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HOMOPOLYMERIZATION OF BENZYL COMPOUNDS

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4 Claims. (Cl. 260-2)

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The present invention relates to a method of producing resinous bodies, and more particularly, to a method of making resinous bodies from aromatic oxy-compounds, especially aromatic alcohols and ethers, and to the products thereof.

It is well known that aromatic alcohols having either a saturated side chain or an unsaturated side chain, such as benzyl or cinnamic alcohols can be polymerized to form resinous bodies by such agents as sulfuric acid, phosphorous acid or phosphorus pentoxide. It is also known that benzyl alcohol is readily converted to a yellow resinous hydrocarbon by contact in the vapor phase with precipitated alumina at temperatures above 300° C.

It has now been discovered that mono-nuclear and polynuclear aromatic alcohols and ethers such as benzyl alcohol, benzyl ether, trimethyl benzyl alcohols, trimethyl benzyl ethers, and especially polyalkyl aralkyl alcohols and ethers of the aromatic constituents of aromatic petroleum stocks, can be converted into resinous products in a liquid phase at temperatures below 300° C.

As those skilled in the art know, large quantities of aromatic petroleum stocks are available. The aromatic constituents of these aromatic petroleum stocks can be converted into the corresponding alcohols and ethers in various ways. Thus, for example, aromatic petroleum stocks derived from Houdry cracking operations and having boiling point ranges varying from 150° C. to 210° C. contain between 50 per cent and 75 per cent of aromatic hydrocarbons of the polyalkyl benzene type. One of these stocks, for example, is believed to be, primarily, polymethyl benzenes ranging from trimethyl benzene to tetramethyl benzene. Small amounts of other aromatic hydrocarbons, such as ethyl methyl benzene also may be present. There are three trimethyl benzenes, mesitylene, 1,3,5-trimethyl benzene; pseudocumene or 1,2,4-trimethyl benzene; and hemimellitene or 1,2,3-trimethyl benzene. There are three tetramethyl benzenes, durene or 1,2,4,5-tetramethyl benzene; isodurene or 1,2,3,5-tetramethyl benzene; and prehnitene, 1,2,3,4-tetramethyl benzene. All of these polyalkyl benzenes are present in the various stocks, boiling between 310 degrees and 395 degrees F. to a greater or lesser degree. The higher boiling cuts of these aromatic stocks, for example those with an initial boiling point of 210° C., contain appreciable quantities of mono- and polyalkyl polynuclear aromatic hydrocarbons such as mono- and di-methyl naphthalene.

The aromatic petroleum stocks can be treated

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to produce the corresponding alcohols, for example, by haloalkylation to the corresponding aralkyl chlorides and the aralkyl chlorides converted to the corresponding alcohols or to ethers.

5 A method of haloalkylating aromatic petroleum stocks is disclosed in the co-pending United States application Serial No. 515,145, filed December 21, 1943, in the name of Howard D. Hartough, now abandoned. A method of converting the aromatic constituents of aromatic petroleum stocks to alcohols and ethers is disclosed in the co-pending United States application for Letters Patent Serial No. 560,365, now abandoned. Aromatic alcohols, ethers and aralkyl esters of hydroxy carboxylic acids, whether produced in the manner described therein or by other methods and whether derived from aromatic petroleum stocks or otherwise, can be converted into resinous bodies in a liquid phase operation not employing any of the conventional condensation agents, sulfuric acid, phosphorous acid or the like.

15 The present method provides satisfactory results when employing aralkyl alcohols of mono-nuclear or polynuclear aromatic compounds whether the hydroxyl group be attached to the ring by a saturated or unsaturated alkyl chain. Typical of such aromatic alcohols are benzyl and cinnamic alcohols. Aralkyl alcohols having alkyl substituted rings likewise readily lend themselves to condensation by the present method. Illustrative of such alkyl substituted mono-nuclear aralkyl alcohols are hemimellitenyl alcohol and its isomers and durenyl alcohol and its isomers. Both of the foregoing homologues are grouped together as polyalkyl benzyl alcohols. Among the polynuclear aralkyl alcohols which likewise may be condensed by the present method are the alcohols which are derivatives of naphthalene and mono- and polyalkyl naphthalene. It is to be understood that the present method is not limited to the treatment of methyl substituted aralkyl alcohols but also provides satisfactory results with mono- and polyalkyl mono- and polynuclear aralkyl alcohols in which the alkyl groups substituted in the ring are other than methyl, for example, ethyl, methyl and ethyl radicals, and in general radicals having up to 24 carbon atoms.

25 The present process produces satisfactory results when aralkyl ethers are treated. Thus, for example, benzyl ether, (C₆H₅CH₂)₂O may be condensed as well as polyalkyl benzyl ether according to the present method. Ethers of mono- and

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polyalkyl polynuclear carbocyclic compounds such as $(C_{10}H_7CH_2)_2O$, $(CH_2C_{10}H_6CH_2)_2O$ and



may also be condensed in accordance with the method disclosed hereinafter. It will be understood by those skilled in the art that mixtures of the various types of aralkyl alcohols and ethers may be condensed as well as mono-component materials. Thus, for example, benzyl alcohol may be condensed with durenyl alcohol or benzyl ether with polyalkyl benzyl ether. Accordingly, in view of the source of the reactants, described hereinbefore, the reactants of the present invention may be defined as benzyl alcohols having not more than 4 nuclear hydrogen atoms replaced with methyl groups, dibenzyl ethers having not more than 4 nuclear hydrogen atoms replaced with methyl groups, and benzyl lactates having not more than 4 nuclear hydrogen atoms replaced with methyl groups, the hydrogen atoms of said benzyl alcohols, dibenzyl ethers, and benzyl lactates being otherwise unsubstituted.

It is an object of the present invention to provide a method of condensing aralkyl alcohols, aralkyl ethers and aralkyl esters of hydroxy carboxylic acids in a liquid phase reaction employing a solid catalyst. It is another object of the present invention to provide a method of producing resinous bodies from aralkyl alcohols, aralkyl ethers and aralkyl esters of hydroxy carboxylic acids in a liquid phase reaction employing natural or synthetic hydrated aluminum hydroxy silicates. It is a further object of this invention to provide a method of producing resinous bodies from aralkyl alcohols, aralkyl ethers and aralkyl esters of carboxylic acids in a liquid phase reaction employing natural or synthetic clays. The present invention also has as an object the provision of a method of producing resinous bodies from aralkyl alcohols, aralkyl ethers and aralkyl esters of hydroxy carboxylic acid employing natural and synthetic clays of the montmorillonite type. The present invention likewise has as an object the provision of a method of producing resinous bodies from aralkyl alcohols, aralkyl ethers and aralkyl esters of hydroxy carboxylic acids employing natural or synthetic clays of the activated montmorillonite type. Other objects and advantages of this invention will become apparent to those skilled in the art after reading the following description.

In accordance with the method of this invention aralkyl alcohols, ethers or aralkyl esters of hydroxy carboxylic acids are condensed by heating the alcohols, ethers or esters in liquid phase in the presence of a solid condensation catalyst. The condensation reaction may be carried out in the presence or absence of a solvent or diluent at temperatures below the boiling point of the reaction mass. The reaction time is of the order of about an hour to several hours. After the reaction is complete the reaction liquid is treated to remove the condensation agent. The solid condensation agent is most readily removed by filtration or centrifugation. The solid condensation catalyst is usually washed with suitable organic solvents to remove resins or oils adsorbed on the clay. When desirable the solid condensation agent or catalyst can be re-used after activation.

The novel catalyst or condensation agent is a solid adsorbent contact mass such as clays of the activated montmorillonite type, fresh burnt Attapulugus clay, silica gel, synthetic alumina-

silica gel catalysts containing about 7 per cent to about 15 per cent alumina, powdered cracking catalyst which is a base exchanged silica-alumina catalyst containing about 7 per cent to about 15 per cent alumina and similar adsorbent materials. The condensation agent is used preferably in finely-divided or powdered form. Illustrative of the clays of the montmorillonite type which have provided satisfactory results is a non-swelling crystalline rather than amorphous bentonite clay which has been activated by an acid treatment in a manner well known to those skilled in the art to give a composition approaching $Al_2Si_4O_{10}(OH)_2 \cdot nH_2O$. The term hydrated aluminum hydroxy silicate is used hereinafter to include all of the catalysts or condensing agents disclosed herein.

Those skilled in the art will instantly recognize that the use of a solid condensation agent in this reaction provides at least two important advantages over the prior art condensation agents as will be more readily appreciated by consideration of the following discussion.

Heretofore the most generally used of the known condensation agents for the condensation of benzyl alcohol and cinnamic alcohols have been the acid catalysts, sulfuric acid and various acids of phosphorus. The known condensation agents for this purpose are liquids miscible with the reaction mass. Consequently, it has been very difficult in the past to separate the acid condensation agent from the resinous material. In distinct contrast the novel condensation agents of the present invention are readily and cheaply separated from the reaction mass.

The present condensation agents provide a second and equally important advantage over prior art agents for the purposes of the present invention. Due to the character of the prior art, soluble, acidic condensation agents, the prior art condensation agents were useless for further employment as catalysts in the condensation reaction. On the other hand, the novel condensation agents are readily re-activated and prepared for re-use. The novel condensation agents of this invention can be readily regenerated or re-activated by methods known to those skilled in the art.

In addition to the foregoing advantages which the solid condensation agents of this invention possess in contrast to the prior art liquid agents, the solid condensation agents of this invention entrain dark colored materials present in the reaction and remove these coloring matters from the resinous reaction products when the solid condensation agents are separated from the reaction mass in any suitable manner. As a result of this absorption or entrainment, the resinous materials thus produced are much lighter in color than prior art products prepared by condensating, for example, aralkyl alcohols such as benzyl alcohol using the prior art liquid acidic condensation agents. To further improve the color, the resin may be dissolved in a suitable solvent and filtered a second time through freshly activated natural hydrated aluminum hydroxy silicate clay using about 10 per cent by weight based upon the weight of the resin solution. The amount of clay employed for the second filtration may vary from about 10 per cent by weight to the amount necessary for use as a catalyst for another batch, say about 30 per cent to about 35 per cent by weight. This clay, used only for decolorization, may be used as the catalyst for another batch if so desired without reactivation.

The following examples are provided for the

guidance of those skilled in the art and to illustrate variations in certain variables which have given satisfactory results.

EXAMPLE I

Benzyl alcohol

A resin has been prepared from benzyl alcohol in the following manner in accordance with the principles of the present invention.

One hundred and fifty (150) grams, about 144 cubic centimeters, (1.4 moles) of benzyl alcohol, 77.5 grams of Stoddard solvent (safety solvent naphtha; boiling point 300° F. to 400° F.) about 0.7 volume and 60 grams of clay of the montmorillonite type which is a hydrated aluminum hydroxy silicate were stirred together at atmospheric pressure for 12 hours at 110° C. The reaction mixture was filtered and the filtrate distilled or topped to a pot temperature of 233° C. at 12 millimeters of mercury pressure to remove solvent, unreacted alcohol and intermediate resins volatile at this temperature. The still residue amounted to 24.5 grams of a brownish-red, tacky, tough solid.

EXAMPLE II

Trimethyl benzyl alcohols

One hundred and fifty grams, above 149.5 cubic centimeters, (1 mole) of trimethyl benzyl alcohols from a petroleum naphtha having a boiling range of 310° F. to 395° F., 77.5 grams (0.7 volume) of Stoddard solvent and 60 grams of clay of the montmorillonite type were stirred at 110° C. under atmospheric pressure for 12 hours. At the end of this period the reaction mixture or mass was filtered and the filtrate distilled or topped to a pot temperature of 300° C. at 7 millimeters of mercury pressure to remove solvent, unreacted alcohols and intermediate resin. Fifty-four grams of reddish-amber, hard, brittle resin was obtained as a still residue.

EXAMPLE III

Benzyl Ether

One hundred and fifty grams (0.76 mole) of benzyl ether, 77.5 grams (0.7 volume) of Stoddard solvent and 60 grams of clay of montmorillonite type were stirred at 110° C. at atmospheric pressure for twelve hours. The reaction mixture was filtered and the filtrate topped to a pot temperature of 300° C. at 10 millimeters of mercury pressure to remove solvent, uncondensed benzyl ether and resin intermediates. The still residue was a tough brown flexible resin and weighed 31 grams.

EXAMPLE IV

Trimethyl benzyl ether

Five hundred and sixty grams, about 571 cubic centimeters (about 2.0 moles) of trimethyl benzyl ether derived from a petroleum naphtha having a boiling range of 310° F. to 395° F., and 150 grams of re-activated "Super Filtrol" clay which is a hydrated aluminum hydroxy silicate (freshly activated at 1050° F.) were stirred together at atmospheric pressure for 2.5 hours at 200° C. to 225° C. The reaction mixture was filtered and the clay washed with a solvent ["Sovasol" #74 (predominantly xylenes)]. The filtrate was topped to a pot temperature of 300° C. at a pressure of 4 millimeters of mercury to remove solvent, unreacted ether and intermediate resin. Three hundred and sixty-six grams of still residue remained which was a brittle reddish amber resin.

EXAMPLE V

Twenty-two and two-tenths grams (0.1 mole) of trimethyl benzyl lactates (made by a standard procedure from trimethyl benzyl chlorides and sodium lactate), 50 cubic centimeters of Stoddard solvent and 10 grams of natural hydrated aluminum hydroxy silicate clay were heated and stirred together at atmospheric pressure for 11½ hours at 110±5° C. The reaction mixture was filtered and the clay washed with benzol. The combined filtrates were distilled to give in addition to recovered trimethyl benzyl lactates and intermediate liquids, 11 grams (49.5 per cent conversion) of a light amber colored solid residue (final pot temperature for topping—300° C. at 10 millimeters) which was hard and brittle.

It is believed desirable to point out that when using a solvent the quantity thereof is not critical, sufficient solvent being used to provide a fluid reaction mass at the condensation temperature. Furthermore, the amount of condensation agent is not critical, sufficient being used to ensure intimate contact between all of the liquid reactant and the solid condensation agent. The amount of condensation agent preferably should be between 0.2 volume and about 0.7 volume based on the volume of the hydroxy-, aralkyloxy-, or oxy-aryl compound, i. e. alcohol or ether or ester or about 0.1 part to about 0.5 part by weight based on the weight of the material to be condensed.

The solid catalyst or condensation agent may be activated or reactivated, as those skilled in the art know, by heating in a kiln or other suitable apparatus at controlled temperatures in the presence of suitable amounts of air for oxidation of carbonaceous deposits.

Although the present invention has been described in conjunction with certain preferred embodiments thereof, those skilled in the art will understand that variations and modifications can be made without departing from the principles thereof. Thus, for example, the principles of the present invention may be employed to condense aralkyl compounds containing an ether linkage or a hydroxy radical such as, for example, aralkyl alcohols, aralkyl ethers and aralkyl esters of hydroxy carboxylic acids.

We claim:

1. The method of effecting the homopolymerization of an organic compound selected from the group consisting of a benzyl alcohol having not more than 4 nuclear hydrogen atoms replaced with methyl groups, a dibenzyl ether having not more than 4 nuclear hydrogen atoms replaced with methyl groups and a benzyl lactate having not more than 4 nuclear hydrogen atoms replaced with methyl groups, the hydrogen atoms of said benzyl alcohol, said dibenzyl ether, and said benzyl lactate being otherwise unsubstituted, which comprises heating said organic compound, in the liquid phase, in the presence of a hydrated aluminum hydroxy silicate clay catalyst, at temperatures below the boiling point of said organic compound, for a period of time sufficient to effect resinification.

2. The method of effecting the homopolymerization of benzyl alcohol, which comprises heating said benzyl alcohol, in the liquid phase, in the presence of a hydrated aluminum hydroxy silicate clay catalyst, at temperatures below the boiling point of benzyl alcohol, for a period of time sufficient to effect resinification.

3. The method of effecting the homopolymerization of trimethyl dibenzyl ether, which com-

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prises heating said trimethyl dibenzyl ether, in the liquid phase, in the presence of a hydrated aluminum hydroxy silicate clay catalyst, at temperatures below the boiling point of trimethyl dibenzyl ether, for a period of time sufficient to effect resinification.

4. The method of effecting the homopolymerization of trimethyl benzyl lactate, which comprises heating said trimethyl benzyl lactate in the liquid phase, in the presence of a hydrated aluminum hydroxy silicate clay catalyst, at temperatures below the boiling point of trimethyl benzyl lactate, for a period of time sufficient to effect resinification.

CHARLES F. FEASLEY.
HOWARD D. HARTOUGH.

REFERENCES CITED

The following references are of record in the file of this patent:

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15 Sabatier et al: Compte Rendu, vol. 147, pages 106-110 (1908).

Certificate of Correction

Patent No. 2,486,831

November 1, 1949

CHARLES F. FEASLEY ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 5, line 29, for the word "above" read *about*;
and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of May, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.