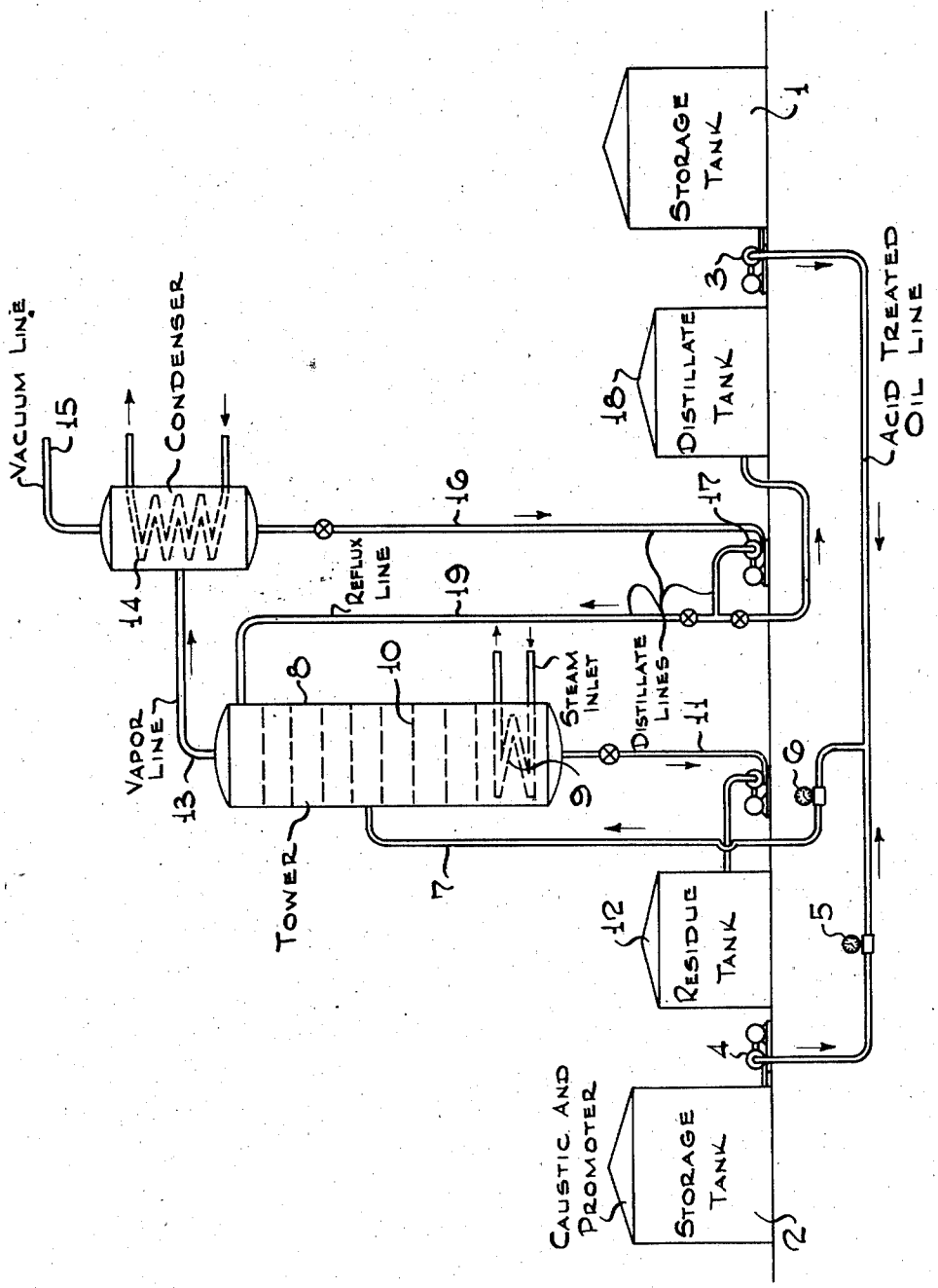
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DISTILLATION OF ACID-TREATED OILS

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DISTILLATION OF ACID-TREATED OILS

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4 Claims. (Cl. 196—35).

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This invention relates to a process of distilling acid treated oils and will be fully understood from the following description when read in conjunction with the drawing, the sole figure of which is a diagrammatic side elevation partly in section of the apparatus used in carrying it out.

The invention may be used in conjunction with the distillation of various types of mineral oils such as naphthas, petroleum lubricating oils, shale oils, hydrogenated tars or coals, etc., which have been acid treated and which on distillation develop certain undesirable characteristics due to decomposition of compounds containing the acid radical. Since the greatest advantages of the present process are obtained when it is applied to the redistillation of acid treated naphthas, and especially of acid treated cracked naphthas, the same will be described in more detail in conjunction with its last mentioned application.

Redistillation of a cracked naphtha which has been treated with sulfuric acid is the usual method employed for improving the color and lowering the gum and sulfur content of the stock, these changes being effected through removal of polymers. In the course of this distillation, sulfur dioxide is often evolved through the thermal breakdown of sulfuric acid esters present in the acid treated charge. This gas passes out of the still in company with the overhead products, resulting in serious corrosion of both overhead equipment and furnace tubes and heaters. Deposits in the tubes in the reboiler section from this decomposition of sulfuric acid esters reduce heat transfer coefficients causing rapid rise in the tube metal temperatures and forcing shutdowns for cleaning after runs of short duration.

The addition of caustic soda with solutizers or contact promoters to acid treated catalytic distillates has the effect of neutralizing the sulfur dioxide formed when the esters decompose on pyrolysis. It has been found that sediment formation causing fouling difficulties in heaters is not materially reduced unless no excess caustic soda is present with the sodium sulfate formed during the neutralization of the sulfur dioxide.

The main object of this invention, therefore, is to produce a product which may be distilled in ordinary plant or other metallic distillation equipment including transfer pipes, heat exchangers, reboilers, condenser coils and the like without causing corrosion and/or fouling of said equipment.

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This and other objects of this invention are accomplished by adding less than the theoretical quantity of alkali, preferably 90–95%, necessary for neutralization of the esters present and completing the neutralization by the addition of sufficient amount of a reactivity promoting material capable of neutralizing the residual acid. Suitable promoters include naphthenic acid soaps, such as sodium naphthenate, amines, alkali phenates, tetra-alkyl ammonium hydroxides, tetra-alkynol ammonium hydroxides, such as tetra ethanol ammonium hydroxide and oil soluble soaps such as corn oil soap, cocoanut oil soap, cotton seed oil soap, etc. It is also advantageous to use a small amount of a heavy oil such as a clean fuel oil along with the caustic and promoter to act as a vehicle to carry along any sediment formation through the heater section of the still.

Referring now to the figure, the apparatus will be briefly described in conjunction with the method of operating the same.

The acid treated oil from tank 1 and the caustic containing the promoter from tank 2 are passed by means of pumps 3 and 4 through meters 5 and 6 and line 7 into the re-run battery. About 0.5% of a heavy oil may be added if desired. The re-run battery, in case of redistilling naphtha, may consist of tower 8 which is heated by means of a closed steam coil 9 at the bottom thereof. The tower is provided with the usual bell cap plates. All of the unvaporized residue is removed through line 11 into residue tank 12. Overhead distillate which leaves the tower through line 13 is condensed in condenser 14 which is connected with a source of vacuum by line 15. The condenser distillate is passed through line 16 by pump 17 to the distillate tank 18. The line 19 serves for the return of reflux condensate to the tower.

Below are tabulated three runs showing the effect of using more than theoretical caustic requirements in the first case, and the stoichiometric amount with a contact promoter in the second, and the above recommended procedure of adding 95% of the stoichiometric amount of caustic soda plus contact promoter in the form of sodium naphthenates from caustic washing naphthenic acids from a suitable heating oil fraction in the third case, in testing acid treated catalytic naphtha in a laboratory type heater fouling test and distillation equipment. Such laboratory equipment reproduces the response

of full scale plant equipment to similar conditions.

NaOH Added as Free Caustic to Stock		Contact Promoter Added, Vol. Percent	Deposit Formed on Heater Fouling Tube Grams	Distillation Test Showing Percent SO_2 Reduction over Stock with No Treatment
Lbs./bbl.	Percent of Theoretical [1]			
0.16	133	None	0.5959	63
0.12	100	2.0% crude sodium naphthenate	0.8843	85
0.114	95	do	0.2368	86

[1] Exactly to neutralize the ester content found by quantitative analysis.

The first run, in which an excess amount of caustic soda only was added, shows a rather high sediment formation in the heater fouling test and only a 63% reduction in sulfur dioxide formation in the distillation test. In the second case where exactly the theoretical quantity of caustic plus the contact promoter was used, the effect of the solutizer was seen in the greater reduction of sulfur dioxide formation. However, sediment formation here was much higher than with caustic soda alone, but some advantage was gained in that the deposit was soft and muddy in appearance and in production furnace and heat exchanger tubes does not build up to a great extent. The third run, where caustic soda and sodium naphthenate were added in the amounts found to be critical, produced the best results. Here sediment formation was less than half than where caustic soda alone was used and sulfur dioxide reduction was excellent.

In experimental distillations made in glass apparatus, the change in color and appearance of the acid-treated gasoline was evident by visual observation. Acid treated gasolines of appreciable ester content, from say 10 to 50 ester number (milligrams of N/10 acidity formed per 100 ml.), were distilled with and without the addition of sodium hydroxide solution for neutralization and tetraethanol ammonium hydroxide as a contact or reaction promoter, in the manner described. When the acid-treated gasolines were distilled, they gradually darkened to a black color (due to decomposition of the esters), with evolution of sulfur dioxide in the overhead. However, when the neutralization and reaction promoter formula and technique was applied, the gasoline in the distillation flask remained clear and of its original color, and only traces of sulfur dioxide were noted. These experiments demonstrated the improvement in deposit formation which is possible in distilling acid-treated petroleum distillates.

By way of illustrative explanation of the mechanism by which the favorable results are attained, it may be postulated that the sulfuric acid esters in the acid treated distillate react to the extent possible with the promoter, say oil soluble sodium naphthenate, releasing oil soluble naphthenic acids. These acids resaponify with the sodium hydroxide present and the reaction is repeated, until all the esters have reacted with (lower cost) sodium hydroxide through the route of the oil soluble promoter. Carbon deposition is thus avoided and sulfur dioxide evolution does not take place. At the same time, the cement-like action of a mixture of sodium hydroxide, sodium sulfate and carbon is avoided, so that hard deposits do not build up in heat exchanger and furnace tubes. However, it is not intended to be bound by any theory of the mechanism of the reaction.

The nature and objects of the present invention having been thus described and illustrated, what is claimed as new and useful and is desired to be secured by Letters Patent is:

1. The process of distilling an acid-treated mineral oil which comprises adding 90–95% of the stoichiometric quantity of caustic alkali necessary to neutralize any acid reacting substance evolved from any residue of the treating acid during the distillation of the oil together with a sufficient amount of a naphthenic acid soap to be capable of completing said neutralization, and carrying out the distillation in the presence of the said caustic alkali and the naphthenic acid soap.

2. The process of distilling an acid treated mineral oil which comprises adding 90–95% of the stoichiometric quantity of caustic alkali solution necessary to neutralize any acid reacting substance evolved from any residue of the treating acid during the distillation of the oil, said caustic alkali solution containing a sufficient amount of a naphthenic acid soap to be capable of completing said neutralization and carrying out the distillation in the presence of said caustic alkali and naphthenic acid soap.

3. The process of distilling an acid-treated mineral oil which comprises adding 90–95% of the stoichiometric quantity of sodium hydroxide necessary to neutralize any acid reacting substance evolved from any residue of the treating acid during the distillation of the oil, together with a sufficient amount of sodium naphthenate capable of completing said neutralization, and carrying out the distillation in the presence of said sodium hydroxide, and sodium naphthenate.

4. The process of distilling an acid treated mineral oil which comprises adding 90–95% of the stoichiometric quantity of sodium hydroxide solution necessary to neutralize any acid reacting substance evolved from any residue of the treating acid during the distillation of the oil, said sodium hydroxide solution containing a sufficient amount of sodium naphthenate capable of completing said neutralization, and carrying out the distillation in the presence of said sodium hydroxide and sodium naphthenate.

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