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METHOD OF CHLORINATION

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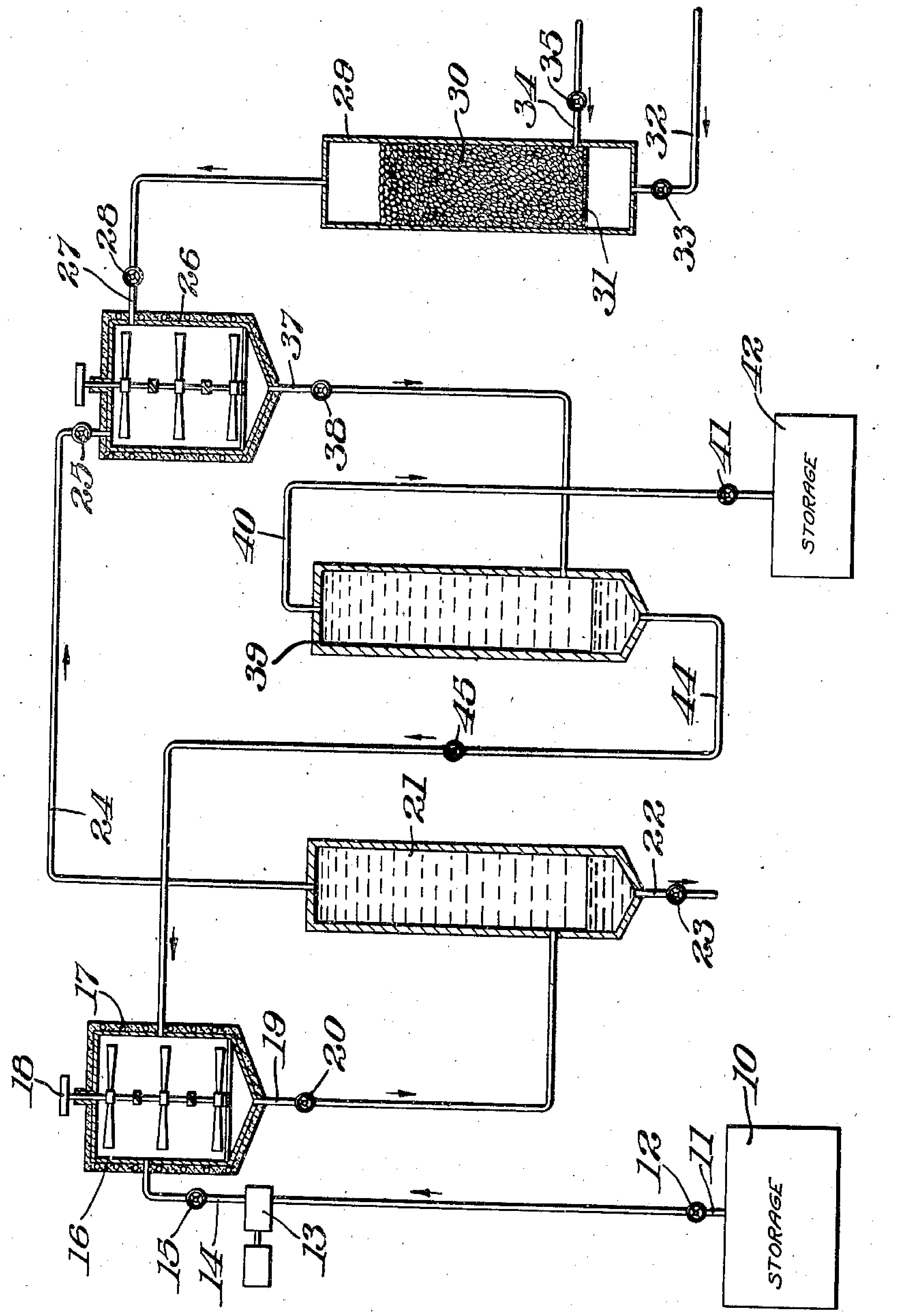

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METHOD OF CHLORINATION

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5 Claims. (Cl. 260—162)

This invention relates to the chlorination of petroleum hydrocarbons and more particularly to the chlorination of petroleum hydrocarbon oils.

More specifically, my invention relates to the chlorination of petroleum hydrocarbon oils by contacting them with an aqueous solution of hypochlorous and hydrochloric acids whereby the petroleum hydrocarbon oils are chlorinated to the desired chlorine content.

A large number of chlorination methods have been proposed in the past. Some of these have featured the chlorination of petroleum hydrocarbons by reacting them with gaseous chlorine in the presence of ultra-violet light or chemical catalysts and promotors. Other methods have disclosed the interaction of hydrocarbon oils and chlorine in the presence of contact catalysts and under varying conditions of temperature and pressure. These methods, when applied to the chlorination of petroleum hydrocarbon oils, have been found to result in the discoloration of the oils, the formation of sludges, as well as in the production of large quantities of undesirable chlorinated by-products. The reactions are either extremely slow or else when accelerated by increasing the temperatures, pressures or chlorine concentration tend to proceed violently and may, in many cases, result in the utter decomposition of the petroleum hydrocarbon oil.

In accordance with my process, petroleum hydrocarbon oils and chlorine may be interacted to yield the desired chlor compounds without the formation of undesirable by-products or the destruction of the petroleum hydrocarbon oils. I achieve, this result by saturating water with chlorine gas to form chlorine water in accordance with the following equation:

$$H_2O + Cl_2 \rightarrow HCl + HClO$$

and then agitating a petroleum hydrocarbon with this chlorine water whereby a smooth and complete chlorination of the petroleum hydrocarbon is effected.

The use of ultra-violet light, reaction catalysts, contact agents or reaction promotors is unnecessary. The reaction proceeds quite rapidly and there is no apparent production of exothermic energy. Petroleum hydrocarbon oils chlorinated in accordance with my invention are not discolored and do not contain any sludge, nor does the chlorinated oil suffer from the formation of undesirable, unsaturated hydrocarbons due to the cracking of the unstable petroleum hydrocarbons. My invention is readily applicable to all types of petroleum hydrocarbons and elaborate apparatus is unnecessary for carrying out the process.

The herein disclosed invention may be applied in a variety of ways. For example, a petroleum hydrocarbon oil may simply be agitated with chlorine water for a sufficient period of time to permit the reaction to take place, or else the oil may be mixed with chlorine water in a tower filled with contact materials such as Raschig rings, coke or refractory materials. The process also lends itself quite successfully to application in a countercurrent process wherein the petroleum hydrocarbon oil is flowed countercurrently to a stream of chlorine water. Here the oil and chlorine water are successively agitated together and separated, the unchlorinated hydrocarbon oil being contacted with chlorine water containing the lowest percentage of hypochlorous acid and the most highly chlorinated hydrocarbon oil coming into contact with the highest concentration of hypochlorous acid.

The accompanying drawing discloses an apparatus suitable for carrying out my invention and the following description taken in connection therewith will serve for a better understanding of my invention.

The numeral 10 indicates a tank for untreated oil. This tank is provided with a drawoff line 11 fitted with a valve 12 which connects the tank with the intake side of the pump 13. This pump discharges through the line 14 controlled by the valve 15 into the mixing chamber 16. This mixing device may be of any suitable construction. It is fitted around its circumference with heating coils through which a suitable heating medium may be circulated. These coils are indicated by the numeral 17. It is also equipped with a mechanical agitating device 18 which is used for bringing the untreated oil into intimate contact with chlorine water. The bottom of the mixing chamber 16 is provided with a draw-off line 19 controlled by the valve 20 which line discharges into the settling chamber 21 wherein the partly chlorinated oil separates from the spent chlorine water. The latter is drawn off from the bottom of the settling chamber through the drawoff line 22 controlled by the valve 23.

The top of the settling chamber 21 is equipped with a drawoff line 24 controlled by the valve 25 through which the partly chlorinated oil drawn off from the top of the settling chamber is delivered into the mixing chamber 26. The mixing chamber 26 may advantageously be of the same construction as the previously described mixing chamber 16.

The mixing chamber **26** is connected by means of the line **27** controlled by the valve **28** with a source **29** of chlorine water. This source consists of a chamber wherein water and chlorine gas are reacted to form an aqueous solution of hydrochloric and hypochlorous acids which is spoken of herein as chlorine water. The chamber is preferably fitted with a filling **30** of refractory material which assists in the proper interaction of the water and gaseous chlorine. This material is preferably supported on the perforated tray **31** at a small distance above the bottom of the chamber. Gaseous chlorine is delivered into the bottom of the tower through the line **32** controlled by the valve **33** while water is injected through the line **34** controlled by the valve **35** at a point above the tray **31**.

The mixing chamber **26** is fitted at its bottom with a drawoff line **37** controlled by the valve **38** which connects it with the settling chamber **39** wherein the chlorinated oil is separated from the partly spent chlorine water. The chlorinated oil is drawn off from the top of the settling chamber through the line **40** controlled by the valve **41** and delivered to the storage tank **42**. The bottom of the settling chamber **39** is fitted with a drawoff line **44** controlled by the valve **45** which leads to the mixing chamber **16**.

In a typical operation of my invention in connection with the apparatus shown in Figure 1, a petroleum hydrocarbon oil which is to be chlorinated, is drawn from the storage tank **10** and passed to the charge pump **13** by which it is delivered under suitable pressure through the line **14** into the mixing chamber **16**. Herein the untreated oil is thoroughly agitated at an elevated temperature with partly spent chlorine water from a succeeding step in the process. The hypochlorous acid readily reacts with the hydrocarbon oil to form substituted chlor compounds. The mixture of partly chlorinated oil and spent chlorine water is drawn off from the bottom of the mixer **16** and delivered into the settling chamber **21** wherein a substantial separation of the oil and water is brought about. The spent chlorine water is drawn off through the bottom drawoff line **22** controlled by the valve **23** and delivered to a suitable storage tank or, if desirable, to a hydrochloric acid concentration system. The partly chlorinated oil which forms the supernatant layer in the settling chamber **21** is drawn off through the line **24** and delivered into the mixing chamber **26** wherein it is agitated with a proportioned amount of fresh chlorine water. The chlorine water used in the operation of this process is prepared in the chamber **29**. Herein correctly proportioned quantities of water and gaseous chlorine are intermixed and interacted to form an aqueous solution of hydrochloric and hypochlorous acids. This solution is delivered into the mixing chamber **26** through the line **27**.

The partly chlorinated oil and fresh chlorine water react quite readily and the mixture which is drawn off from the mixing chamber **26** through the drawoff line **37** consists essentially of chlorinated oil and partly spent chlorine water. These two materials are substantially separated in the settling chamber **39**, the partly spent chlorine water being delivered to the mixing chamber **16** through the line **44** while the chlorinated oil is drawn off from the top of the chamber through the line **40** and delivered to the storage tank **42**.

The chlorination process may be applied to any petroleum hydrocarbon oil irrespective of its viscosity, the only requirement being that it be fluid enough at elevated temperatures to permit of its being readily reacted with the chlorine water. As an example of how the process may be applied to various petroleum hydrocarbons, an oil having the following tests may be submitted to treatment:

Gravity, A. P. I.	26.7
Visc. Univ. at 100° F.	183
Pour, °F.	25

By interacting this oil with a chlorine water at a temperature of approximately 150° F. and under a pressure of 25 lbs. per sq. in., a chlorinated oil having the following tests may be produced:

Gravity, A. P. I.	20.2
Visc. Univ. at 100° F.	305
Visc. Univ. at 210° F.	52
Pour, °F.	15
Chlorine, per cent	5.37

Paraffin waxes and similar compounds may be readily chlorinated by interacting them with chlorine water at an elevated temperature. For example, a paraffin wax having a melting point of 102.5° F., a flash of 410° F. and a fire point of 480° F. was subjected to reaction until it contained 23.26% of chlorine. This material had the following tests:

Specific gravity at 60° F.	1.014
Flash	535
Fire	570
Visc. Univ. at 100° F.	328
Solid point °F.	30
Chlorine content per cent	23.26

The temperatures used in the operation of the process lie preferably in the range of from 100 to 200° F. although higher or lower temperatures may be found especially applicable in chlorinating certain hydrocarbons. Similarly, the pressures used while interacting petroleum hydrocarbon oils and chlorine water are preferably below 500 lbs. per sq. in.

In actual practice it is found that certain hydrocarbons are less reactive than others and that their hydrogen atoms are not as readily replaced by chlorine. Such oils require longer time of contact with the chlorine water as well as higher temperatures and pressures. The longer time of contact in an apparatus such as that shown in Figure 1 is readily obtainable by reducing the rate of flow of the oil while substantially increasing the quantity of chlorine water used. In this manner smaller volumes of petroleum hydrocarbon oil are contacted with proportionately larger quantities of chlorine water and the flow rates being low, these two materials will be contacted for proportionately longer periods of time.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of chlorinating hydrocarbons which comprises agitating petroleum hydrocarbons selected from the group consisting of lubricating oils and paraffin wax with an aqueous solution of hydrochloric and hypochlorous acids at a temperature in the range of 150° to 200° F. and under a pressure of between 25 and 500 pounds per square inch.

2. The method of chlorinating hydrocarbons

which comprises agitating petroleum hydrocarbons selected from the group consisting of lubricating oils and paraffin wax with chlorine water at a temperature of about 150° F. and under a pressure of about 25 pounds per square inch.

3. The method of chlorinating hydrocarbons which comprises agitating petroleum hydrocarbons selected from the group consisting of lubricating oils and paraffin wax with chlorine water at a temperature of between 150° and 200° F. and under a pressure of between 25 and 500 pounds per square inch to form a mixture, and then subjecting the mixture to settling to effect the separation of the chlorinated hydrocarbons from the spent chlorine water.

4. The method of chlorinating hydrocarbons which comprises alternately mixing petroleum hydrocarbons selected from the group consisting of lubricating oils and paraffin wax and separating them from a countercurrently flowing stream of chlorine water while maintained at a temperature in the range of 150° to 200° F., and under superatmospheric pressure, the unchlorinated hydrocarbons coming into contact with partly spent chlorine water and the partly chlorinated hydrocarbons coming in contact with fresh chlorine water.

5. The method of chlorinating hydrocarbons which comprises flowing petroleum hydrocarbons selected from the group consisting of lubricating oils and paraffin wax while maintained at a temperature in the range of 150° to 200° F. and under a pressure of between 25 and 500 pounds per square inch countercurrently to a stream of chlorine water, the relatively unreacted hydrocarbons coming into contact with partly spent chlorine water and the partly chlorinated hydrocarbons coming into contact with relatively fresh chlorine water, separating the chlorinated hydrocarbons from the fresh chlorine water and returning the latter to the process.

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