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TREATMENT OF ACID SLUDGE

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This invention relates to certain improvements in the manufacture of a heating fuel from acid sludge which is formed in the refining of mineral oils, tars, benzene or benzol and similar distillation or residue products by sulphuric acid monohydrate or fuming sulphuric acid.

It is an object of my present invention to produce from waste acids, formed by the refining of petroleum products and usually referred to as "acid sludge," a fuel which can be burnt through nozzles.

Another object of my invention is to govern the viscosity of the acid sludge and to prevent undesirable increase of the viscosity on storing or heating the acid sludge.

Still another object of the invention is to eliminate as much as possible any decomposition of the acid sludge by heating and to prevent attacks on the brickwork of the furnace as the acid sludge is burnt.

The by-product obtained by refining mineral oils besides polymerisation, oxidation and sulphurisation products constituting organic compounds contains also larger or smaller proportions of free concentrated sulphuric acid which have not been used up in the refining operation. This acid on extended storage acts upon the organic products, whereby the viscosity is strongly increased as a result of decomposition. Owing to its contents of highly concentrated acid the acid sludge cannot be heated for facilitating the re-pumping, since the decomposition phenomenons in this case are particularly heavy. At the elevated temperatures required for the re-pumping owing to the viscosity of the acid sludge, coke-like separations may easily occur in the pipes and in the pump.

It already has been proposed to use the waste acids as a fuel. To this end, the acid sludge has been mixed under action of heat with a relatively large quantity of a normal fuel oil, soda or lime being admixed, for example, in a proportion insufficient for neutralizing the available acid.

I have now found that acid sludge can be readily and cheaply converted into a fuel which is combustible through nozzles, by adding to the acid sludge relatively small proportions of water. If desired, a hydrocarbon oil may be admixed to waste acids of high viscosity, for governing the viscosity. The process is particularly suitable for the treatment of acid sludges occurring in the refinement of hydrocarbon oils by sulphuric acid monohydrate, but it is also readily applicable to products obtained by the refining with fuming sulphuric acid, provided that the content of free acid is not so high as to render the products incombustible. In general, waste acids having a content of free acid of less than about 40 percent may be treated.

The amount of water to be admixed is relatively small, since it is sufficient to reduce the concentration of the acid in the acid sludge by about 20 to 30 percent. In general, quantities of water not exceeding 10 percent of the acid sludge are sufficient to reach this end. Anyhow, the admixed quantity of water by no means should be as high as to form two layers in the acid sludge. In other words, in my novel process no layer containing dilute acid is separated from the organic products. The admixed water rather is intimately mixed with the waste acids, forming a stable emulsion or colloidal solution therewith.

A special advantage of my novel process consists in the fact that no ash-forming constituents are added to the acid sludge. Admixtures of soda and the like serving as a neutralizing agent would entail the disadvantage that the alkaline substances on combustion of the fuel would react with the masonry of the furnace.

Moreover, a high ash content of the fuel oil would cause obstruction or incrustation in the tubes and in the channels of the boilers.

I wish it to be understood that while in the preferred form of my invention the acid sludge is diluted merely with water, for reducing the strength of the sulphuric acid, my invention also comprises modifications in which, together with, or besides, the water, agents are added to the acid sludge which do not increase the ash contents of the fuel. Such substances may be, e.g., ammonia or organic bases.

Where reduction of the viscosity of the waste acids is required, suitable hydrocarbonic oils, having a lower viscosity than the acid sludge may also be added to the acid sludge. Such oil admixtures are either intended to dissolve the waste acids or, by slight mixing, to form stable emulsion therewith. Suitable oil admixtures are, for instance, extracts produced from mineral oils by means of solvents which are selective with respect to aromatic and naphthenic hydrocarbons, as for instance, liquid SO_2, furfurol, or the oils of medium viscosity occurring by the blowing of bitumen.

The following table stating the temporal change of the viscosity of acid sludge with and without admixtures of water will show the favourable effect of small admixtures of water and

the fact that even by small proportions of water the free sulphuric acid not only is deprived of any further capability of reacting with the waste acid, but the viscosity of the waste acid is even reduced on prolonged heating. The solvent has been an extract obtained by extraction of mineral oils with liquid sulphuric dioxide.

Heating of waste acid with and without additions of water and solvent. Initial material: Acid sludge from the refining of machinery oil with sulphuric acid monohydrate. Solvent: SO_2-extract E°3 at 100° C.

Test No.	Acid sludge from—	Solvent percent by weight	Water percent by weight of acid sludge used	Flowing-out time [1] in seconds after storage at 80° C. hours			
				0	16	40	112
1	Light machinery oil.	No-solvent.	No water	200	Thickened		
2	do	do	10 percent	26	15	16	18
3	do	10	No water	200	Thickened		
4	do	10	10	150	120	120	120
5	do	40	10	27	27	34	33
6	Cylinder oil E° 3 at 100°.	No-solvent.	No water	---	Plastic		
7	do	40	20	105	52	60	60

[1] The flowing-out time has been determined by means of a pipette in which 33 seconds at 100° C correspond to E° 14. (E°=degrees Engler.)

The following example of one mode of carrying my novel process into effect will illustrate the invention, but it is to be understood that the invention is not limited to the details set out in this example nor to a product having the specific properties recited.

500 kgs of acid sludge from the refining of heavy and light mineral oils (heavy spindle oil to cylinder oil E°4 at 100° C) having a content of free sulphuric acid of about 35 precent is intimately admixed with 50 kgs of water and 100 kgs of an extract obtained by refining mineral oils with liquid sulphur dioxide (viscosity E° 2.8 at 100° C).

The mixture even after heating at 70 to 80° C for several days did not practically show any increase of its viscosity, it can be readily conveyed through pumps and pipes, without forming residues, and can be burnt through nozzles without formation of residues and with full utilization of its calorific value.

It is desirable to use the acid sludge immediately after its formation, so as to avoid thickening which of course takes place also if the acid sludge is in contact with the free sulphuric acid at room temperature for a long time. It is also possible, however, to use acid sludges which have been stored for a longer time and thus already have been somewhat thickened; it is merely required in this case that the amount of oil added for dilution is rated accordingly.

The method of the present invention has been described in detail with reference to specific embodiments. It is to be understood, however, that the invention is not limited by such specific reference but is broader in scope and capable of other embodiments than those specifically described.

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