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TREATMENT OF HYDROCARBONS WITH
RADIOACTIVE MATERIALS

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This invention relates to the production of valuable resinous materials, synthetic resins, film forming materials and plastic materials particularly useful as rubber substitutes. The invention is particularly concerned with a process of polymerization of unsaturated materials.

This invention is also concerned with production of chlorinated materials useful as a substitute for rubber, as resins, in coating compositions, paints and the like. The materials of the present invention are characterized by certain physical characteristics which render them particularly desirable in surface coating compositions, being non-tacky, stable, acid- and alkali-resistant.

The present invention can be practiced on pure unsaturated hydrocarbons available as individual hydrocarbons. I have also successfully practiced the invention on hydrocarbon mixtures which included unsaturated hydrocarbons as olefins as well as other hydrocarbons as paraffins, aromatics and naphthenes although the first two were preponderantly present.

It is in general the broad object of the present invention to provide a novel process for the production of a resinous material particularly a chlorinated material of high stability.

Another object of the present invention is to provide for the production of a stable, non-tacky chlorinated resin.

Another object of the present invention is to provide a process for polymerizing the unsaturated content of a hydrocarbon mixture containing olefins and paraffins and possibly aromatics and naphthenes.

Another object is to provide a process for polymerizing and condensing the unsaturated and the saturated content of a hydrocarbon mixture of which various petroleum oils are typical.

The invention includes other objects and features of advantage, some of which, together with the foregoing, will appear hereinafter wherein I have set forth by way of example and not by way of limitation, the present preferred manner of practicing the process of my invention to produce the desirable chlorinated material of the present invention.

In producing the material of the present invention I have found it desirable to polymerize and condense a mixture of paraffins and olefins, such as can be found in a petroleum oil, by treatment with a radioactive material particularly of the thorium series. In place of thorium as such, radioactive materials, including thorium are useful as auerlite, braggerite, calcio-thorite, cary-

ocerite, erdmannite, erikite, eschynite, eucrasite, euxenite, hydrothorite, kochelite, mackintoshite, maitlandite, monazite sand, naegelite, nicolayite, orangite, pilbarite, steenstrupine, thorianite, thorite, thorogummite, thorotungstite, thucholite, uraninite, urananiobite, yttrialite, yttracrasite, can be employed as can radioactive thorium compounds as a radioactive dioxide. Uranium and radium materials are also useful including amparagabite, autunite, bassetite, becquerelite, betafite, blomstrandine, brannerite, carnabite, clarkite, curite, davidite, dewendite, dumantite, ellsworthite, ferghanite, fergusonite, fourmarierite, gummite, hatchettalite, hielmite, ianthinite, ishikawaite, johannite, kasolite, medjdite, mendelyevite, metatarbermite, metazeunenite, nivenite, parsonsite, phosphuranyle, pilbarite, plumbaniobite, polycrase, priorite, randite, renardite, rutherfordite, samarskite, samiresite, schroeckeringite, sklodowskite, soddyite, torbernite, trogerite, uraconite, uranacanite, uraninite, uranochalcite, uranocercite, uranoniobite, uranophane, uranopillite, uranospathe, uranosphaerite, uranospinite, uranathallite, uvanite, voglite, walpurgite, zeunerite and zippeite.

So far as I am aware I am the first to employ the radioactive properties of these materials; their use is to be distinguished because of dependence on this property in these material which I employ as polymerization and/or condensation and/or hydrogenation and/or dehydrogenation catalysts. Because of the complex nature of the materials and reactions I cannot say at this time what is the exact nature or mechanism of the reactions involved and one or more probably occur concurrently or successively during the period that the hydrocarbon mixture is undergoing treatment or is in contact with or is exposed to action of the catalytic material.

The polymerizing agent becomes inactive, apparently by taking on an acid condition from the oil because I have found that by washing with an alkaline wash the agent is again rendered effective although its life is usually fairly long.

Example 1

One thousand parts of a gulf coast naphthene base oil containing largely only olefins and paraffins were mixed with 30 parts of fuller's earth as a carrier and surface extender for 10 parts of radioactive thorium dioxide. The oil had a viscosity of 100 seconds Saybolt Universal and contained 27.8% of unsaturated hydrocarbons, and had a specific gravity of 28° Baumé. The

mixture was heated to 265° F. for 30 minutes with agitation. Twenty parts of trichloroethylene were added and the mixture agitated for 5 minutes, then filtered. This treatment was given the material to effect olefin polymerization therein. This product contained valuable resinous products, film forming materials and plastics.

The mixture was then chlorinated to effect addition chlorination. Any process can be employed to effect this but I prefer a liquid phase operation. Chlorine was passed through the filtrate until it had increased over 60% in weight and preferably about 65% by weight. In the presence of the trichloroethylene, the chlorine acts as if in the liquid phase, the chlorine being dissolved in the oil miscible trichloroethylene. The mixture was then permitted to stand until a heavy precipitate had separated out as a heavy syrupy mass. This required about 72 hours. The top layer was largely constituted of the liquid saturated hydrocarbon while the bottom layer contained the materials of the present invention.

One portion of the bottom layer was distilled in vacuum and a tough rubbery mass of specific gravity 1.5 and of a light amber color was obtained. This mass was a combination of about 94.5% of a rubbery hydrocarbon mixed with oils and resins to make up the remainder, the mixture containing a trace of thorium dioxide. This material was insoluble in petroleum hydrocarbons of the nature of gasoline, painter's naphtha, and alcohols, but was soluble in chlorinated hydrocarbons and coal tar solvents, benzene, toluene and the like.

The second portion of the bottom layer, a liquid having a viscosity of 500 seconds Saybolt Universal, was painted as a thin film on metal. It dried in the air in several minutes to touch. This film, when dry, was resistant to commercial muriatic acid, 50% sulphuric acid, saturated solutions of trisodiumphosphate, sodium metasilicate, paint removers, 50% sodium hydroxide, ethyl alcohol, gasoline, and painter's naphtha.

The liquid produced is non hygroscopic and water insoluble. It contains about 20.4% solids, is heavy, syrupy and amber in color, of 1.54 specific gravity (66° F.) and 9.613 pounds per gallon. Its iodine number and saponification value are zero, while the acid number dissolved in benzol is 2. Because of characteristics it is suitable as a transformer oil, its dielectric strength is equivalent to that of 25,000 volt oil; it is fire resisting, charring and decomposing at 480° F.

Example 2

Two thousand parts of a California fuel oil were mixed with 40 parts of fuller's earth as a carrier and 10 parts of radioactive thorium dioxide. While the mixture was maintained at 225° F. it was stirred for an hour. After this it was filtered. Ten per cent by weight of trichloroethylene was added and chlorine gas passed through the filtrate until 60% weight increase had occurred. This mixture was allowed to stand about 72 hours, at the end of which time 32% of the mixture had settled to the bottom as a heavy syrupy layer. This layer was drawn off, its properties and qualities being much the same as those discussed under Example 1, being, as with the liquid product of Example 1, soluble in acetone, xylol, benzol, hiflash naphtha, the usual ketone solvents, secondary butyl acetate, butyl cellosolve, ethylene dichloride, and other satu-

rated chlorinated hydrocarbons, both chain and ring, including aliphatic and aromatic compounds.

The material to be polymerized can be varied and I have successfully treated the bottom fraction remaining after recovery and separation of a gasoline from a liquid formed by the usual and known phosphoric acid polymerization of a mixture of olefins after the manner described by Ipatieff (Ind. & Eng. Chem. 27, 1077, 1935). This bottom fraction, composed of about 20%-25% olefins and about 20% aromatics with the remainder largely paraffins, was treated with a monazite sand catalyst at about 225° F. for several hours, usually about two hours, and at about 150 pounds pressure. The fraction had an initial boiling point of 346° F., an end point of 625° F. and a gravity of about 22° A. P. I. on the average.

The polymerization treatment results in alteration of the initial fraction. Depending on the period of treatment a 10%-20% solid fraction is produced, the remainder being liquid. The solid is hard, black and resinous; it is useful as a paint base, particularly heat resistant paints, as a core oil additive when dissolved in a suitable solvent. The liquid fraction can be distilled into various useful fractions useful as solvents, paint thinners, drying oils, wetting materials, lubricating oils, as coating compositions suitable for direct application to surfaces, particularly metal surfaces, as well as sources of further chemicals.

A lubricating oil fraction can be recovered from the product. For example, a neutral, lemon colored oil having a viscosity of 93 seconds Saybolt at 130° F. and 44 at 210° F., and a viscosity index of 45 was recovered. This oil had desirable lubricating and "oiliness" characteristics.

I have found the polymerized material should be chlorinated in the liquid phase, either with a body of liquid chlorine or with chlorine carried in a suitable chlorine solvent so that the oil chlorinates as in the liquid phase.

I have discovered that if the chlorination operation be conducted in the presence of a saturated chlorinated hydrocarbon such as trichloroethylene, ethylene dichloride, propylene dichloride, carbon tetrachloride, chloroform, methyl chloride or a chlorinated saturated aromatic hydrocarbon as a dichlor benzene or a hydrocarbon in which the chlorine present has been acquired by way of substitution and not by way of addition, the production of tacky, sticky and relatively unstable products is avoided. Instead the air-drying, non-tacky relatively stable product of the present invention results.

I have further found that to secure the maximum effect from the chlorinated solvent it is highly desirable that the temperature of chlorination approximate closely the boiling point of the chlorine solvent. While it is not absolutely essential, nevertheless the most efficient operation occurs when chlorination is effected at or close to the boiling point of the chlorinated solvent. The presence of the chlorinated hydrocarbon enables high percentages of chlorine to be introduced, and I have successfully formed end products having as high as 75% chlorine. The high chlorine content results in a more commercially stable product with respect to breakdown, for example, when subjected to strong acid and alkali.

While I have previously mentioned that a small amount of the hydrocarbon is employed, usually

about 10%, this is only by way of illustration and either more or less of the solvent can be employed. For example, I have utilized as much as 25% of the solvent and as little as 1% without harmful effects in the case of employing the larger percentage and without losing the beneficial effect in the case of the smaller percentage. However, it is preferred that the operation be conducted with about 10% of the material present.

If a portion of the amber syrupy liquid resulting from the chlorination is mixed with an alcohol, for example, ethyl alcohol, a pearly white mass coagulates instantly. When the alcohol is separated, the pearly mass remains. It is slightly tacky but air dries fairly rapidly.

The hydrocarbon mixture undergoing polymerization can be advantageously subject to oxidation to increase production of oxygen containing compounds therein, particularly carboxylic acids. To achieve this air, or other oxygen containing gas, is introduced into the hydrocarbon material. I have found the proportion of a pound of air per pound of hydrocarbon material preferable, giving a high increase in organic acid content and providing a source material from which ketones and esters can be manufactured readily.

The bottoms remaining after gasoline removal from a liquid formed by phosphoric acid polymerization of olefins in a cracked refinery gases were polymerized and treated according to the process of this invention. One hundred fifteen pounds were held for about two hours at 220 pounds at 160°-250° F. The pressure can go as low as 50 pounds but a longer time is required. Air was introduced substantially continuously until the weight of air passed slowly into the oil mass was equal to that of the original oil charge. The mass of oil was vented with a small vent to release inert nitrogen and unreacted air.

It is neither reasonable to demand that an inventor know all of the art at the present time upon which he may supposedly—but erroneously so—select the words of this disclosure nor possible for any human to anticipate what direction the future development of the art may take, which may make the language here used inapt. Therefore, the disclosure of this invention should not be construed as limited by mere interpretation of the words used. It is contemplated that changes in form may be made with variations and departures from the illustrated examples without departing from the scope of this invention. Such variations and departures include those made possible by the discovery of improved materials and better uses and forms of present materials, as well as practices and results which may be possible in fabrication and handling.

I claim:

1. A process for treatment of a hydrocarbon mixture rich in olefins and aromatics comprising maintaining said mixture in contact with a finely divided radioactive material as substantially the sole effective catalyst at an elevated non-cracking temperature to effect polymerization and condensation in said mixture.

2. A process for treatment of a hydrocarbon mixture rich in olefins and aromatics comprising maintaining said mixture in contact with a finely divided radioactive material as substantially the sole effective catalyst while subjecting said mixture to oxidation at an elevated non-cracking temperature to effect polymerization and condensation in said mixture.

3. A process for treatment of a hydrocarbon

mixture rich in olefins and aromatics comprising maintaining said mixture in contact with a finely divided radioactive material as substantially the sole effective catalyst while subjecting said mixture to oxidation with about an equal weight of air at an elevated non-cracking temperature to effect polymerization and condensation in said mixture.

4. A process for production of valuable materials comprising polymerizing a mixture of olefin and aromatic hydrocarbons in the presence of a radioactive material as the only effective polymerization catalyst present to give a liquid having a final boiling point of about 625° F., distilling off of said liquid a fraction boiling over the range 346° F.-625° F., and further polymerizing said distilled fraction to produce a polymerized fraction containing about 20% solids.

5. A process for production of valuable materials comprising polymerizing a mixture of olefin and aromatic hydrocarbons as the only effective polymerization catalyst present to give a liquid having a final boiling point of about 625° F., distilling off of said liquid a fraction boiling over the range 346° F.-625° F., and further polymerizing said distilled fraction until it contains about 20% solids, and simultaneously oxidizing said polymerized fraction.

6. A process for producing valuable materials comprising polymerizing in the presence of a monazite sand as the only effective polymerization catalyst a liquid fraction having a boiling point range of about 346° F. to 625° F. and containing about 20% olefins and 20% aromatics at about 150 pounds pressure and at about 225° F. for about two hours.

7. A process for production of valuable materials from olefin and aromatic hydrocarbon mixture comprising maintaining said material at a temperature of about 160° F. to about 265° F. for about a half hour to two hours in the presence of a finely divided radioactive material as substantially the only effective catalytic material present.

8. A process for production of valuable materials from olefin and aromatic hydrocarbon mixture comprising maintaining said material at a temperature of about 160° F. to about 265° F. for about a half hour to two hours in the presence of a finely divided radioactive material as substantially the only effective catalytic material present and admitting an oxygen carrying gas into said mixture to oxidize at least some components thereof.

9. A process for production of valuable materials from olefin and aromatic hydrocarbon mixture comprising maintaining a mass of said material at a temperature of about 160° F. to about 265° F. for about a half hour to two hours in the presence of a finely divided radioactive material as substantially the only effective catalytic material present and admitting about an equal weight of air as an oxygen carrying gas into said mixture to oxidize at least some components thereof.

10. A process for production of valuable materials from a petroleum fraction heavier than gasoline comprising maintaining a mass of said fraction at a temperature of about 160° F. to about 265° F. for about a half hour to two hours in the presence of a finely divided radioactive material as substantially the only effective catalytic material present.

11. A process for production of valuable materials from a petroleum fraction heavier than

gasoline comprising maintaining a mass of said fraction at a temperature of about 160° F. to about 265° F. for about a half hour to two hours in the presence of a finely divided radioactive material as substantially the only effective catalytic material present and admitting an oxygen carrying gas into said mixture to oxidize at least some components thereof.

12. A process for production of valuable materials from a petroleum fraction heavier than 10

gasoline comprising maintaining a mass of said fraction at a temperature of about 160° F. to about 265° F. for about a half hour to two hours in the presence of a finely divided radioactive material as substantially the only effective catalytic material present and admitting about an equal weight of air as an oxygen carrying gas into said mixture to oxidize at least some components thereof.

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