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PROCESS FOR RECOVERY OF PHOSPHORIC ACID

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The present invention relates to a process for the recovery of phosphoric acid from acid sludge containing the same.

The use of phosphoric acid in the refining of hydrocarbon distillates is known. For example, hydrocarbon distillates either in the liquid or vapor phase may be conducted at temperatures between about 300° and 750° F. over or through a stationary bed of a contact reagent comprising phosphoric acids deposited on firebrick, metallurgical coke, or the like. In contact with the hydrocarbons, the acid catalyst is gradually spent, and when it is finally exhausted the treatment is interrupted. Residual phosphoric acid may be removed from the carrier by washing it with water, acetone or other suitable solvent for phosphoric acid and may thus be recovered in part. The coke is then drenched with a strong solution of fresh phosphoric acid and the resulting mass is dried. Thereafter the refining treatment may be resumed.

While the above method is capable of effectively refining hydrocarbons containing unstable compounds to yield distillates of satisfactory stability, it is somewhat cumbersome in the matter of regenerating the refining reagent, the cost of the regeneration of the catalyst constituting a large part of the total refining cost.

In a more recently discovered phosphoric acid treating process, for example, as described in detail in co-pending application U. S. Patent 2,224,636, issued December 10, 1940, in the name of George A. Lorenz, it has been found that unstable hydrocarbon distillates can be refined satisfactorily by contacting them in a suitable refining zone, while in a heated condition, with an aqueous solution of phosphoric acid in an amount which is just sufficient to effect the desired degree of refining and which is completely consumed, i. e. converted to acid sludge, in a once through operation, and to produce two layers only, a hydrocarbon layer and a sludge layer. The hydrocarbon layer may consist of two phases, i. e. it may be gaseous or liquid or both. If an excess of phosphoric acid is used, then three layers will separate, namely a hydrocarbon layer which also may be vapor or liquid or both, a layer consisting essentially of free phosphoric acid with varying amounts of water, and a sludge layer. It is an essential of this particular refining process that the maximum amount of phosphoric employed be less than that required to cause the separation of free phosphoric acid layer after prolonged standing, i. e., in the successful operation of the process there will be no layer of free phosphoric acid separated.

The purpose of the present invention relates particularly to the recovery of phosphoric acid from an acid sludge such as is produced in the last outlined process above. Another purpose of the instant invention is to provide a process for recovering phosphoric acid from such a sludge wherein a minimum amount of the phosphoric acid is consumed. Still further it is the purpose of this invention to provide a recovered phosphoric acid which is suitable for reuse in the treating process, all of these purposes being realized in an efficient and relatively simple manner, utilizing equipment requiring a minimum capital outlay.

Oils susceptible to the above treatment are in particular cracked gasoline distillates, although the process is applicable as well to special aromatic solvents, cracked tractor fuels having boiling ranges from about 200° F. up to about 575° F., distillate fuels such as the No. 1 to No. 3 fuel oils by the A. S. T. M. specification D396–34T, which oils may boil between about 300°–700° F., etc. A common defect of burners designed to operate on distilled fuel oils is a clogging of the screen through which the fuel must pass before combustion. This difficulty is largely overcome with treating the distillate fuel oils by the above process. Moreover, as a result of the treatment, carbon forming bodies which have a tendency to cause soot are at least partially eliminated.

The sludge formed in the above process as the result of the contact between a small amount of the phosphoric acid and the hydrocarbons is substantially free from water, has the appearance of a homogeneous mass, but actually contains substantial amounts of free or very loosely bound phosphoric acid, which is insufficient in amount, however, to form a separate phase. This sludge may be semi-solid or liquid under the conditions of the treatment. It dsposits on the packing, and if sufficiently liquid, runs down to the bottom of the treating zone from which it can be withdrawn. If it is semi-solid, it may clog the packing and force a shut-down of the treating operation. Obviously, for a continuous operation, the sludge should be sufficiently liquid so that the clogging will not occur. It has been found that formation of a liquid, though viscous sludge, is favored if nitrogen bases are removed from the distillates prior to subjecting them to treatment. This may be accomplished by washing the distillates at about normal room temperature with aqueous solutions of sulphuric or other suitable acids which

are sufficiently diluted so that they will not substantially react with unsaturated hydrocarbons under the conditions of the washing. Removal of the nitrogen bases has the additional obvious advantage of materially reducing the consumption of the rather expensive phosphoric acid.

Besides nitrogen bases, mercaptans, and other acidic compounds may be, if desired, removed by a suitable pretreatment such as washing with aqueous caustic alkali. However, acidic impurities do not normally materially influence the effectiveness of my treatment; except that certain acidic compounds such as alkyl phenols which are powerful natural gum inhibitors, when allowed to stay in the distillate, improve its stability after treatment.

As previously mentioned, the sludge is free from water, and although apparently homogeneous when emerging from the treating zone, is acid reacting and contains substantial amounts of free or very loosely bound phosphoric acid which amounts, however, are insufficient to form a separate phase. It is corrosive to many materials in contrast to the sludge formed by similar treatment with sulfur acids described in my copending applications Serial No. 208,697, filed May 18, 1938, and Serial No. 208,698, filed May 18, 1938.

The treater bottoms (including the "sludge") may vary from a very fluid liquid containing a large proportion of gasoline to a thick, viscous mass resembling an asphaltic flux. Whatever their physical condition, the treater bottoms contain practically all the unreacted phosphoric acid and phosphoric acid derivatives that are removed from the treating tower. Whereas phosphoric acid is insoluble in the hydrocarbons constituting the treater bottoms, the phosphoric acid derivatives (phosphates of nitrogen bases and possibly alkyl phosphates) are slightly soluble in the hydrocarbons of high molecular weight so that this combined phosphoric acid does not separate quantitatively from the treater bottoms. This material, insoluble in the hydrocarbon layer, or "sludge," separates from the treater bottoms, the rapidity of the separation depending upon the greater or lesser fluidity of the latter.

If the treating distillate is substantially free from nitrogen bases, due to pretreatment of the feed with acids as hereinbefore mentioned, a large portion, usually about 90% or more, of the phosphoric acid consumed in the treatment may be recovered in the following manner: The acid sludge is first separated from entrained hydrocarbon oil by any of the known gravitational separation methods, after being first diluted with a suitable diluent to facilitate separation if necessary; the upper oil layer is then decanted and the sludge layer washed, repeatedly, if necessary, with a light hydrocarbon oil such as naphtha, gasoline or the like and the sludge layer finally hydrolyzed at an elevated temperature, preferably not below about 200° F., as by steaming or heating it with water, if desired, under superatmospheric pressure sufficient to materially raise the treating temperature to above the normal boiling point of water.

It has been found that to attempt to hydrolyze the sludge in the known manner, i. e., without the above described pretreatment, is impractical, due to the presence of oil soluble emulsifiers (apparently phosphates) in the sludge. When these compounds have not been removed from the sludge, addition of water or a diluent and water results in such stable emulsions that they have not broken in some cases after as long as two weeks standing. By first extracting these emulsification agents with a suitable solvent, emulsions are no longer observed. As extracting agents, practically all solvents in which these oil-soluble phosphates are soluble are useful. Relatively water-soluble normally liquid compounds such as lower molecular weight alcohols, for example, isopropyl; ketones, for example, acetone and methyl ethyl ketone; ethers, for example, morpholine and dioxane and in fact any similar materials having the desired solvent properties for such phosphate compounds will usually be found acceptable for the present purpose. On the other hand, relatively water-insoluble normally liquid compounds such as the higher molecular weight alcohols, ketones, ethers, etc., as well as aromatic hydrocarbons having less than 10 carbon atoms, such as benzene, may be used equally well. The preferred solvents for these undesirable compounds, however, are light hydrocarbon oils, such as gasolines, naphthas, etc., and in fact the hydrocarbon being treated according to the described stabilizing process will, in most cases, be found satisfactory.

At substantially atmospheric pressure, a treating time of about 1 to 8 hours and more often 2 to 4 hours for hydrolysis and liberation of readily hydrolyzable phosphoric acid is usually sufficient. After complete hydrolysis, water should be present in such quantity that the concentration of phosphoric acid in the aqueous layer be from 2 to 30%, preferably about 10%. Such a solution will easily separate from the organic residue. The hydrolyzed mixture is allowed to settle, preferably while hot, whereby a lower aqueous solution of phosphoric acid is formed, which may be used in the above described refining process without further purification, concentration or other treatment, or, may if desired be further concentrated by the known methods. The upper hydrocarbon layer which forms comprises various polymers, some of which have the properties of useful resins, as well as higher alcohols, tars, etc.

As a specific example of a preferred method of recovering phosphoric acid, the following may be cited:

10 gallons of acid sludge obtained in the described refining process were first washed with 50 gallons of untreated gasoline, which was decanted after proper settling, then with 30 gallons of gasoline which was also decanted after settling. The gasoline washed sludge was then mixed with 50 gallons of water, the mixture being agitated and simultaneously held at approximately 212° F. for 30 minutes. The hydrolyzed sludge was then allowed to settle while hot and the lower aqueous phosphoric acid layer drawn off.

Subsequent analysis revealed that approximately 97% of the titratable phosphoric acid (free and partially combined phosphoric acid) was recovered in the dilute phosphoric acid solution.

I claim as my invention:

1. In a process for recovering phosphoric acid from acid sludge containing the same, said sludge being obtained in a refining process wherein hydrocarbons are treated with phosphoric acid under conditions to produce a sludge which contains insufficient free acid to form a separate layer of free acid upon standing, the steps comprising washing said acid sludge with a solvent

for oil soluble phosphates to form two liquid layers, an upper solvent layer containing substantially all oil soluble phosphates originally present in such acid sludge and a lower sludge layer substantially free of oil soluble phosphates, separating said upper solvent layer from said lower sludge layer, hydrolyzing said lower sludge layer to form two liquid layers, an upper layer containing hydrolyzed organic material and a lower aqueous phosphoric acid layer and subsequently separating said last named two layers.

2. In a process for recovering phosphoric acid from acid sludge containing the same, said sludge being obtained in a refining process wherein hydrocarbons are treated with phosphoric acid under conditions to produce a sludge which contains insufficient free acid to form a separate layer of free acid upon standing, the steps comprising washing said acid sludge with a substantially water-immiscible solvent for oil soluble phosphates to form two liquid layers, an upper solvent layer containing substantially all oil soluble phosphates originally present in said acid sludge and a lower sludge layer substantially free of oil soluble phosphates, separating said upper solvent layer from said lower sludge layer, hydrolyzing said lower sludge layer to form two liquid layers, an upper layer containing hydrolyzed organic material and a lower aqueous phosphoric acid layer and subsequently separating said last named two layers.

3. In a process for recovering phosphoric acid from acid sludge containing the same, said sludge being obtained in a refining process wherein hydrocarbons are treated with phosphoric acid under conditions to produce a sludge which contains insufficient free acid to form a separate layer of free acid on standing, the steps comprising washing said acid sludge with a substantially water-soluble solvent for oil soluble phosphates to form two liquid layers, an upper solvent layer containing substantially all oil soluble phosphates originally present in said acid sludge and a lower sludge layer substantially free of oil soluble phosphates, separating said upper solvent layer from said lower sludge layer, hydrolyzing said lower sludge layer to form two liquid layers, an upper layer containing hydrolyzed organic material and a lower aqueous phosphoric acid layer and subsequently separating said last named two layers.

4. In a process for recovering phosphoric acid from the acid sludge containing the same, said sludge being obtained in a refined process wherein hydrocarbons are treated with phosphoric acid under conditions to produce a sludge which contains insufficient free acid to form a separate layer of free acid on standing, the steps comprising washing said acid sludge with a light hydrocarbon oil to form two liquid layers, an upper hydrocarbon layer containing substantially all oil soluble phosphates originally present in said acid sludge and a lower sludge layer substantially free of oil soluble phosphates, separating said upper hydrocarbon layer from said lower sludge layer, hydrolyzing said lower sludge layer to form two liquid layers, an upper layer containing hydrolyzed organic material and a lower aqueous phosphoric acid layer and subsequently separating said last named two layers.

5. In a process for recovering phosphoric acid from acid sludge containing the same, said sludge being obtained in a refining process wherein hydrocarbons are treated with phosphoric acid under conditions to produce a sludge which contains insufficient free acid to form a separate layer of free acid upon standing, the steps comprising washing said acid sludge with a solvent for oil soluble phosphates to form two liquid layers, an upper solvent layer containing substantially all oil soluble phosphates originally present in said acid sludge and a lower sludge layer substantially free of oil soluble phosphates, separating said upper solvent layer from said lower sludge layer, hydrolyzing said lower sludge layer with approximately five volumes of water at a temperature of at least 200° F. to form two liquid layers, an upper layer containing hydrolyzed organic material and a lower aqueous phosphoric acid layer and subsequently separating said last named two layers.

6. In a process for recovering and utilizing phosphoric acid from acid sludge containing the same, said sludge being obtained in a refining process wherein unstabilized hydrocarbons are contacted in a treater with phosphoric acid under conditions to produce a sludge which contains insufficient free acid to form a separate layer of free acid upon standing, the steps comprising washing said acid sludge with a solvent for oil soluble phosphates to form two liquid layers, an upper solvent layer containing substantially all oil soluble phosphates originally present in said acid sludge and a lower sludge layer substantially free of oil soluble phosphates, separating said upper solvent layer from said lower sludge layer, hydrolyzing said lower sludge layer to form two layers, and upper layer containing hydrolyzed organic material and a lower aqueous phosphoric acid layer, separating said last named two layers and thereafter returning said aqueous phosphoric acid layer to said treater for further contact with unstabilized hydrocarbons.

7. In a process for recovering and utilizing phosphoric acid from acid sludge containing the same, said sludge being obtained in a refining process wherein unstabilized hydrocarbons are contacted in a treater with phosphoric acid under conditions to produce a sludge which contains insufficient free acid to form a separate layer of free acid upon standing, the steps comprising washing said acid sludge with at least five volumes of a light hydrocarbon oil to form two liquid layers, an upper hydrocarbon layer containing substantially all oil soluble phosphates originally present in said acid sludge and a lower acid sludge layer substantially free of oil soluble phosphates, separating said upper hydrocarbon layer from said lower acid sludge layer, hydrolyzing said acid sludge layer with approximately five volumes of water at a temperature of at least 200° F. to form at least two layers, an upper layer containing hydrolyzed organic material and a lower aqueous phosphoric acid layer, separating said last named two layers and thereafter returning said aqueous phosphoric acid layer to said treater for further contact with unstabilized hydrocarbons.

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