This invention relates to the treatment of hydrocarbon oils, such as petroleum oils, or distillate derived from crude petroleum oils, shale oil, or similar sources, in which a certain percentage of the constituents are unsaturated hydrocarbons which may have been produced by thermocracking processes, with sulphuric acid in the presence of liquid sulphur dioxide dissolved in said petroleum oil, at relatively low temperatures, and under sufficient pressure to retain said sulphur dioxide dissolved in said petroleum distillate in a liquid state, to remove therefrom polymerizable, unstable and sulphur bearing hydrocarbons, without any substantial removal of the stable unsaturated hydrocarbons therefrom, and to produce a hydrocarbon oil which will be stable without change of color when stored in tanks, or other containers for a period of time.

By well known methods for the purification of naphtha or gasoline made by thermocracking operation, much difficulty has been found in stabilizing the stock produced, without a considerable loss of the stable unsaturated hydrocarbons, in which sulphuric acid, caustic soda and various oxidizing agents are usually employed. By these well known methods the sulphuric acid used, not only extracts the unstable hydrocarbons, but also a certain percentage of the stable unsaturated hydrocarbons which if conserved would be serviceable and usable for motor fuel.

By our invention these difficulties are overcome and a stable gasoline or naphtha stock is obtained without any substantial loss of the stable unsaturated hydrocarbons, by the employment of a sulphuric acid treatment on the naphtha or gasoline stock containing dissolved liquid sulphur dioxide, and at relatively low temperature, by means of which the chemical action of the sulphuric acid is modified and a selective action obtained, whereby the said sulphuric acid reacts substantially only with the unstable unsaturated and sulphur bearing hydrocarbons with the formation of sulpho-acids or sludge, which is separated from the treated gasoline or naphtha, and then finished by methods well known in the art, such as treatments with neutralizing agents, distillation, or the employment of oxidizing agents such as hypochlorite of soda.

Various further objects and advantages of the present invention will be understood from a description of a preferred process of treating hydrocarbon oils containing dissolved sulphur dioxide with sulphuric acid at low temperatures. For this purpose there is hereafter set forth a specific example of one form of process which embodies the invention. The process is described as it is carried out in the apparatus illustrated in the accompanying drawing.

The drawing represents a diagrammatical view of an apparatus for carrying out the invention.

Referring to the drawing, 1 indicates a pipe for conveying the petroleum oil distillate to be treated, from a source not shown, through a cooler or pipe heat exchanger coil 2, contained in the tank 3. 4 indicates a gauge glass connected to tank 3 for observing the oil level in said tank 3. 5 indicates a pipe or a continuation of cooler coil pipe 2, which conveys the cooled oil to be treated into the bottom of treating tank 6. 7 indicates a gauge glass connected to the treating tank 6 for observing the sludge level 55. 56 indicates a distributor plate so that the incoming oil may be uniformly distributed as it passes up through the treating tank 6. 8 is a pipe connected to the top of treating tank 6 and conducts the oil for further treatment into the bottom of treating tank 9, which in like manner is provided with a distributor plate 10, the acid sludge level being indicated by the number 13. The sludge level in treating tank 9 is observed by means of the gauge glass 12 which is connected to said treating tank 9. 11 indicates a distributor plate in the top of treating tank 9, by means of which the sulphuric acid introduced is evenly distributed as it passes downward through the oil in said treating tank 9. 16 is an acid tank which is filled with sulphuric acid of the desired strength through the pipe 18 which leads to a source not shown, and controlled by the valve 19. 17 is a gauge glass by means of which the level of the acid contained in said acid tank 16 may be observed.

Connected to the bottom of acid tank 16 is a pipe 14, controlled by a valve 15, which connects to the treating tank 9. 20 is a pipe connected to the top of treating tank 9 which conveys the treated cold oil into the cooler tank 3. The cooler tank 3 is provided with a dome at the top to which is connected a pipe.
2. A tank provided with a steam heating coil 24 and controlled by valves 26 and 28, the pipe 23 leading to a source of steam not shown, and the pipe 27 leading to a steam trap not shown. The tank 23 is provided with a gauge glass 29 by means of which the level of the treated oil may be observed. The pipe 21 controlled by valve 22 connects the cooler tank 3 to the tank 23 at the top, by means of which the treated oil after cooling the incoming oil overflows into the said tank 23 where it is heated and most of the sulphur dioxide is expelled from the treated oil, and then compressed to a liquid by the compressor 33 which takes suction on the top of the said tank 23 through a dome as shown. The heater tank 25 is provided with an outlet pipe 31 controlled by a valve 30 which conducts the treated oil to a source of storage not shown. The pipe 32 is connected to the top of the heater tank 23 and leads to the suction side of the sulphur dioxide compressor 33 controlled by the valve 33. 39 is a pipe connected to the discharge side of compressor 33 and is connected to the sulphur dioxide condenser passing through the cooling coil 40 which is a prolongation of the pipe 39 in the condenser box 41, from whence the liquid sulphur dioxide is conducted through the pipe 42 into a liquid sulphur dioxide storage tank 46. The tank 46 is provided with a gauge glass 43, by means of which the level of the liquid sulphur dioxide may be observed. 44 is a pipe which is connected to the liquid sulphur dioxide tank 46 at the top controlled by a valve 45 and leading to a source of liquid sulphur dioxide not shown. 36 is a pipe which connects the tank 46 at the top, controlled by a valve 37 which leads to the suction side of the compressor 33. 47 is a pipe controlled by the valve 48 which connects the bottom of said tank 46 to pipe 5, by means of which the required quantity of liquid sulphur dioxide may be introduced into the flow of oil coming through the said pipe 5.

The pipe 49 connects the treating tank 6 at the bottom to an acid sludge tank 51 and controlled by a valve 50. The acid sludge tank 51 is connected at the top with the pipe 52 which leads to the suction side of a compressor not shown, and is employed to liquefy the sulphur dioxide given off by the sludge. 53 is a pipe, controlled by valve 54, connecting treating tank 9 with treating tank 6.

The preferred process as carried out with the apparatus thus described is as follows:

Petroleum oil or petroleum oil distillate, such as gasoline stock, made by any of the well known cracking operations, which has preferably had a preliminary treatment with caustic soda, sodium-hypochlorite or similar reagents, for the removal or partial removal of hydrogen sulphide and mercaptans therefrom, is conducted from pipe 1 through cooler or exchanger coil 2 into the bottom of treating tank 6, passing through the pipe 5 which is a prolongation of heat exchanger coil 2. Heat exchanger coil 2 is surrounded by the outgoing treated oil, which is maintained at approximately 17°C F., by taking suction on said tank 3 through the line 54 which leads to the suction side of a compressor 33, controlled by valve 35. By means of this said suction taken on the tank 3 a portion of the liquid sulphur dioxide contained in the treated oil changes to a gas thereby cooling the solution to the desired temperature, by means of which the petroleum distillate to be treated passing through this exchanger may be cooled to the desired degree. The cooled oil passing from the exchanger 3 is introduced into the said treating tank 6 along with a regulated flow of liquid sulphur dioxide coming from tank 46 and passing through pipe 47 controlled by the valve 48. The said liquid sulphur dioxide, at the rate of approximately 25% by volume of the oil, which is continuously introduced along with the petroleum distillate to be treated is maintained at approximately 17°C F., by means of evaporating a portion of the liquid sulphur dioxide contained in tank 46, which is accomplished by opening the valve 37 which admits the sulphur dioxide gas into the suction side of the compressor 38 thereby cooling the liquid sulphur dioxide to the desired degree.

The petroleum distillate containing the requisite quantity of sulphur dioxide at the required temperature passes into the treating tank 6 and up through a distributor plate 56 which is provided with openings so that the petroleum oil containing the liquid sulphur dioxide may pass upward in uniform droplets through the sludge contained in said tank 6, whereby a partial treatment of the petroleum distillate or gasoline is obtained by contact with said acid sludge coming from treating tank 9. The partly treated oil containing the dissolved sulphur dioxide passes through the pipe 8 into the bottom of a second treating tank 9 where in like manner it passes through a distributing plate 10 through a 115 body of acid and acid sludge the level of which is indicated by the figure 13. At the same time sulphuric acid in the desired quantities is introduced into the top of said treating tank 9 passing through the distributor plate 11 so that the same may pass downward through the oil in small droplets or streams. The acid treated petroleum distillate or gasoline passes out of treating tank 9 through the pipe 20 and into tank 3 where the aforesaid heat exchange takes place, the said treated cold gasoline stocks absorbing a part of the heat from the incoming petroleum gasoline or distillate. As heretofore stated the temperature of the treated oil coming into
the said exchanger tank 3 may be further cooled by the employment of a vacuum, which is produced by taking suction through line 34 which is connected to the said tank 3 at the top. The treated oil passes from tank 3 into the tank 23 where the balance of the liquid sulphur dioxide is removed by means of heating said oil to the required temperature by means of the heater coil 24, and taking suction on said tank 23 through the pipe 32 which leads to the suction side of compressor 38. The treated oil from tank 23 is conducted to a storage not shown by means of the pipe 31 controlled by the valve 30, where said treated oil may be further treated if necessary by processes well known in the art.

By this process the sulphur dioxide employed is utilized repeatedly and only such quantities that are lost are replaced. The sulphur dioxide evolved during the operation from the tanks 3, 23, 51 and 46 is compressed by the compressor 38 and then passed through the cooling coil 40 which is surrounded by a cooling medium contained in the condenser box 41. By this said compression and cooling the sulphur dioxide gas is liquefied and passes through the pipe 42 which is a prolongation of the said cooler coil 40 and connects to the liquid sulphur dioxide tank 46.

The sulphuric acid employed in this operation may be of varying strength depending upon the stock treated and the product desired, in case a gasoline stock containing a very high percentage of unsaturated hydrocarbons. With certain gasoline stocks produced by the cracking of a petroleum oil distillate under a pressure of 1000 pounds or higher we preferably use fuming sulphuric acid containing 3 to 15% SO₃, although 60 to 66° Baume sulphuric acid may be successfully employed.

For example, in the treatment of a gasoline stock, made by cracking a petroleum oil distillate at a pressure of approximately 1000 pounds gauge, by our process approximately 5 to 10 pounds of 3% fuming sulphuric acid was required to obtain a stable water white gasoline product with a treating loss ranging from 1 to 4% by volume; while by the employment of well known methods of acid treating a loss of from 2 to 6% by volume was obtained employing the same quantities of acid.

The acid sludge produced by the operation may be recovered by any of the well known methods of hydrolysis and employed again for this treatment or other treatments of hydrocarbon oils.

It is to be understood that a preliminary treatment of the gasoline stock, which is to be treated by our process with caustic soda or other agents, may not be necessary for gasoline stocks derived from relatively low sulphur content crude petroleum oils.

It is also to be understood that this treating process may be carried intermittently, or in batch lots, and that the treatment of the gasoline stock, containing the requisite amount of sulphur dioxide, may be carried out by commingling the said gasoline stock with the required amount of sulphuric acid by any preferred method.

While the process herein described is well adapted for carrying out the objects of the present invention it is understood that various modifications may be made without departing from the invention and the invention includes all such modifications and changes as come within the scope of the appended claims.

We claim:

1. A process of treating hydrocarbon oils with sulphuric acid in the presence of liquid sulphur dioxide which comprises commingling the hydrocarbon oil containing added liquid sulphur dioxide with the requisite amount of sulphuric acid, and then separating the products of reaction, sulphur dioxide and the uncombined acid from the treated oil.

2. A process of treating gasoline or naphtha derived from cracking petroleum oil which comprises simultaneously treating the same with liquid sulphur dioxide and sulphuric acid at temperatures not substantially in excess of the boiling point of liquid sulphur dioxide, and then separating the treated oil from the sulphur dioxide and the products of reaction.

3. A process of purifying gasoline or naphtha derived from cracking petroleum oil which comprises simultaneously treating the same with liquid sulphur dioxide and sulphuric acid in quantities sufficient to dissolve unstable hydrocarbons and sulphur bearing hydrocarbons in the gasoline or naphtha, the sulphur dioxide being kept substantially in the liquid state during the treatment, separating the treated oil from the acid and substances dissolved therein and then separating the sulphur dioxide from the purified gasoline or naphtha.

4. A continuous process of treating gasoline or naphtha derived from cracking petroleum oils at high temperatures and pressure which comprises treating said gasoline or naphtha containing added dissolved liquid sulphur dioxide with sulphuric acid, at a temperature not substantially in excess of the boiling point of liquid sulphur dioxide, and then separating the treated oil from the residue of acid and sulphur dioxide.

5. A continuous process of treating gasoline or naphtha derived from the cracking of petroleum oil which comprises simultaneously treating the same with sulphur dioxide and sulphuric acid in quantity suf-
sufficient to dissolve the unstable hydrocarbons and sulphur bodies desired to be removed, dissolving constituents of the same therein, and then separating the treated oil from the sulphur dioxide and acid dissolved constituents, the temperature, during the sulphuric acid treatment, being kept at about 17° F.

6. A continuous process of treating hydrocarbon oil which comprises passing the said hydrocarbon oil in heat exchange relationship with cold hydrocarbon oil subsequently produced, continuously introducing into said first mentioned hydrocarbon oil, cooled liquid sulphur dioxide, passing said hydrocarbon oil containing the sulphur dioxide in counter current flow with sulphuric acid, and then separating the sludge formed and the sulphur dioxide from the treated oil.

7. A process of treating gasoline or naphtha derived from cracking petroleum oil which comprises continuously passing said gasoline or naphtha in heat exchange relationship with cold gasoline or naphtha subsequently produced, introducing cooled liquid sulphur dioxide into said first mentioned gasoline or naphtha, passing the gasoline or naphtha containing the dissolved sulphur dioxide in counter current flow with sulphuric acid, and then separating the sludge formed and the sulphur dioxide from the treated gasoline or naphtha.

8. The method of separating unstable, unsaturated hydrocarbons from petroleum oils containing the same together with stable unsaturated hydrocarbons without removing the latter which comprises simultaneously subjecting the oil to the action of liquid sulphur dioxide and sulphuric acid at temperatures approximating the boiling oil of liquid sulphur dioxide.

9. The method of separating unstable, unsaturated hydrocarbons from oils containing the same together with stable hydrocarbons without removing the latter which comprises adding liquid sulphur dioxide to the oil to be treated, commingling said oil containing liquid sulphur dioxide with sulphuric acid at temperatures not substantially in excess of the boiling point of liquid sulphur dioxide, and thereafter separating the treated oil from the sulphuric acid reaction products and the sulphur dioxide.

In testimony whereof we affix our signatures.

JOHN C. BLACK.

MARVIN L. CHAPPELL.