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PURIFICATION OF GASES

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This invention relates to the treatment of gases and refers more particularly to the treatment of fuel gases intended for domestic use.

In a more particular sense the invention has reference to a process for removing gum-forming hydrocarbons from domestic gases so that difficulties in the manipulation of fine control valves and the clogging of the tips of pilot flame burners is prevented.

A great many of the gases employed domestically as fuel contain considerable percentages of olefinic hydrocarbons, particularly those gases produced by the intensive heat decomposition of hydrocarbon oils. The various carbureted gases such as carbureted water gas and carbureted producer gas also contain olefins, they are present in gases made by the partial combustion of oils and in gases that have been subjected to reforming operations to increase their hydrogen content and decrease their heating value. Gases from oil cracking processes aimed primarily at the production of gasoline are notably rich in olefins and since these gases are coming into prominence as blending material for increasing the heating and illuminating value of other gases their treatment is comprised within the scope of the present invention.

While the presence of the more stable olefins such as ethylene is not always undesirable since they possess a high heating value and give considerable luminosity when burned, there are usually present minor percentages of less stable olefins such as the dienes and traces of mixed type hydrocarbons such as styrene and indene, these compounds being ethylene and propylene derivatives of benzol, respectively. When gases containing appreciable quantities of these olefinic hydrocarbons which tend to resinify are burned for long periods of time in the fine tipped pilot flames of automatic heaters and stove lighters, resinous material gradually accumulates in the fine tip of the burner (which is usually only of capillary dimensions) and these accumulations in time may cause a complete stoppage of the opening and the extinction of the flame with resultant hazard, due to escaping gas and the concurrent danger of explosions. For this reason the removal of compounds of pronounced gum-forming tendencies is a problem of importance.

In one specific embodiment the invention comprises treatment of gases containing gum-forming olefins with aromatic hydrocarbons in the presence of sulfuric acid to remove the gum-forming constituents by condensation reactions between them and the aromatics to form hydrocarbon derivatives of a mixed alkyl-aryl character.

The mechanism of the reactions involved in the production of alkyl derivatives of aromatics from olefins and aromatics in the presence of condensing agents such as sulfuric acid may be specifically illustrated by the case involving the interaction of propylene and benzol. In the presence of sulfuric acid and at atmospheric or slightly subatmospheric temperatures the propylene combines additively to form a mixture of mono and dipropyl benzols, according to the equations:

(1) $$C_3H_6 + C_6H_6 = C_6H_5.C_3H_7$$

Propylene Benzol Mono-Benzol propyl

(2) $$2C_3H_6 + C_6H_6 = C_6H_5.(C_3H_7)_2$$

Propylene Benzol Dipropyl Benzol

The relative amounts of mono and dialkyl products will depend largely upon the relative proportions of the olefin and aromatic employed, though yields of the two compounds will also be influenced by the conditions of treatment such as the amount and concentration of the sulfuric acid employed, the temperature, the efficiency of contact, etc. The above equations are quite general for olefins containing more than two carbon atoms, that is, the higher homologs of ethylene such as butylene, amylenes, hexylenes, etc., and for some of the corresponding series of di and tri olefins, which are many times the chief offenders in the production of gummy deposits from gas mixtures. The reactions are also quite general for benzol and its homologs on the side of the aromatics. Thus in place of benzol, toluol, xylols and polynuclear ring compounds such as naphthalene, anthracene, etc. may be used insofar as their physical properties permit under the temperature and pressure conditions of treatment. While polymerization of olefins among themselves and oxidation reactions occasioned by the sulfuric acid are never entirely absent, they may be minimized by suitable control of operation conditions so that the major trend of the reactions is of the character indicated by the equations.

The process of the invention is preferably applied as a supplementary purification step in the preparation of gases for domestic consumption. In the case of manufactured gases such as the oil gas and the carbureted and reformed gases mentioned, it may be employed as a final step to insure the complete removal of gum-forming compounds which are undesirable for the reasons already stated.

The reactions of condensation of the gum-forming olefines and aromatics may be brought about in ordinary types of gas washing equipment with perhaps minor modifications in some instances. In the simplest type of operation the gases to be treated for the removal of gum-forming constituents may be bubbled through a mixture of sulfuric acid of commercial grade and some aromatic hydrocarbons such as benzol, the acid and hydrocarbon being kept in more or less thorough admixture by means of mechanical agitation or stirring devices or by circulation through centrifugal pumps placed exteriorly to the treater. During the passage of the gases through the acid-hydrocarbon mixture the reactions of condensation are effected and may continue until the aromatic hydrocarbon is alkylated to a definite extent, after which the reactions may slow up and economy demand that the gas stream be diverted to other treaters arranged in parallel and containing fresh quantities of aromatic hydrocarbons. The quantity of sulfuric acid available for catalyzing the reactions may also be gradually depleted, due to ester formation and the reducing effect of the hydrocarbons, even though special precautions are taken to maintain low temperatures, and replenishment of the acid may be necessary at intervals.

The gases may also be treated in treating towers by being caused to rise countercurrent to descending streams of both aromatic hydrocarbons and acid and treatment thus effected with a smaller pressure drop than when the gases are bubbled through a relatively long column of acid-oil mixture.

Ordinarily the process may be conducted at ordinary temperatures and pressure though as already stated a higher yield of valuable by-products consisting of the alkyl-aromatic compounds may be obtained by maintaining the temperatures slightly below atmospheric. In regard to pressures there is usually no special advantage to be gained by using pressures greater than ordinary atmospheric though the invention is not confined to such use of pressure and at times the reactions may be accelerated by increasing the total pressure on the system.

The mixed type hydrocarbons produced in removing the gum-forming hydrocarbons from gases are quite uniformly of high antiknock value when used as blending materials in commercial gasolines, many of the compounds having an antiknock value equivalent to from 75 to 100 percent of that of iso-octane which is employed at the present time as a reference standard in evaluating engine fuels.

As an example of the improvement produced in a commercial fuel gas by treating it by the process of the present invention, the case of a gas produced by blending water-gas with gases from an oil cracking plant to produce a mixture containing 75 percent of the former and 25 percent of the latter may be considered. The gas of the cracking plant may have the following approximate composition:

	Per cent
Hydrogen	12
Methane	45
Ethane	16
Ethylene	5
Propane	7
Propylene	4
Butanes	3
Butylenes	1
Pentanes	2
Amylenes	1
Miscellaneous heavier hydrocarbons	4

In using this blend considerable gummy deposit was noticed around the tip of a small pilot burner which was kept continuously in operation to insure the ignition of the main burner in a hot water heater after a period of about a month. In another two weeks the flame had decreased considerably in size, due to tarry deposits and was in danger of being blown out by accidental drafts.

The blend of water-gas and cracked gas was then treated according to the process of the invention by passing it through a well agitated mixture consisting of 20% by volume of 66 Bé. sulfuric acid and 80% by volume of a commercial toluol fraction, the temperature being held at approximately 50° F. during the treatment. When the gas thus treated was used in the same pilot burner, as before, there was no evidence of gummy deposit after a period of three months continuous service.

The novel character and utility of the process of the present invention is evident from the foregoing description of its character and the example of results obtainable by its use, but the invention is broad in scope and may be applied in many different ways to other gas mixtures than the one mentioned in the example. Hence, the invention is not limited to the descriptive material nor the numerical data presented.

I claim as my invention:

1. A process for purifying fuel gases containing gum-forming olefins and for converting the latter into more valuable products, which comprises contacting the fuel gas with an aromatic hydrocarbon and reacting the latter with the gum-forming olefin content of the gases, separating the resultant alkylation products from the gas, and recovering the thus purified gas and separated alkylation products.

2. A process for purifying fuel gases containing gum-forming olefins and for converting the latter into more valuable products, which comprises contacting the fuel gas with benzol and alkylating the latter with the gum-forming olefin content of the gas, separating the resultant alkylation products from the gas, and recovering the thus purified gas and separated alkylation products.

3. A process for purifying fuel gases containing gum forming olefins and for converting the latter into more valuable products, which comprises scrubbing the fuel gas with a mixture of sulphuric acid and aromatic hydrocarbon to form alky-acyl derivatives whereby the gum-forming olefins are separated from the gas, and recovering the thus purified gas and said derivatives.

4. The process as defined in claim 2 further characterized in that the alkylation of the benzol with said gum-forming olefins is effected in the presence of sulphuric acid.

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