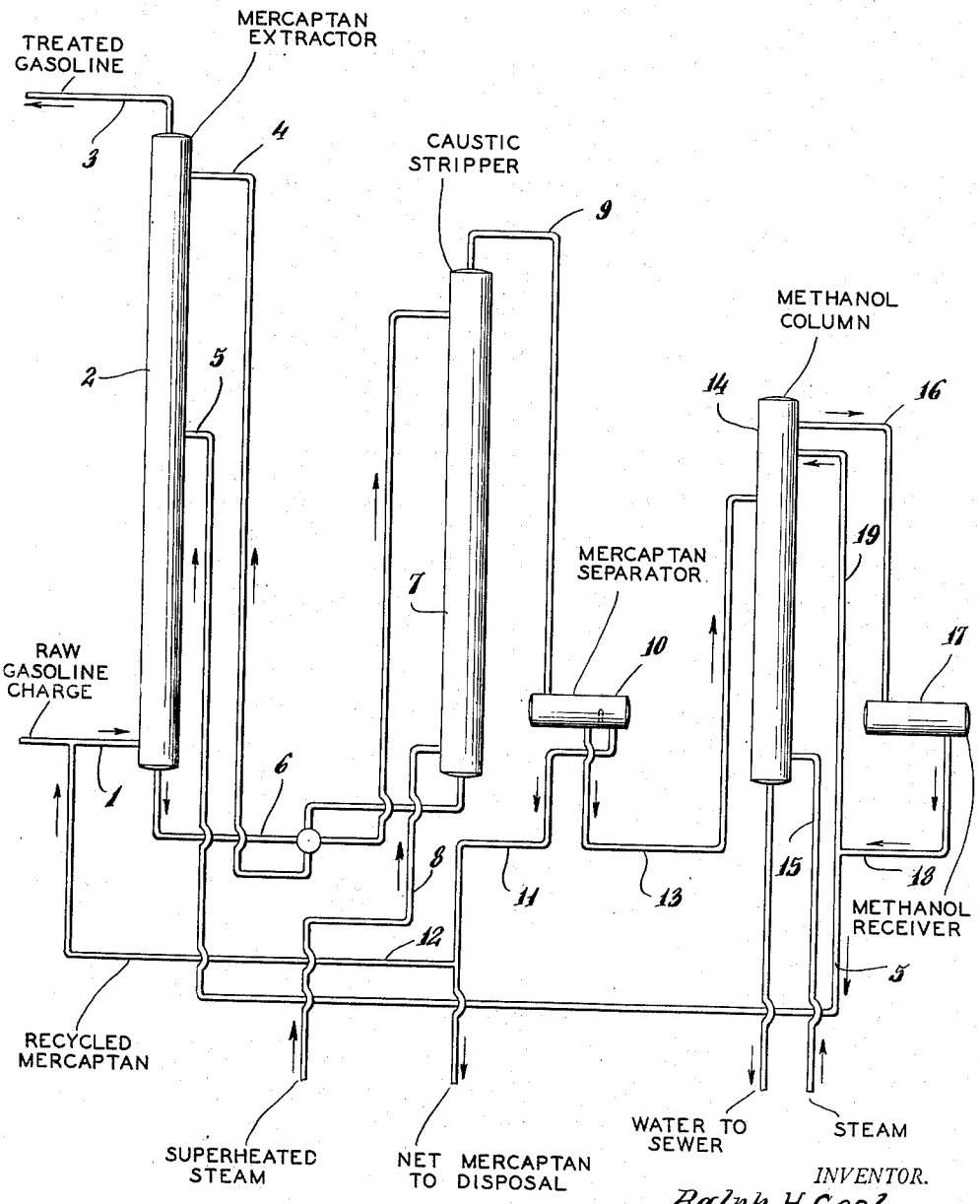
April 22, 1952 R. H. COOL 2,593,851

METHOD OF REMOVING MERCAPTANS FROM HYDROCARBONS

Filed March 20, 1948



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Patented Apr. 22, 1952 2,593,851

UNITED STATES PATENT OFFICE

2,593,851

METHOD OF REMOVING MERCAPTANS FROM HYDROCARBONS

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Application March 20, 1948, Serial No. 15,992

2 Claims. (Cl. 196—32)

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This invention relates to the removal of acidic organic impurities from raw hydrocarbon oils and more particularly to the removal of mercaptan impurities contained therein.

Conventionally, raw gasoline containing mercaptan impurities is treated with a solution of an alkaline reagent such as caustic soda and methanol or other aliphatic alcohol containing less than four carbon atoms in order to extract the major portion of the mercaptans from the gasoline. The mercaptan oil together with hydrocarbons dissolved in the solvent solution is then separated from the caustic and alcohol solution used as the extracting agent and is run off to waste. Such a method of treating hydrocarbon oils is described in U. S. Patent 2,309,651 to McCullogh, Birkhimer, and Leum.

It is an object of this invention to provide a method of treating hydrocarbon oils whereby the loss of hydrocarbons per unit of mercaptan extracted from the hydrocarbon oils may be substantially reduced.

Other and further objects and advantages of this invention will be apparent as the disclosure proceeds.

I have found that the mercaptan oil always contains some hydrocarbons as a diluent and over a period of operation the hydrocarbons lost in the process represents a considerable economic waste. The amount of hydrocarbons dissolved in the solvent solution seems to be a function of the amount of salts of acid oils, including phenol and naphthenic acids, that has built up in the caustic as a result of extraction of these acid oils from the hydrocarbon oil being treated, and is apparently independent of the amount of mercaptan extracted by the solvent solution. I have further found that the ratio of mercaptan to hydrocarbons in the waste stream from the mercaptan separator can be substantially increased by recycling a portion of the waste stream to the mercaptan extractor, thereby decreasing the amount of hydrocarbons run off to waste per unit of mercaptans extracted from the raw gasoline stream.

In order that those skilled in the art may more fully understand the nature of my invention, reference is made to the accompanying drawing in which the single figure is a diagrammatic representation of an apparatus in which my new and improved system for the extraction of mercaptans from raw hydrocarbon oils may be practiced.

A hydrocarbon oil, such as a raw gasoline charge stock, which may be straight run gasoline

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or gasoline produced by conventional cracking processes, is introduced through line 1 into mercaptan extractor tower 2 where it is treated in countercurrent by caustic soda solution introduced into the mercaptan extractor 2 near the top through a line 4. Methanol or other aliphatic alcohol containing less than four carbon atoms is introduced into the mercaptan extractor 2 through a line 5 near the midpoint of the mercaptan extractor 2. The treated gasoline is withdrawn from the top of the mercaptan extractor 2 through a line 3 to storage.

The mixture of caustic soda solution and methanol, containing dissolved mercaptans and gasoline is withdrawn from the bottom of the mercaptan extractor 2 through a line 6, and is introduced into causic stripper 7. The solution of caustic and methanol together with dissolved gasoline and mercaptans is stripped in the caustic stripper 7 by means of super heated steam introduced through steam line 8, and methanol, gasoline, mercaptans and water are recovered as an overhead product, the stripped caustic being continuously removed from the bottom of the caustic stripper 7 and returned to the mercaptan extractor 2 through the line 4.

The overhead products from the caustic stripper 7 are taken through line 9 to a mercaptan separator 10, in which the mercaptans will separate as an oily layer together with the gasoline present, the mercaptan-gasoline mixture being withdrawn through line 11. The methanol layer is withdrawn from the mercaptan separator and is led to a fractionating column 14, which is heated by steam introduced through line 15. Purified methanol is recovered as an overhead product through line 16 and is led to a methanol receiver 17. The methanol is reintroduced into the system through a line 18, a portion of it being reintroduced into the methanol fractionating column 14 as reflux through line 19, and the remainder being returned to the mercaptan extractor 2 through the methanol line 5. Water is withdrawn from the methanol column 14 as a bottoms product.

When the system as described above is operated as described above, I have found that the mercaptan mixture withdrawn from the mercaptan separator through line 11 will contain from about 75 per cent to about 95 per cent gasoline. However, I have discovered that when from about 50 per cent to about 90 per cent of the mercaptan-gasoline mixture from the mercaptan separator is recycled to the mercaptan extractor through line 12, the system will soon arrive at an equi-

librium in which the mercaptan mixture withdrawn from the mercaptan separator will contain but 25 per cent of gasoline, thus cutting the gasoline lost when the separated mercaptans are withdrawn to waste to from one third to one fifteenth of the amount which would be lost per unit of mercaptan extracted if the mercaptan mixture were not recycled.

Surprisingly, the addition of mercaptans to the charge stock prior to introducing it into the mercaptan extractor does not adversely affect the quality of the treated gasoline which will show a mercaptan content of from 0.0002 per cent to 0.0009 per cent, a mercaptan content comparable to that obtained when no additional mercaptans are added to the charge stock.

Having now described my invention, what I claim is:

1. In the process of treating a stream of hydrocarbon oils containing mercaptans with methanol and an aqueous solution of caustic soda to extract a major portion of the mercaptans therefrom, the steps of continuously removing methanol-caustic solution from contact with the hydrocarbon oil stream, separating mercaptans and dissolved hydrocarbons from the methanol and caustic solution, and recycling from about 50 to 90 per cent of the mercaptan and hydrocarbon mixture to the stream of hydrocarbon oils prior to treatment with methanol and caustic soda.

2. The method of removing mercaptans from hydrocarbon oil containing the same which comprises introducing methanol into a stream of said hydrocarbon oil, countercurrently contacting the said oil stream with a stream of an aqueous solution of caustic soda whereby the methanol-caustic solution will remove mercaptans therefrom, separating the methanol-caustic solution containing mercaptans and dissolved hydrocarbons from the hydrocarbon oil stream, stripping the methanol, mercaptans, and gasoline from the caustic soda solutions, separating the mercaptans and hydrocarbons from the methanol, and recycling from about 50 to 90 per cent of the mercaptan and hydrocarbon mixture to the stream of hydrocarbon oil prior to treatment with methanol and caustic soda.

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