $\text{AlCl}_3\text{-NaCl}$, $\text{AlCl}_3\text{-BaCl}_2$, $\text{AlBr}_3\text{-KCl}$, $\text{AlCl}_3\text{-AgCl}$, $\text{AlF}_3\text{-NaCl}$, $\text{AlBr}_3\text{-AgBr}$, $\text{AlBr}_3\text{-BaCl}_2$, $\text{AlCl}_3\text{-nitromethane}$, $\text{AlCl}_3\text{-nitrobenzene}$, $\text{AlCl}_3\text{-nitrobenzen-NaCl}$, $\text{AlCl}_3\text{-acetone}$, $\text{AlCl}_3\text{-acetophenone}$, $\text{AlCl}_3\text{-benzophenone}$, $\text{AlCl}_3\text{-benzoyl chloride}$, $\text{AlCl}_3\text{-diphenyl sulphone}$, $\text{AlCl}_3\text{-dibenzyl sulphone}$ and the like.

A preferred subgroup of acid-acting condensation catalysts containing a boron halide embraces the following: BF_3 , BCl_3 , BEr_3 , $\text{BF}_3\text{-NaCl}$, $\text{BCl}_3\text{-NaCl}$, $\text{BF}_3\text{-AgF}$, $\text{BF}_3\text{-BaCl}_2$, $\text{BF}_3\text{-nitromethane}$, $\text{BF}_3\text{-nitrobenzene}$, $\text{BF}_3\text{-acetone}$, $\text{BF}_3\text{-benzoyl chloride}$, $\text{BF}_3\text{-dibenzyl sulphone}$ and the like.

In addition to the above-mentioned catalysts, many other condensation catalysts as benzoyl peroxide, etc., are suitable. In some instances, the absorptive materials as silica gel, alumina, activated charcoal, Fuller's earth, kieselguhr, Death Valley clay, bentonite, activated aluminum hydrosilicate and similar partially hydrated silicates and silicic acid compounds are suitable condensation catalysts. The absorptive materials may be used in admixture with the other condensation catalysts or the other catalysts, such as the acid-acting metal halides, may be precipitated on or otherwise deposited on the surface of the absorptive material.

As an example of a suitable mode of executing the process of the invention, the following procedure may be followed: The materials to be condensed are charged, separately or in admixture, to a suitable reaction vessel. The mixture to be treated in the reaction vessel may comprise one species of olefine and one species of a polyolefinic organic compound containing a polar radical, or it may comprise a plurality of different olefines and one or a plurality of different polyolefinic polar compounds. In the latter case, a mixture of condensation products may be obtained.

A preferably employed reactor comprises a re-

action kettle of the requisite size, equipped with mechanical stirring means, means for heating and cooling its contents, and suitable inlet and outlet means. The reaction is preferably effected with one or all of the reactants in the liquid phase. The proportion of the olefine to the polyolefinic polar compound in the reaction mixture may vary considerably depending upon the nature of the product desired. Preferably, we employ a considerable molecular excess of the olefine or olefines. The reaction may or may not be effected in the presence of a solvent or diluent. When olefine-containing hydrocarbon fractions as pressure distillates and the like are used as starting materials, the inert hydrocarbons may act as solvents or diluents. A substantially inert solvent such as a saturated hydrocarbon mixture as benzol, gasoline, mixtures of hexanes, etc., may be added to the reaction mixture to give a more freely flowable mixture during the condensation, or to afford better contact of the catalyst and reactants. The solvent or diluent used should be substantially inert under the conditions of the polymerization.

The condensation catalyst may be added to the reaction mixture in any convenient manner as a solid, as a fluid, or suspended or dissolved in a suitable medium or solvent therefor. The catalyst may be added to the reaction mixture all at once, or it may be added slowly in a continuous or intermittent manner until the required amount has been added. By a suitable regulation of the rate of admittance of the catalyst, the temperature of the reaction mixture may be more effectively maintained within the desired temperature range. The amount of the catalyst to be used in each particular case will depend upon the particular catalyst, the materials to be condensed, the conditions of the condensation reaction, etc.

The process may be executed at any suitable temperature. Generally, the temperature is adjusted with respect to the activity of the catalyst selected so that the desired polymerization is effected at a practical rate. The optimum temperature will depend upon the nature of the reactants. For example, the tertiary olefines may be advantageously condensed with halogenated diolefines, as chloroprene, at temperatures of -80°C . and lower. The reaction may be effected at atmospheric, subatmospheric or superatmospheric pressure. The condensation is conveniently effected under superatmospheric pressure when relatively high reaction temperatures are employed.

When the condensation reaction whereby the valuable high-molecular weight polar compounds are formed has proceeded to substantial completion or to the desired extent, the operation is terminated and the product or products recovered in any suitable manner.

The following specific example illustrates a suitable mode of executing the process of the invention to obtain a valuable oil-soluble polar organic compound of high-molecular weight. It is to be understood that the invention is not to be regarded as limited to the specific reactants, catalyst, or mode of operation disclosed in the example:

Example

About 22.5 parts by weight of isobutene were charged to a suitable reaction vessel equipped with means for cooling its contents to a low temperature, and with means for mechanically stirring its contents, and about 2.5 parts by weight

of chloroprene (chloro-2-butadiene-1,3) were added thereto. The mixture was stirred and cooled to a temperature of about -80°C . while boron fluoride was added slowly until the required amount sufficient to effect the polymerization had been added. When all of the catalyst had been added, the stirring was continued until the reaction was substantially complete.

The product was a high-molecular weight polychlorinated compound which was soluble in most hydrocarbon oils. The product, when added in an amount of about 4.4% by weight to a turbine oil, raised the viscosity index of the oil from 26 to about 111.

While we have described our invention in a detailed manner and illustrated suitable modes of executing the same, it is to be understood that modifications may be made and that no limitations other than those imposed by the scope of the appended claims are intended.

We claim as our invention:

1. A process for the production of valuable high-molecular weight polar compounds soluble in hydrocarbon oils which comprises condensing an unsaturated hydrocarbon of the general formula C_nH_{2n} with a polyolefinic organic compound containing at least one polar radical in its molecule.

2. A process for the production of valuable high-molecular weight polar compounds soluble in hydrocarbon oils which comprises condensing an unsaturated hydrocarbon of the general formula C_nH_{2n} with a polyolefinic organic compound containing at least one polar radical in its molecule in the presence of a condensation catalyst.

3. A process for the production of valuable high-molecular weight polar compounds soluble in hydrocarbon oils which comprises condensing an unsaturated hydrocarbon of the general formula C_nH_{2n} with a polyolefinic organic compound containing at least one polar radical in its molecule in the presence of a condensation catalyst containing an acid-acting halide of the class consisting of the acid-acting metal halides and the boron halides.

4. A process for the production of valuable high-molecular weight polar compounds soluble in hydrocarbon oils which comprises condensing an unsaturated hydrocarbon of the general formula C_nH_{2n} with a polyolefinic compound containing at least one sulphur atom in the presence of a condensation catalyst containing an acid-acting halide of the class consisting of the acid-acting metal halides and the boron halides.

5. A process for the production of valuable high-molecular weight polar compounds soluble in hydrocarbon oils which comprises condensing an unsaturated hydrocarbon of the general formula C_nH_{2n} with a polyolefinic organic compound containing at least one halogen atom in its molecule in the presence of a condensation catalyst.

6. A process for the production of valuable high-molecular weight polar compounds soluble in hydrocarbon oils which comprises condensing an unsaturated hydrocarbon of the general formula C_nH_{2n} with a chlorinated conjugated double bond diolefin in the presence of a condensation catalyst containing an acid-acting halide of the class consisting of the acid-acting metal halides and the boron halides.

7. A process for the production of valuable high-molecular weight polar compounds which comprises condensing tertiary base olefine of the

general formula C_nH_{2n} with a chlorinated conjugated double bond diolefin in the presence of a condensation catalyst containing a boron halide.

8. A process for the production of valuable high-molecular weight polar compounds which comprises condensing a substantial molecular excess of isobutene with chloroprene at a temperature of about -80°C . in the presence of boron fluoride.

9. A process for the production of valuable high-molecular weight polar compounds which comprises condensing an unsaturated hydrocarbon of the general formula C_nH_{2n} with a polyolefinic compound containing at least one carboxy group in its molecule in the presence of a condensation catalyst containing an acid-acting halide of the class consisting of the acid-acting metal halides and the boron halides.

10. As a composition of matter: the high-molecular weight condensation product of an unsaturated hydrocarbon of the general formula C_nH_{2n} with a polyolefinic organic compound containing at least one polar radical per molecule, the product being of polar character and substantially soluble in hydrocarbon oils.

11. As a composition of matter: the high-molecular weight condensation product obtained by condensing an unsaturated hydrocarbon of the general formula C_nH_{2n} with a halogenated polyolefinic organic compound in the presence of a condensation catalyst containing an acid-acting halide of the class consisting of the acid-acting metal halides and the boron halides, the product being of polar character and substantially soluble in hydrocarbon oils.

12. As a composition of matter: the high-molecular weight condensation product obtained by condensing isobutene with chloroprene in the presence of boron fluoride, the product being a polychlorinated compound substantially soluble in hydrocarbon oils.

13. As a composition of matter: the high-molecular weight condensation product obtained by condensing isobutene with a chlorinated diolefin in the presence of boron fluoride, the product being a polychlorinated compound substantially soluble in hydrocarbon oils.

14. As a composition of matter: the high-molecular weight condensation product obtained by condensing isobutene with a chlorinated diolefin in the presence of an acid-acting metal halide, the product being a polychlorinated compound soluble in hydrocarbon oils.

15. As a composition of matter: the high-molecular weight condensation product obtained by condensing a tertiary olefine containing from four to eight carbon atoms with a halogenated diolefin in the presence of boron fluoride, the product being a polyhalogenated compound soluble in hydrocarbon oils.

16. A process for the production of valuable high-molecular weight polar compounds which comprises reacting a tertiary olefine containing from four to eight carbon atoms with a chlorinated diolefin in the presence of a boron halide.

17. A process for the production of high-molecular weight polar compounds which comprises reacting an unsaturated hydrocarbon of the general formula C_nH_{2n} with a polyolefinic organic compound containing at least one halogen atom per molecule.

18. A process for the production of higher-molecular weight polar compounds which comprises

reacting an unsaturated tertiary olefin of the general formula C_nH_{2n} with chloroprene.

19. A process for the production of high-molecular weight polar compounds which comprises reacting an unsaturated hydrocarbon of the general formula C_nH_{2n} with a polyolefinic organic compound containing at least one carboxy group per molecule.

20. The high-molecular weight product of the reaction of an unsaturated hydrocarbon of the general formula C_nH_{2n} with a diolefinic organic compound containing at least one halogen atom per molecule.

21. The high-molecular weight product of the reaction of a tertiary olefin of the general formula C_nH_{2n} with chloroprene.

22. The high-molecular weight product of the reaction of an unsaturated hydrocarbon of the general formula C_nH_{2n} with a polyolefinic organic compound containing at least one carboxy group per molecule.

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