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REFINING HYDROCARBONS

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This invention relates to an improved method of refining hydrocarbons and in particular to the use as refining agents of certain addition compounds of alkali metals with polycyclic aromatic hydrocarbons such as naphthalene, diphenyl, phenanthrene and the like.

Heretofore, various methods for refining hydrocarbons by treatment with alkali metals, particularly sodium, have been proposed. However, for various reasons, there has been little practical use of sodium for this purpose. One disadvantage that has hindered the adoption of sodium as a refining agent is the fact that it reacts readily with water to liberate hydrogen, simultaneously liberating heat, thus creating a fire hazard. In order to avoid this hazard, it has been proposed to use compounds made by reacting sodium with substances having hydrogen atoms replaceable by sodium. Such compounds includes sodium alcoholate and sodamide. Such compounds, however, as a class either are less effective than sodium, as is the case with sodium ethylate or have disagreeable or hazardous properties of their own, as in the case of sodamide.

One object of this invention is to provide an improved process for refining hydrocarbons. A further object is to provide a novel method for polymerizing unsaturated hydrocarbons having conjugated ethylenic linkages. Other objects will be hereinafter apparent.

I have now found that the addition compounds formed by the reaction of alkali metals with polycyclic aromatic hydrocarbons such as naphthalene, diphenyl and phenanthrene, have decided advantages as refining agents in that they are easily prepared, can be handled as solutions, do not ignite in contact with air under ordinary conditions, do not evolve hydrogen or ignite on contact with water, yet react instantly with a large number of undesirable impurities commonly occurring in hydrocarbons and are in general more effective than the free alkali metal itself in polymerizing gum forming constituents. Certain methods of forming these addition compounds are disclosed and claimed in my copending applications Serial Numbers 638,524 and 678,261. One convenient method is to dissolve sodium in a solution of naphthalene or other polycyclic aromatic hydrocarbon in liquid dimethyl-ether at a temperature somewhat below —24° C., while stirring or abrading the sodium in contact with the mixture to start the reaction. When the reaction is once started, the solution becomes highly colored and solution of the metal occurs at a rapid rate. The amount of sodium readily dissolved will range in general from one to two gram atoms per gram molecule of the aromatic hydrocarbon. Various other aliphatic ethers may be used as solvents in place of dimethyl ether, as for example, methyl ethyl ether, poly ethers such as dimethyl or diethyl glycol ethers, or cyclic ethers such as dioxane.

When the solution of the sodium hydrocarbon compound or mixture of compounds has been prepared, it either may be mixed with the hydrocarbon to be refined, or as is usually preferable to avoid wasting solvent, the methyl ether or other special solvent used in preparing the sodium compound may be partly distilled off and recovered before contacting the sodium compound with the hydrocarbon to be refined. In the latter case, it is advisable to leave a small amount of the solvent ether in contact with the sodium compound, e. g., equivalent to around 20% by weight of the compound, as this increases the stability of the sodium compound.

The best method of carrying out the refining treatment will vary to a considerable extent with the nature of the materials involved. In general it can be stated that the sodium compound will react instantly, even in the cold, with water, acids and other substances containing hydrogen atoms replaceable by sodium, with CO_2 or CS_2 and with dissolved oxygen. The latter, for example, gives mainly sodium monoxide and naphthalene by reaction with the sodium naphthalene compound. When the sodium hydrocarbon compound reacts with water or other substances having replaceable hydrogen, no hydrogen evolution occurs; the replaceable hydrogen appears to exchange places with the sodium, thus:

$$R—Na_2+2H_2O \rightarrow R—H_2+2NaOH$$

I have discovered that the herein described addition compounds of alkali metals and polycyclic aromatic hydrocarbons have a marked polymerizing effect when contacted with an unsaturated hydrocarbon which has conjugated double bonds, at least one of the conjugated double bonds occurring in an aliphatic radical. Further, I have found that these addition compounds have little or no polymerizing effect on unsaturated hydrocarbons which do not have conjugated double bonds as described above. Examples of hydrocarbons with conjugated unsaturation which may be readily polymerized by treatment with small amounts of the alkali addition compounds are butadiene, dimethyl butadiene, styrene, cyclopentadiene and 1,2-dihydronaphthalene. This polymerizing action is rapid and complete, even at relatively low temperatures, e. g., 20 to 30° C. Alkali metals are known to cause polymerization of unsaturated compounds, but my herein described alkali metal addition compounds differ from the alkali metals in that they cause more rapid and more complete polymerization of the conjugated unsaturates than do alkali metals. For example, a small amount of an ether solution of the sodium naphthalene addition compound added to 1,2-dihydronaphthalene at 20 to 30° C.

rapidly and substantially completely polymerizes the latter to a resinous substance, while an equivalent amount of sodium metal, under similar conditions polymerizes this hydrocarbon only very slowly and incompletely, even at elevated temperatures.

I have found that the herein described alkali metal addition compounds are selective in their polymerizing action in that they readily polymerize the conjugated unsaturates, while having substantially no polymerizing action on non-conjugated unsaturates.

The selective polymerizing action of the herein described alkali metal addition compounds is illustrated by the fact that whereas the sodium naphthalene compound causes rapid polymerization of butadiene, it has substantially no action on amylene.

The above described selective polymerizing action is of especial importance in the use of the herein described alkali metal addition compounds as agents for refining motor fuel grades of petroleum hydrocarbons. It is known that the undesirable gum forming characteristics of gasoline and the like is due to the presence of conjugated unsaturates. On the other hand, it is desirable to leave unsaturated bodies in motor fuel on account of their anti-knock properties. I have found that because of the above mentioned selective polymerizing action, my herein described refining agents materially decrease the gum-forming characteristics of petroleum hydrocarbons, while leaving the non-conjugated unsaturates present substantially unchanged. Thus my herein described method of refining is an improvement over prior methods adapted to decrease gum-formation, e. g. treatment with sulfuric acid, which tend to remove all unsaturated aliphatic hydrocarbons, whether conjugated or not.

The efficient removal of sulfur occurring in the form of thiophene or other particularly stable sulfur compounds is best effected by treating the crude hydrocarbon with the sodium hydrocarbon addition compound at somewhat elevated temperatures, for example 100–150° C. Hence, while the refining treatment may be affected at various temperatures, ranging from ordinary room temperature up to temperatures close to the cracking point of the hydrocarbon to be refined, I prefer to operate at 100–200° C., especially when it is desired to remove sulfur compounds.

My novel treating agent may be contacted with the hydrocarbon to be refined by various methods, which will be apparent to those skilled in this art. Preferably, the alkali metal hydrocarbon compound is thoroughly mixed by efficient agitation with the material to be refined at the desired temperature until well-known tests indicate that the desired degree of refinement has been attained.

The amount of the alkali metal hydrocarbon compound required will vary over a wide range, depending upon the temperature, time of contact, the nature and amounts of impurities in the hydrocarbon to be refined and the degree of refinement desired. In general, when a highly refined product is desired, the amount of sodium hydrocarbon compound in contact with the hydrocarbon to be refined should be equivalent to one pound of sodium metal to about 10 to 50 gallons of the hydrocarbon to be refined. As shown by the following examples, the time of the treatment may vary widely, for example from 2 to 60 hours, depending mainly on the temperature employed. In general, for a given degree of refining, the time required to complete the treatment is inversely proportional to the temperature.

The separation of the refined product generally is best effected by distillation in the absence of water at a pressure suitable for the material being distilled. The refining treatment in general improves the color and odor of the hydrocarbons, decreases tendency for gum formation and decreases the sulfur content.

The invention is illustrated by the following examples, although variations of the method will be obvious.

Example 1

Sodium naphthalene addition compound was made by reacting sodium with a solution of naphthalene in liquid dimethyl ether at a temperature of around −30° C. The resulting green solution was separated from unreacted sodium and sufficient of the solvent ether was allowed to evaporate to leave an amount equivalent to about 20% by weight of the sodium naphthalene compound. The product, a dark, granular, solid, wet with the solvent, was stored out of contact with the air until used.

A cracked gasoline (A) with a very high sulfur content was mixed with a quantity of sodium naphthalene prepared as described above in the ratio equivalent to one pound of sodium metal to 4.68 gals. of gasoline and the mixture was allowed to stand for about 60 hours at 20–30° C. The mixture then was heated under a reflux condenser at about 150° C. for four hours. The refined gasoline then was recovered by distillation at atmospheric temperature.

Another cracked gasoline (B) was refined by the same procedure, except that the amount of sodium naphthalene used was equivalent to one pound of sodium metal to 9.6 gals. of gasoline and after standing about 15 hours at room temperature, the mixture was refluxed at 125° C. for six hours.

The following data indicate the degree of refining obtained:

	A	B
	Operating conditions	Operating conditions
Ratio of refining agent to gasoline.	1 lb. Na/4.68 gals.	1 lb. Na/9.60 gals.
Time standing in cold	60 hrs.	15 hrs.
Time refluxed	4 hrs.	6 hrs.
Refluxing temperature.	150° C.	125° C.

	Results		Results	
	Crude	Refined	Crude	Refined
Color (Saybolt)	Yellow	28	Orange	24.
Odor	Sour	Sweet	Sour	Sweet.
Gum (copper dish test)		0.0082		
Doctor test	Positive.	Negative.	Positive.	Negative.
Sulfur content	1.120%	0.136%	0.423%	0.031%
Boiling range		40–205° C.		40–210° C.
Recovery of refined product.		89%		

I have obtained similar results by utilizing this method to refine straight-run gasoline with the sodium addition compound of naphthalene. Likewise, I have successfully refined cracked gasolines by similar treatment with the sodium addition compounds of diphenyl and anthracene.

Example 2

A "light oil" obtained from coal distillation was refined with sodium naphthalene prepared by the method of Example 1. A quantity of the sodium naphthalene equivalent to one pound of sodium metal to 25 gals. of light-oil was mixed with the oil at room temperature and the cold mixture allowed to stand over night. The mixture then was refluxed at 125 to 150° C. for four hours and then distilled to recover the refined product. The following results were obtained:

	Crude light oil	Refined product
Color (Saybolt)	Yellow	25
Odor	Sour	Sweet
Gum (copper dish test)	0.2480	0.0015
Sulfur content	0.332%	0.245%

As mentioned above, part of the solvent may be recovered from the ether solution of the alkali metal hydrocarbon compound before using the compound as refining agent, in order to avoid loss of the solvent ether. It should be mentioned that if the solvent is completely distilled off, the alkali metal compound will decompose to form a mixture of aromatic hydrocarbon and a colloidal form of the metal. This mixture will function as an active refining agent because of the colloidal alkali metal present. However, I prefer to avoid the formation of substantial amounts of free metal in my refining agent and I have found that such decomposition may be prevented by leaving in the mixture a small amount of the solvent, e. g. an amount equal to about 20% by weight or more of the alkali metal-hydrocarbon compound.

While the above description has dwelt chiefly on the use of the sodium naphthalene addition compound for refining hydrocarbons, it is to be understood that my invention is not restricted thereto. The various polycyclic aromatic hydrocarbons other than naphthalene may be reacted with sodium or other alkali metal (e. g., potassium or lithium) by the method described and the resulting alkali metal addition compounds may be used to refine hydrocarbons in accordance with my herein described invention. Examples of polycyclic aromatic hydrocarbons which may be used in place of naphthalene in my invention are: diphenyl, anthracene, acenaphthene, phenanthrene and methyl naphthalene.

I claim:

1. A process for refining hydrocarbons comprising contacting a hydrocarbon with an addition compound of an alkali metal and a polycyclic aromatic hydrocarbon.

2. A process for refining hydrocarbons comprising contacting a hydrocarbon with an ether solution of an addition compound of an alkali metal and a polycyclic aromatic hydrocarbon.

3. A process for refining hydrocarbons comprising contacting a hydrocarbon with an addition compound of sodium and a polycyclic aromatic hydrocarbon at a temperature of 100–200° C.

4. A process for refining hydrocarbons comprising contacting a hydrocarbon with an addition compound of sodium and naphthalene.

5. A process for refining hydrocarbons comprising contacting a liquid hydrocarbon with an ether solution of an addition compound of sodium and naphthalene.

6. A process for refining hydrocarbons comprising contacting a hydrocarbon with an addition compound of sodium and anthracene.

7. A process for refining hydrocarbons comprising contacting a hydrocarbon with an addition compound of sodium and diphenyl.

8. A process for refining hydrocarbons comprising contacting a liquid hydrocarbon with an addition compound of sodium and naphthalene at a temperature of 100–200° C.

9. A process for refining hydrocarbons comprising contacting a liquid hydrocarbon with a solution of an addition compound of sodium and naphthalene which contains as solvent an ether selected from the group consisting of dimethyl ether, methyl ethyl ether, polyethers and cyclic ethers.

10. A process for refining hydrocarbons comprising contacting a liquid hydrocarbon with a solution of an addition compound of sodium and naphthalene which contains as solvent an ether comprising a dialkyl glycol ether having a molecular weight not in excess of that of diethyl glycol ether.

11. A process for refining hydrocarbons comprising contacting a hydrocarbon with an addition compound of an alkali metal and a polycyclic aromatic hydrocarbon, said addition compound being in the solid state and wet with a solvent therefor.

12. A process for refining hydrocarbons comprising contacting a hydrocarbon with an addition compound of sodium and naphthalene, said addition compound being in the solid state and wet with a solvent comprising an ether selected from the group consisting of dimethyl ether, methyl ethyl ether, polyethers and cyclic ethers.

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