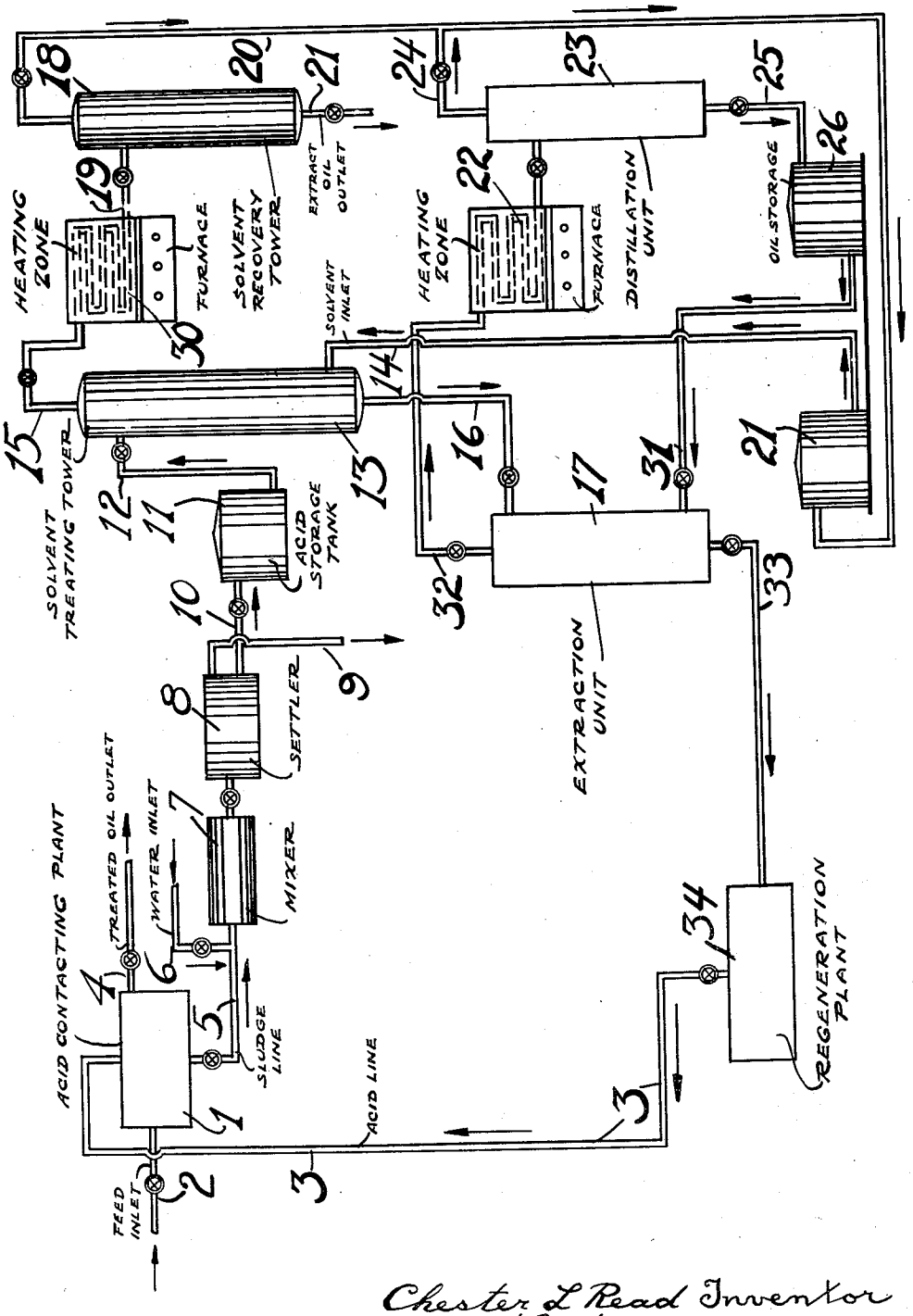
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PROCESS OF RECOVERING SULPHURIC ACID FROM SPENT SULPHURIC ACID

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PROCESS OF RECOVERING SULPHURIC ACID FROM SPENT SULPHURIC ACID

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8 Claims. (Cl. 23—173)

The present invention relates to the refining of mineral oils. The invention is especially concerned with the recovery of mineral acids used in the refining of petroleum oils. In accordance with the present process, spent acids secured in the refining of mineral oils and in the manufacture of intermediate products such as alcohols, esters, and ethers from olefins are re-extracted in an efficient and economical process in a manner whereby increased yields of high quality regenerated acids are secured. The process essentially comprises a two-stage operation in which the spent acid secured from these operations is treated in an initial stage with a primary solvent of the character of phenol and further treated in a secondary stage with a secondary mineral oil solvent. The acid after removal from the mineral oil is reconcentrated in any desirable manner and recycled to the system.

It is well known in the art to refine mineral oils, utilizing various inorganic acids. For example, it is known to remove sulphur compounds and various other deleterious substances from petroleum fractions, particularly those fractions boiling in the motor fuel boiling range, by treating the same with sulphuric acids of various concentrations. It is also known to produce various products, as for example, alcohols, esters, and ethers from olefins utilizing sulphuric acid as a reagent. These processes are commercially justified to a large extent upon the efficiency and the cost of regenerating the various reagents, particularly the sulphuric acid. Thus, suggestions have been made that spent acids secured in the processing of mineral oils be hydrolyzed and treated with a selective solvent of the class which have a preferential selectivity for the relatively more aromatic constituents as compared to the relatively more paraffinic constituents as for example phenols, beta-beta-dichlor-diethyl ether and nitro benzene prior to concentrating the acid by the application of heat or other means. Processes of this character represent distinct improvements in the acid regeneration cycle. Suitable selective solvents for extracting the spent acid are quite expensive and every effort is exerted to avoid loss of the same. However, loss of solvent has not been entirely prevented in processes of this character due to the fact that an appreciable quantity is soluble in the acid liquor, is thus removed with the same and lost when the acid is re-concentrated by the application of heat. I have now discovered an improved process by which spent acids may be economically processed for the production of high quality acids which may be readily recycled to the system and in which loss of valuable reagent is substantially completely eliminated. The process of my invention may be readily understood by reference to the attached drawing illustrating modifications of the same. Feed oil, which for the purposes of illustration is taken to be a petroleum oil boiling in the motor fuel boiling range, is introduced into acid treating plant 1 by means of feed line 2, wherein it is contacted with sulphuric acid which is introduced by means of feed line 3. The treated oil is removed from acid treating plant 1 by means of line 4, while the acid sludge is removed by means of line 5. The acid sludge containing tarry hydrocarbon materials is then hydrolyzed with water which is introduced by means of line 6. The mixture is then passed through mixer 7 and into settler or equivalent means 8. The precipitated tarry hydrocarbon materials are withdrawn from settling unit 8 by means of line 9, while the hydrolyzed spent acid is withdrawn by means of line 10 and introduced into acid storage 11. The spent weak acid is withdrawn from storage 11 by means of line 12, and passed to solvent treating plant 13, which for the purposes of description is taken to be a countercurrent solvent treating tower. The spent acid flows downwardly through tower 13 and contacts an upflowing solvent of the character of phenol as for example cresol, which is introduced into solvent treating tower 13 by means of line 14. Temperature and pressure conditions are adapted to secure the formation of a solvent phase which is withdrawn from tower 13 by means of line 15 and an acid phase substantially free of oily materials which is withdrawn by means of line 16. The solvent phase may be passed through heating zone 30 and is then introduced into solvent recovery tower 18 by means of line 19. Temperature and pressure conditions are adjusted in tower 18 adapted to remove overhead substantially pure phenol by means of line 20 and to remove as a bottoms a solvent-free extract oil by means of line 21. The solvent removed overhead from solvent recovery tower 18 by means of line 20 is passed to solvent storage 21 from which it is preferably recycled to solvent treating tower 13. The acid phase withdrawn from tower 13 by means of line 16 containing dissolved therein an appreciable amount of the cresol is then passed to secondary extraction unit 17, wherein it is contacted with a secondary non-reactive petroleum oil solvent which is in-

troduced by means of line 31. For purposes of illustration it is assumed that contacting plant 17 comprises a countercurrent solvent treating tower. Temperature and pressure conditions are adapted to remove by means of line 32 a secondary oil solvent and cresol phase substantially free of acid and to remove by means of line 33 an acid phase substantially free of secondary oil solvent and cresol. This latter phase is passed to regeneration plant 34 which may comprise any desirable number and arrangement of stages in which the acid is concentrated to the desired extent by the removal of water. The regenerated acid is withdrawn from regeneration plant 34 by means of line 3 and recycled to acid treating plant 1. The secondary oil solvent phase withdrawn by means of line 32 is passed to heating zone 22 and introduced into distillation unit 23. Temperature and pressure conditions are adapted to remove overhead from unit 23 by means of line 24 the phenolic solvent which is passed to storage 21. The secondary petroleum oil solvent is withdrawn from unit 23 by means of line 25 and passed to secondary solvent storage 26 from which it is recycled to extraction zone 17 by means of line 18.

The process of the present invention may be widely varied. The invention may be readily adapted to the recovery of phenolic type solvents utilized in the regeneration of spent acids secured in various refining and related operations. The process, however, is particularly applicable in the recovery of phenol utilized in the regeneration of spent acids secured in the refining of petroleum oils boiling in the motor fuel boiling range. Although the present process may be adapted under certain conditions for the treatment of acids of any concentration particularly desirable results are secured providing the spent acid be diluted to a concentration of from 30% to 60% preferably to about 40% to 50% prior to extracting the same with a phenol. The preferred concentration will vary to some extent since as the molecular weight of the monophenols is increased the solubility in weak sulphuric acid solutions is decreased. Methyl phenol, for example, is 50% as soluble as monohydroxy phenol. The solubilities of the high molecular weight phenols are low but as the molecular weight increases the boiling point likewise increases and the difficulty of recovering the solvent from the extract oil is similarly increased.

Although in general solvents selected from the class of solvents which have a preferential selectivity for the relative more aromatic constituents of a petroleum oil as compared to the relative more paraffinic constituents may be used for extracting the spent acid as for example nitro benzene and beta-beta-dichlor-diethyl ether it is preferable to employ phenolic type solvent. The amount of the phenolic type primary solvent employed to extract the spent acid may vary considerably, depending upon the concentration of the acid and the character of the impurities dissolved therein. In general, when treating sulphuric acid having a concentration in the range from about 30% to 60% with a phenol it is preferred to use from 0.1 to 1.0 volume preferably from 0.4 to 0.6 volume of a phenol per volume of spent acid. The temperature and pressure conditions likewise may vary considerable, depending upon operating conditions. In general, it is preferred to employ atmospheric temperatures and pressures.

The secondary solvent utilized comprises a petroleum oil which is substantially non-reactive with the spent acid. The secondary solvent is preferably a highly paraffinic petroleum oil fraction having a gravity in the range from about 25° A. P. I. to 35° A. P. I. It is likewise preferred that the boiling range be from about 500° F. to 700° F. Any highly paraffinic petroleum oil having an initial boiling point of about 50° F. or more above the boiling range of the primary solvent however may be used. The quantity of secondary solvent employed will depend upon the particular primary solvent used, as well as upon other operating conditions. In general, it is preferred to use from 0.1 to 1.0 volume preferably from 0.4 to 0.6 volume of secondary solvent per volume of spent acid.

In order to further illustrate the invention, the following examples are given which should not be construed as limiting the same in any manner whatsoever:

Example 1

Various tests were made to determine the solubility of methyl phenol and phenol in sulphuric acid of varying concentrations. The results of these tests are as follows:

Solubility of phenol and cresol in H_2SO_4 at +75° F.

Acid conc. percent	Cresol solubility		Phenol solubility	
	Percent by wt.	Percent of H_2SO_4	Percent by wt.	Percent of H_2SO_4
0	3.2		8.5	
11	1.6			
26	0.5	1.9	0.8	3.1
40	0.45	1.15	1.0	2.4
64	0.8	1.25	1.85	2.9
80	(1)	(1)	(1)	(1)

[1] Miscible.

Example 2

A spent sulphuric acid secured in the treatment of a petroleum naphtha boiling in the motor fuel boiling range was hydrolyzed to approximately 40% concentration. The spent acid had a 5% carbon content. This acid was batch extracted with 50% of cresylic acid which produced an acid product having 0.2% carbon and 0.5% of cresylic acid dissolved in the sulphuric acid. The cresylic acid was substantially completely recovered from the acid by extracting the same with a petroleum oil secondary solvent derived from a Mid-Continent lube distillate. The secondary solvent had a Saybolt viscosity at 210° of 60 and a 450° flash. The results of these operations were as follows:

Percent of secondary solvent based on weak acid solution	Percent of cresylic acid recovered
10	40
25	82
50	96

The process of the present invention is not to be limited by any theory or mode of operation, but only in and by the following claims in which it is desired to claim all novelty in so far as the prior art permits.

I claim:

1. Process for the regeneration of a spent sulphuric acid secured from petroleum oil refining operations comprising hydrolyzing said spent acid and then countercurrently contacting the same with a primary phenol solvent under con-

ditions to form a solvent phase and an acid phase containing an appreciable amount of the primary solvent, countercurrently contacting said acid phase with a highly paraffinic oil fraction having a gravity in the range of about 25° A. P. I. to 35° A. P. I. under conditions to form a highly paraffinic oil phase containing dissolved therein said appreciable amount of primary solvent and an acid phase, reconcentrating said acid and separating said appreciable amount of the primary solvent from the highly paraffinic oil fraction.

2. Process in accordance with claim 1 in which said spent acid is hydrolyzed to an acid concentration of from 30% to 60%.

3. Process in accordance with claim 1 in which said spent acid is hydrolyzed to about 40% to 50% acid concentration and said primary solvent is cresol.

4. Process in accordance with claim 1 in which said spent acid is contacted with from 0.4 volume to 0.6 volume of primary solvent per volume of spent acid and in which said acid phase derived from the initial extraction is contacted with from 0.4 volume to 0.6 volume of a highly paraffinic petroleum oil fraction having a gravity in the range from about 25° A. P. I. to 35° A. P. I. per volume of acid phase.

5. Process in accordance with claim 1 in which said primary solvent is cresol.

6. Process in accordance with claim 1 in which said primary solvent is cresol and in which from about 0.4 volume to 0.6 volume of phenol and highly paraffinic petroleum oil are employed per volume of feed to the respective extraction stages.

7. Process for the regeneration of a spent sulphuric acid containing dissolved carbonaceous constituents secured in the treatment of petroleum oils comprising contacting a spent sulphuric acid with a primary solvent selected from the class consisting of phenols, nitrobenzene, and beta-beta-dichlor diethyl ether under conditions to form a primary solvent extract phase containing said carbonaceous constituents and a spent acid phase containing an appreciable amount of said primary solvent, separating the spent acid phase from the primary solvent extract phase and contacting said spent acid phase with a highly paraffinic petroleum oil solvent having a gravity in the range from about 25° A. P. I. to about 35° A. P. I. under conditions substantially completely to remove this primary solvent from said spent acid and to form a highly paraffinic petroleum oil phase containing dissolved therein said primary solvent and a spent acid phase, separating the respective phases, regenerating said spent acid phase and recovering said primary solvent from said highly paraffinic petroleum oil.

8. Process for the regeneration of a spent sulphuric acid containing dissolved carbonaceous constituents secured in the treatment of petroleum oils comprising contacting a spent sulphuric acid with phenol under conditions to form a phenol phase containing said carbonaceous constituents and a spent acid phase containing an appreciable amount of said phenol, separating the spent acid phase from the phenol phase and contacting the spent acid phase with a highly paraffinic petroleum oil fraction having a gravity in the range from about 25° A. P. I. to about 35° A. P. I. under conditions to substantially completely remove said phenol from said spent acid phase and to form a highly paraffinic petroleum oil phase containing dissolved therein said phenol and a spent acid phase, separating the respective phases, regenerating said spent acid phase and recovering said phenol from said highly paraffinic petroleum oil.

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