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2,742,402

**SOLID CAUSTIC ALKALI AND PHENOL REAGENT
FOR TREATMENT OF HYDROCARBONS****Lewis M. Browning, Jr., Woodbury, N. J., assignor to
Socony Mobil Oil Company, Inc., a corporation of New
York****No Drawing. Application December 26, 1951,
Serial No. 263,465****4 Claims. (Cl. 196—32)**

The present invention relates to the treatment of hydrocarbons with solid caustic to remove weakly acidic organic compounds and, more particularly, to the treatment of hydrocarbons with an improved solid caustic to remove weakly acidic organic compounds, especially mercaptans.

The problem of removing acidic organic materials and particularly mercaptans from hydrocarbon mixtures has received considerable attention in recent years. In general, removal of mercaptans from mixtures of hydrocarbons is accomplished by extracting the mercaptans from the hydrocarbon mixture with a solution of alkali metal hydroxide. Initially, aqueous solutions of sodium or potassium hydroxide were used. The extractive ability of such aqueous solutions was improved later by the addition of organic compounds, known to the art as solutizers, such as isobutyric acid, tannic acid, naphthenic acids and alkyl phenols. More recently the use of isobutyric acid has ceased apparently because of its disappearance from the competitive market. On the other hand, the use of alkyl phenols has probably increased due to the fact that alkyl phenols are present in most catalytically cracked gasolines and are readily adsorbed in or extracted by aqueous caustic solutions with which the petroleum fractions are brought in contact. Generally speaking, aqueous caustic solutions used for the extraction of mercaptans from admixtures with hydrocarbons, such as petroleum fractions and particularly gasoline contaminated with mercaptans, usually contain an amount of alkyl phenols sufficient to neutralize about 20% to about 50% of the alkali metal hydroxide. The maximum alkyl phenol content is limited by the viscosity of the aqueous alkali metal hydroxide-alkylphenolate solution and is different for sodium hydroxide solutions and potassium hydroxide solutions of the same phenolate concentration.

More recently, it has been proposed that weakly organic material be removed from mixtures with hydrocarbons with finely divided solid anhydrous alkali metal hydroxide. The use of finely divided solid anhydrous alkali metal hydroxide for the removal of weakly acid organic material from admixture with hydrocarbons is disclosed and claimed by Kalichevsky et al. in U. S. Patent No. 2,311,593. These patentees disclose the use of finely divided alkali metal hydroxides for the removal of mercaptans from hydrocarbon mixtures such as petroleum fractions. Kalichevsky and his colleagues state:

"Anhydrous sodium hydroxide is capable of removing quantitatively mercaptans from petroleum oils provided sufficient time is allowed for completing the reaction. With some gasolines containing higher mercaptans, from two to twenty-four hours of continuous agitation may be necessary to sweeten the gasoline, depending upon the state of sub-division of the reagent. In addition, the

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surface of the sodium hydroxide particles is quickly coated with the adsorbed layer of mercaptides, thus preventing further reaction. For this reason, the quantity of sodium hydroxide required to sweeten gasoline is much greater than theoretical. We have found that both the time of the reaction and the quantity of sodium hydroxide required for sweetening gasoline depends primarily on the surface of sodium hydroxide exposed to gasoline rather than on the total quantity of sodium hydroxide present."

These patentees then state that the maximum diameter of particles of alkali metal hydroxide used for the purpose of removing mercaptans from gasoline containing 0.0092% mercaptan sulfur in 30 minutes should not be greater than 0.000048 centimeter. However, in general, the particles of finely divided solid anhydrous alkali metal hydroxide should be of colloidal size, i. e., the particles should have diameters between 0.00001 centimeter and 0.0000001 centimeter.

The present invention is concerned with a finely divided solid anhydrous alkali metal hydroxide reagent of enhanced capability to extract weakly acidic organic material such as mercaptans from mixtures of hydrocarbons such as petroleum fractions.

The finely divided solid anhydrous alkali metal hydroxide can be prepared either by the methods suggested in U. S. Patent No. 2,311,593 or by the method described in co-pending application for United States Letters Patent No. 263,461, filed December 26, 1951, now U. S. Patent 2,718,458, in the name of Lewis M. Browning, Jr. The finely divided solid anhydrous caustic is then treated to incorporate a small amount of cresols in the particles of caustic. However, it is preferred to add small amounts of alkyl phenols to aqueous solutions of alkali metal hydroxide and then to dehydrate the aqueous solution as disclosed in the aforesaid co-pending application.

The finely divided solid anhydrous alkali metal hydroxide containing not more than about 0.135 pound of cresol per pound of MOH (where M is an alkali metal) calculated as NaOH (dry basis), is contacted with the mixture of hydrocarbon or hydrocarbons and weakly acidic organic material either in batch or continuous operation. Thus, for example, gasoline can be placed in a container equipped with a stirrer, and the calculated dosage (say 200% of theory) of finely divided solid anhydrous sodium hydroxide, containing not more than 0.135 pound of alkyl phenols per pound of sodium hydroxide, is introduced into the gasoline and the mixture stirred until the mercaptan-sulfur content of the gasoline has been lowered to a predetermined value. The treated gasoline is then separated from the finely divided solid anhydrous sodium hydroxide-phenolate, water-washed, and sent to storage or further treatment.

On the other hand, a column of hydrocarbon to be treated is established and finely divided solid anhydrous caustic-phenolate is introduced into the column near the top thereof and withdrawn at the bottom whilst withdrawing treated hydrocarbon at the top and introducing hydrocarbon to be treated near the bottom.

The temperature of treatment is substantially that used in conventional liquid-liquid extraction of mercaptans from petroleum fractions.

Indicative of the critical limits of the concentration of alkylphenols in the particles of finely divided solid anhydrous alkali metal hydroxide necessary to produce the improved reagent are the following data obtained when treating in a single stage extraction a mixture of isooctane

and n-butyl mercaptan with 200% of the theoretical amount of NaOH except where otherwise noted.

liquid, withdrawing said cooled particles, introducing said particles into a petroleum fraction containing mercaptans,

Test No.	Percent Wt. NaOH Converted to Na ϕ	Lbs. Na ϕ per Lb. NaOH	Wt. Percent NaOH in Solid Caustic	Lbs. NaOH Per 1,000 lbs. (1)	Extraction		
					RSH-S Original	Percent Wt. After Treatment	Removed
1.....	0	0.00	93.0	608+	0.095	0.0060	93.7
2.....	1	0.02	87.0	922+	0.144	0.0008	99.4
3.....	5	0.135	83.0	640+	0.100	0.0033	96.7
4.....	10	0.27	76.0	608+	0.095	0.0123	87.2
5.....	50	1.35	60.9	608+	0.095	0.0426	55.2
6.....	50	1.35	60.9	1,280*	0.100	0.0214	78.6

Na ϕ —Sodium alkyl phenolates.

(*)—200% theoretical dosage.

(*)—400% theoretical dosage.

(1)—Caustic dosage based upon total alkalinity of solid caustic.

Structurally, the alkyl phenols have a benzene ring with an OH-group attached to one of the carbon atoms of the benzene ring with or without one or more alkyl groups attached to one or more of the remaining carbon atoms of the ring. Accordingly, the cresylic acid, or alkyl phenols or cresols, use of which is disclosed herein, contain some phenol, i. e., C₆H₅OH as well as CH₃C₆H₄OH and/or higher homologues.

It is to be noted that aqueous solutions containing as much as 65 to 70 per cent alkali metal hydroxide can be used in preparing the finely divided solids, or solutions containing about 20 to about 30 weight per cent alkali metal hydroxide can be used. When the finely divided solid anhydrous alkali metal hydroxide is prepared from aqueous solutions containing about 20 to about 30 weight per cent alkali metal hydroxide, the particles of solid alkali metal hydroxide obtained therefrom tend to be smaller in particle size.

I claim:

1. A method of removing mercaptans from a petroleum fraction which comprises establishing a column of water-immiscible liquid, introducing heated vapors of said water-immiscible liquid into the base of said column in an amount sufficient to raise the temperature of said column to the boiling point of said water-immiscible liquid, introducing into said column at the upper surface thereof a plurality of fined droplets of an aqueous solution containing about 20 to about 70 per cent alkali metal hydroxide and 0.02 to about 0.135 pound of alkyl phenols per pound of alkali metal hydroxide, thereby forming a suspension of droplets of said aqueous solution in said column of water-immiscible liquid, evaporating water from said droplets thereby raising the density of said droplets as said droplets fall in said column until substantially all of the water of the droplets is evaporated and particles of a solid mixture of alkali metal hydroxide and alkali metal alkyl phenolate containing 0.02 to about 0.135 pound of alkyl phenols per pound of alkali metal hydroxide are formed, allowing said particles to fall below the point of introduction of said heated vapors into a cooling zone containing said water-immiscible liquid, cooling said particles as a suspension in said water-immiscible

and separating treated petroleum fraction from particles of a solid mixture of alkali metal hydroxide and alkali metal alkyl phenolate.

2. The method of removing mercaptans from a petroleum fraction as set forth and described in claim 1 wherein the water-immiscible liquid is a petroleum naphtha.

3. In the method of preparing a reagent for the extraction of mercaptans from hydrocarbons admixed therewith which comprises establishing a column of water-immiscible liquid, introducing heated vapors of said water-immiscible liquid into said column at the base thereof in amounts sufficient to raise the temperature of said column to the boiling point of said water-immiscible liquid, introducing into said column at the upper surface thereof a plurality of fine droplets of an aqueous solution containing alkali metal hydroxide, evaporating water from said droplets as said droplets fall through said column of water-immiscible liquid until substantially all of said water is evaporated and particles of solid sodium hydroxide are formed, allowing said particles to continue to fall through said water-immiscible liquid past said point of introduction of heated vapors of said water-immiscible liquid into a cooling zone and cooling said particles of alkali metal hydroxide suspended in said water-immiscible liquid and withdrawing said cooled particles of solid alkali metal hydroxide, the improvement which comprises employing a solution of alkali metal hydroxide containing about 20 to about 70 per cent alkali metal hydroxide and 0.02 to about 0.135 pound of alkyl phenols per pound of alkali metal hydroxide.

4. The method of preparing a reagent for the extraction of mercaptans from hydrocarbons admixed therewith and set forth and described in claim 3 wherein the alkali metal hydroxide is sodium hydroxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,535,833	Bond	Dec. 26, 1950
2,538,287	Voorhees	Jan. 16, 1951
2,574,122	Ryder	Nov. 6, 1951
2,596,175	Rosenstein	May 13, 1952
2,623,008	Kleiss	Dec. 23, 1952