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PHOTOCHEMICAL CHLORINATION OF HYDROCARBONS

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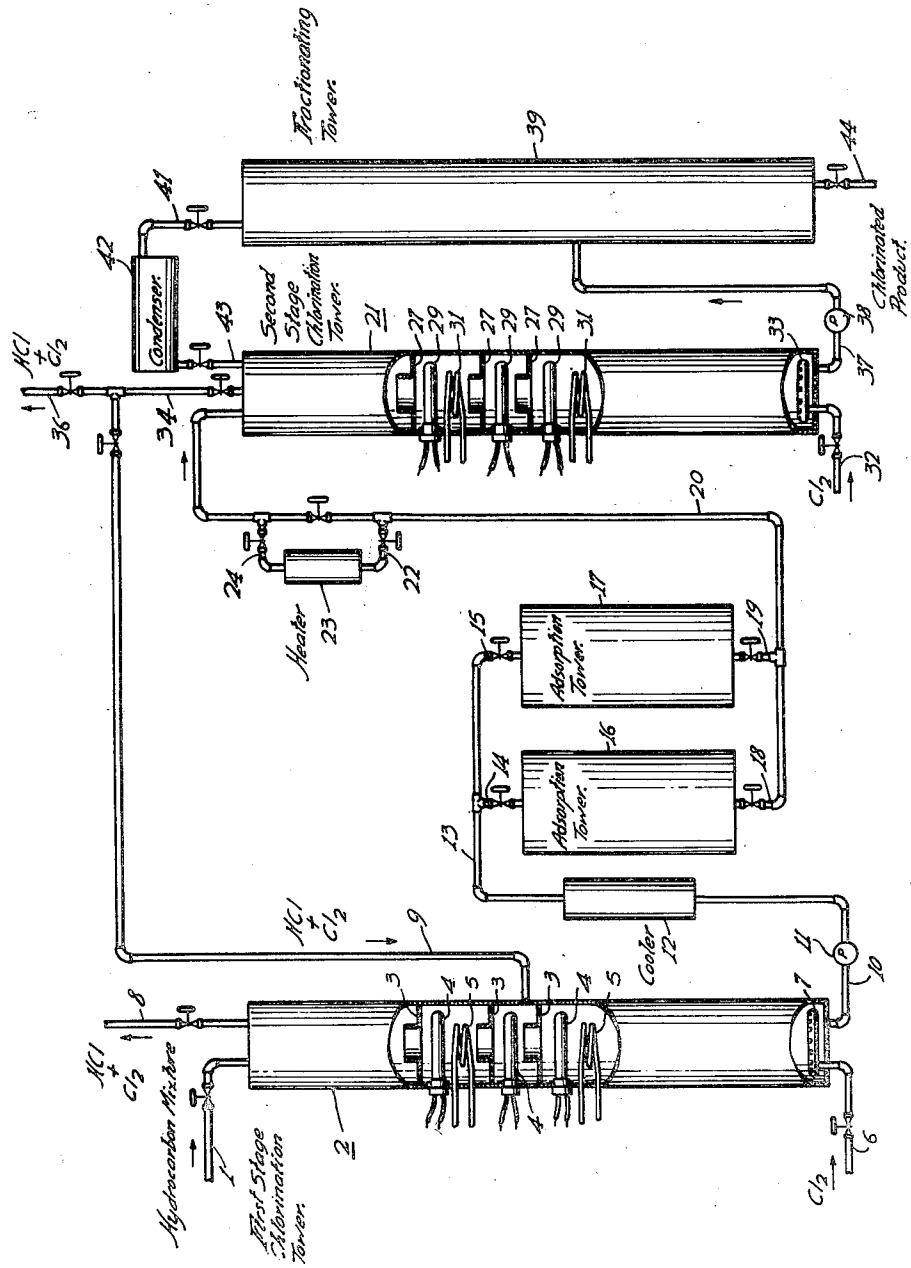

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PHOTOCHEMICAL CHLORINATION OF HYDROCARBONS

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This invention relates to a process of chlorinating hydrocarbons, and more particularly to a process of photocatalytically chlorinating an industrial mixture of hydrocarbons such as a liquid petroleum fraction to a high chlorine content.

It has previously been proposed to accomplish photocatalytic chlorination of petroleum fractions, but in general such operations have involved the introduction into the hydrocarbons of a relatively small percentage of chlorine. The addition of a large percentage of chlorine has presented difficulties because as the chlorine content of the mixture increases, the ability of the mixture to absorb chlorine is reduced and product decomposition occurs so that as a practical matter additional effective chlorination is not accomplished by conventional procedures.

In accordance with the present invention, industrial mixtures of hydrocarbons such as liquid petroleum fractions are efficiently chlorinated to a high chlorine content by intimately contacting the hydrocarbons with chlorine in the presence of active light rays, subjecting the partially chlorinated hydrocarbon mixture to the action of a solid adsorbent, and then intimately contacting the mixture with chlorine in the presence of light to accomplish additional chlorination. We have found that by practicing this process a petroleum fraction can be effectively chlorinated to a chlorine content of 70 per cent or more by weight in a relativly short time and with the use of simple equipment.

The hydrocarbon mixtures that may advantageously be chlorinated by the present process include light liquid petroleum fractions such as gasoline and kerosene fractions. The fractions may boil over a relatively wide temperature range, such as 300° F. or more between the initial and final boiling points, but for most purposes somewhat narrower boiling range fractions are more valuable. Thus a fraction having a boiling point range of from about 30° to about 100° F. may be chlorinated to yield especially useful chlorinated compounds. The process may also be used with value for the chlorination of heavier petroleum fractions, such as lubricating oil fractions, but the extent of chlorination easily attained is not as great as in the cases of the lighter fractions. Other hydrocarbon mixtures, such as light coal tar oils and the like, may be chlorinated effectively. The process may also be applied to the chlorination of relatively pure hydrocarbons. In the chlorination of such hydrocarbons, the process frequently has the advantage of materially reducing the time required for maximum chlorination. Pure hydrocarbons may usually be chlorinated effectively by conventional procedures, and therefore the degree of improvement may not be sufficient to justify use of the present process. However, there is usually an

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important advantage when the hydrocarbon being chlorinated is a technical grade material which may be only 90 to 95 per cent pure.

In the chlorination of a liquid petroleum fraction by conventional photocatalytic procedures the acceptance of chlorine continues with a progressive coloring or darkening of the solution which appears to proceed so long as the chlorine is introduced under conditions causing acceptance of the chlorine by the hydrocarbons. Under such conditions there is a relatively low limit to the amount of chlorine that the mixture will absorb without concomitant product decomposition. While the invention is not limited to any theory of operation, we have reason to believe that during the initial stages of conventional chlorination, condensation or polymerization of unstable compounds in the mixture is effected and that the resulting polymers adversely affect the chlorination and also tend to induce continuing condensation or polymerization in the mixture throughout the chlorination. Thus, the difficulty of chlorinating is continuously increased. We have discovered that by treating the partially chlorinated mixture with a solid adsorbent the mixture obtained may be chlorinated to a high chlorine content while avoiding the indicated decomposition or condensation and polymerization of constituents of the mixture. For example, while in the initial stages darkening or coloring of the mixture takes place, after the adsorption treatment the mixture is capable of absorbing additional quantities of chlorine in a relatively short period of time, and, even though the chlorine content of the mixture is increased to a high value, the mixture remains substantially clear and free from any color other than that due to the chlorinated compounds themselves.

The present process may be carried out in various ways. In accordance with one manner of proceeding, the hydrocarbon mixture is introduced into a vessel provided with a source of violet or ultra-violet rays or related short wave light rays of about 2000 to 5000 A. units. The vessel is also provided with a dispersing device for chlorine, this device being placed in the lower portion of the vessel. The pressure in the vessel is preferably maintained at about the pressure of the atmosphere and where the initial boiling point of the petroleum fraction is above the maximum temperature reached during the initial part of chlorination no special precautions need be taken regarding evolution of vapors. In cases where a relatively light fraction is subjected to chlorination, the pressure may be atmospheric or other pressure at which vapors of the mixture are evolved but in these cases the reaction vessel should be provided with a reflux condenser in which the vapors are condensed and returned to the vessel. Alternatively, the pres-

sure may be maintained sufficiently high so that the initial boiling point of the fraction at the pressure in question is above the maximum chlorination temperature. The vessel is provided with heating means and may also be provided with cooling means, although we have found the latter not to be necessary if the rate of chlorine addition is controlled.

The introduction of chlorine through the dispersing device is preferably begun at a rate such that the exothermic reaction involved in the chlorination of the hydrocarbons is not sufficient to raise the temperature of the mixture above about 125° C.; the temperature preferably is between about 80 and 110° C. The rate of introduction of chlorine is generally such that only a very small amount of unreacted chlorine passes through the mixture, and it is preferred to continue the introduction of chlorine until a major reduction in the rate at which the chlorine is being accepted is noticed. At this stage the partially chlorinated mixture may contain about 35 to 45 per cent chlorine by weight.

The mixture is then removed from the vessel and may be passed through a body of a solid adsorbent in the form of granules; for example 20 to 4 mesh particles. Alternatively, the mixture may be mixed with the adsorbent in finely divided form and then filtered. The solid adsorbent may be, for example, an activated carbon, or an activated clay such as an acid treated montmorillonite clay. The activated clay of this type marketed under the trade name "Super Filtrol" is excellent for the purpose. When using fresh "Super Filtrol" it has been found that effective treatment is accomplished when 1 to 2 volumes of clay are employed for 20 volumes of the chlorinated mixture. It will be understood that other solid adsorbents may be used, among which fuller's earths and high surface area inorganic gels may be mentioned as examples. No particular precautions need be taken with respect to the adsorbent. For example, the adsorbent clay for use may be stored in contact with the atmosphere and contain several per cent adsorbed moisture. The advantageous results obtained do not appear to be dependent in any important respect upon a drying or dehydrating action of the adsorbent.

After treatment with the adsorbent the mixture is returned to the vessel in which the initial stages of chlorination were carried out and the introduction of chlorine is started. At the beginning of the second stage of chlorination the exothermic reaction may be sufficient to maintain a satisfactory chlorination temperature or heating may be necessary. In any case, as the mixture becomes more heavily chlorinated, the reaction rate will begin to slow down. At this time the temperature of the mixture should be raised. This may be done gradually over the period of time required to accomplish the desired amount of chlorination or the temperature may be quickly raised to the maximum and maintained at that point. Thus the temperature during this second stage may vary from about 70° to 200° C., preferably from about 110° to about 130° to 170° C. and the selected maximum temperature employed is dependent upon the extent of chlorination desired.

Inasmuch as the boiling point of the initial charge material has been raised due to the introduction of chlorine, it is generally feasible to maintain atmospheric pressures in the chlorination vessel without the use of a reflux condenser even though the boiling range of the starting material extends below the temperatures reached during the latter stages of chlorination. It has been found in general that if the chlorination is to be effected over a reasonable period of time, it should not be continued beyond the point where the mixture contains between about 65 and 75 per cent chlorine by weight. On the other hand, the advantages of the invention are not fully realized unless the chlorination is continued until the mixture contains in the order of at least 50 per cent chlorine. Depending upon the type of charge material and extent of chlorination, the chlorination product may be a viscous liquid or a waxlike solid which generally has a reddish color.

As discussed above, the process has preferably been carried out under atmospheric pressure because the use of such pressure has been found to result in satisfactory chlorinated materials. However, the invention is not limited to the use of atmospheric pressures; for example, higher pressures are equally operable and may be used if desired. With regard to the point at which it is desirable to subject the mixture to treatment with a solid adsorbent, it is preferred to do this only after as great an amount of chlorine has been absorbed as can be done effectively under the conditions. Nevertheless, since the adverse effects that develop in the mixture occur in the very early stages of the chlorination, satisfactory results are obtained by carrying out the initial chlorination to a relatively small extent, for example to a point substantially short of that where darkening and coloring of the mixture has proceeded to the extent characteristic of maximum initial chlorination.

The time required for effective chlorination to a high chlorine content will vary depending upon the nature of the charge material, the rate of introduction of chlorine, the efficiency of the apparatus, and other factors. We have found that when a light liquid petroleum fraction is chlorinated in the first stage to substantially the maximum extent possible in that stage and the overall chlorination is continued until the mixture contains about 70 per cent chlorine, the entire process will usually require about 45 to 50 hours when the chlorination is interrupted, and about 30 to 45 hours when carried out continuously.

In order that the invention may be understood more fully, reference should be had to the following specific examples.

Example I

500 parts by weight of Stoddard Solvent, a petroleum fraction boiling within the range of about 310° to 410° F. at atmospheric pressure and being obtained by distillation from a paraffinic crude oil, were placed in a narrow glass vessel. Disposed about this vessel were four elongated light sources emitting active light rays. The vessel was positioned above a heater, and was provided with a diffusion device for the introduction of chlorine. A conduit connected the upper end of the vessel with an atmospheric pressure reflux condenser.

Chlorine was introduced into this vessel over a period of 15 hours in three increments of about 5 hours each on three successive days. During most of this period the chlorine was introduced at a rate such that a very small amount of unreacted chlorine passed through the vessel. The exothermic chlorination reaction caused the temperature to rise to about 90° C. but the rate of

chlorine addition was controlled so that the temperature did not exceed 100° C. during this period. Towards the end of the period, the chlorination had substantially ceased and most of the introduced chlorine was passing through the vessel. At this time the weight of the mixture was about 863 parts; the chlorine content being about 42 per cent by weight. At this stage the mixture was black in color and contained small sludge-like flocs.

This mixture was then agitated with 5 per cent, by weight of the mixture, of finely divided "Super Filtrol," and was then filtered. A clear, very slightly colored product, was obtained. This product was then recharged to the chlorinating vessel. The chlorination was continued over a period of about 32 hours (in five successive daily periods of about six hours each). During most of this chlorination period the temperature of the mixture was maintained at from about 130° to 150° C. At the end of this period the chlorine content of the mixture was 70.5 per cent by weight of the mixture. The mixture at this stage in the process was a clear red viscous oil. It was a valuable product as it could be used as a raw material for the production of heavily fluorinated compounds. Such fluorinated compounds may be used as special lubricants.

A portion of the chlorinated mixture prepared as described was returned to the chlorination vessel and the chlorination was continued for an additional 12½ hours while maintaining the temperature at about 170° C., to produce as a product a red, waxy material, solid at ordinary temperatures. The material contained 74.75 per cent chlorine by analysis.

Example II

180 parts by weight of a mineral seal oil, a lubricating oil fraction of a Mid-Continent crude and boiling within the range of about 520° to 615° F. at atmospheric pressure, were introduced into a chlorinating vessel such as described in Example I. Chlorine was passed through the oil at a rate such as to maintain an excess of chlorine over a period of about 22½ hours distributed over four days. During substantially all of this period the temperature was maintained above about 70° C. and did not rise above about 125° C. Toward the end of the period the reaction product was, at room temperature, an extremely viscous, dark red liquid. The product had gained 266 parts in weight, indicating a chlorine content of about 60 per cent. Since the product was too viscous at room temperature to permit filtering from an absorption agent, it was diluted with about 100 parts of CCl_4 and then agitated with 10 per cent of its weight of "Super Filtrol" for about 20 minutes at about 60° F. and then filtered. The filtered solution was recharged to the chlorination vessel and the CCl_4 was removed by passing an excess of chlorine through the solution heated to a temperature within the range of about 60° to about 80° C. The introduction of chlorine in excess was continued for 15¾ hours at a temperature of about 150° to 160° C. At the end of this time the rate of chlorine absorption was rapidly decreasing and the introduction of chlorine was discontinued. The product showed a gain in weight over the original mineral seal oil of 318.5 parts, had a chlorine content of 66.8 per cent, and was a dark red solid.

Another chlorination operation was carried out under conditions similar to those described in Example II except that the step of contacting the partially chlorinated hydrocarbon mixture with "Super Filtrol" was omitted. At the end of a total of 40¼ hours of contacting the mixture with chlorine a black carbonaceous material had collected in the mixture, indicating that the product formed was decomposing and therefore the introduction of chlorine was stopped. The net gain in weight was only 225 parts. However, because considerable material was lost due to decomposition, the chlorine content of the product was 62.5 per cent. This chlorination product was a black semi-solid.

It will be understood that the foregoing examples are merely illustrative of the invention. The procedures described may be employed for the chlorination of others of the types of hydrocarbon mixtures previously mentioned. Also, various changes may be made in the procedures. For example, the rate of introduction of chlorine in the initial stage may be increased without excessive temperature rise provided the mixture is cooled; for example, by indirect heat exchange. Also, the initial chlorination may be moderated by using a diluent such as hydrogen chloride or carbon dioxide. With respect to the temperatures employed in the examples and those previously discussed, it will be understood that the invention is not limited to the use of specific temperatures as in general the temperatures employed in conventional chlorinations may be used. We have found, however, that when the temperatures referred to are employed the process yields good products in a simple manner.

The advantages of the invention may be obtained in other ways. Thus, instead of proceeding as described—subjecting a hydrocarbon mixture in succession to a first stage of chlorination, to treatment with an adsorbent, and then to a second stage of chlorination—the process may be carried out by circulating the hydrocarbon mixture downwardly through the chlorination vessel in contact with upwardly rising chlorine gas, then passing the partially chlorinated mixture from the bottom of the chlorination vessel through a body of adsorbent and returning the treated mixture to the top of the vessel. When operating in this way, it is not necessary to continue the circulation of the hydrocarbon mixture after the chlorine content of the mixture has reached about 30 to 45 per cent by weight, as passage of the mixture through the adsorbent in the early stages is sufficient to condition the mixture for accepting chlorine until the desired amount of chlorine has been added.

The invention may also be practiced in a continuous manner. In order that this method of operation may be easily understood, reference should be had to the accompanying drawing in which the single figure is a diagrammatic illustration, with parts in section, of equipment employed in this embodiment.

Referring to the drawing, the hydrocarbon mixture to be subjected to chlorination, in this case a kerosene fraction of petroleum boiling from about 500° to 600° F., is introduced through line 1 into first stage chlorination tower 2 and caused to flow downwardly through this tower. Tower 2 is provided with means such as trays 3 for insuring intimate contact between the hydrocarbon mixture and the chlorine gas. There is positioned between each pair of trays a source of active light rays shown as elongated light tubes 4, and between every other pair of trays heat exchange coils 5. Chlorine gas is introduced into the tower through line 6 and gas diffusion device 7, shown

as a perforated circular tube. The chlorine passes upwardly through tower 2 in intimate contact with the descending hydrocarbon mixture and accomplishes the desired first stage chlorination. Unreacted chlorine and hydrogen chloride formed in the reaction are removed from tower 2 through line 8. Additional hydrogen chloride and chlorine gas are introduced at an intermediate point in tower 2 through line 9. This hydrogen chloride and chlorine are recycled from a second stage chlorination as will presently be described.

The conditions maintained in the first stage chlorination tower are preferably substantially the same as those described in Example I above. Thus the pressure is preferably about atmospheric and the temperature between about 80° and 110° C. The rate of flow of the hydrocarbon mixture through the tower and the rate of introduction of chlorine are preferably such as to produce at the bottom of the tower a hydrocarbon mixture containing 30 to 45 per cent chlorine. It is preferred to maintain a temperature gradient from the top to the bottom of this tower of at least 30° C.; e. g., varying from about 80° to 110° C. Such a gradient is insured by heat exchange coils 5. Thus, in the upper section of the tower when chlorinating reactive hydrocarbons the coils are used for cooling the mixture, and in lower section containing the partially chlorinated and therefore less reactive compounds the coils are used for heating the mixture.

This partially chlorinated mixture is removed from tower 2 through line 10 provided with a pump 11 and leading to a cooling zone 12 where the temperature of the chlorinated mixture may be reduced, for example to about 20° to 30° C. The cooled mixture is then passed through line 13 and through either valved line 14 or valved line 15 leading respectively to an adsorption tower 16 and a similar tower 17. These adsorption towers contain an activated clay such as "Super Filtrol" in the form of 16 to 8 mesh granules. The towers are used alternately, one being regenerated while the other is in use.

The treated partially chlorinated mixture is removed either through valved line 18 or 19, depending upon which treating tower was employed, which are connected with line 20 leading to second stage chlorinating tower 21. It is usually desirable to heat the hydrocarbon mixture before introducing it into tower 21. To accomplish this the mixture is passed through valved line 22 and heater 23 and returned to line 20 through valved line 24. The temperature of the mixture is preferably raised in this heater to about 90° to 110° C. Tower 21 is constructed similarly to tower 2 previously described. Thus it is provided with trays 27, sources of light 29, and with heat exchange coils 31. Chlorine gas is introduced through valved line 32 leading to a diffusion device 33. In this tower the downwardly flowing partially chlorinated hydrocarbon mixture is contacted with chlorine gas in countercurrent fashion at a pressure which may be substantially atmospheric and at elevated temperature conditions. Heat is supplied to the tower through the heating coils so that the temperature at the bottom of the tower is the maximum desired for effective chlorination; for example, a temperature within the range of about 150° to 200° C. As indicated above, the temperature of the hydrocarbons entering this tower may be substantially atmospheric temperature or it may be a temperature of about 90° to 110° C. In any case, it is preferred to control the operation so that there is a temperature gradient from the top to the bottom of the tower of from about 50° to 100° C.

Since a high degree of chlorination is accomplished in tower 21, chlorine is introduced through line 32 in substantial excess of that taken up by the mixture. The excess chlorine together with hydrogen chloride formed in the reaction is removed through line 34. A part of this mixture is passed to a recovery system, not shown, through valved line 36, and the remainder is passed through valved line 9 leading to first stage chlorination tower 2 as previously described. The chlorinated mixture is removed from the bottom of tower 21 through a line 37 provided with a pump 38 and is passed into a fractionating tower 39.

In the fractionating tower the chlorinated mixture is separated into a heavily chlorinated fraction and a less-heavily chlorinated fraction. As is well known, in the chlorination of hydrocarbons, the addition of chlorine goes unevenly so that a part of the mixture is more heavily chlorinated than another part. The partially chlorinated hydrocarbons are passed overhead from the fractionating tower through valved line 41 to a condenser 42 and are returned to second stage chlorination tower 21 through valved line 43. The desired heavily chlorinated product is removed from the fractionating tower through valved line 44. In many cases where the presence of partially chlorinated hydrocarbons in the final product is not undesirable, the use of the fractionating tower may be dispensed with.

When chlorinating a heavy hydrocarbon oil by the continuous process described, the partially chlorinated mixture leaving tower 2 is preferably thinned before contact with the adsorbent, with an unreactive solvent such as CCl_4 which is vaporized and removed in the second stage chlorination tower.

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

We claim:

1. The process of chlorinating a hydrocarbon to a high chlorine content which comprises reacting the hydrocarbon in liquid phase with chlorine under irradiation by actinic light rays to accomplish substantial chlorination, removing the resulting chlorinated hydrocarbon from contact with free chlorine, then flowing the resulting chlorinated hydrocarbon through an amount of an adsorbent in active condition thereby removing from said resulting chlorinated hydrocarbon more easily adsorbed bodies formed in said chlorination, and then reacting the treated product free from said more easily adsorbed bodies with chlorine under irradiation by actinic light rays to accomplish additional chlorination.

2. The process of chlorinating a hydrocarbon mixture to a high chlorine content which comprises reacting the mixture in liquid phase with chlorine under irradiation by actinic light rays until the rate of acceptance of chlorine by the hydrocarbon mixture has substantially decreased, removing the resulting chlorinated hydrocarbon mixture from contact with free chlorine, then flowing the resulting chlorinated hydrocarbon mixture through an amount of an adsorbent in active condition thereby removing from said resulting chlorinated hydrocarbon mixture more easily adsorbed bodies formed in said chlorina-

tion, and then reacting the treated product free from said more easily adsorbed bodies with chlorine under irradiation by actinic light rays to accomplish additional chlorination.

3. The process of chlorinating a liquid petroleum fraction to a high chlorine content which comprises reacting the petroleum fraction in liquid phase with chlorine under irradiation by actinic light rays to accomplish substantial chlorination, removing the resulting chlorinated petroleum fraction from contact with free chlorine, then flowing the resulting chlorinated petroleum fraction through an amount of an adsorbent in active condition thereby removing from said resulting chlorinated petroleum fraction more easily adsorbed bodies formed in said chlorination, and then reacting the treated product free from said more easily adsorbed bodies with chlorine under irradiation by actinic light rays to accomplish additional chlorination.

4. The process of chlorinating a liquid petroleum fraction to a high chlorine content which comprises reacting the petroleum fraction in liquid phase with chlorine under irradiation by actinic light rays until the rate of acceptance of chlorine by the petroleum fraction has substantially decreased, removing the resulting chlorinated petroleum fraction from contact with free chlorine, then flowing the resulting chlorinated petroleum fraction through an amount of an adsorbent in active condition thereby removing from said resulting chlorinnated petroleum fraction more easily adsorbed bodies formed in said chlorination, and then reacting the treated product free from said more easily adsorbed bodies with chlorine under irradiation by actinic light rays to accomplish additional chlorination.

5. A continuous process of chlorinating a hydrocarbon mixture which comprises, in a first chlorination zone, flowing the mixture downwardly in liquid phase in intimate admixture with an upwardly flowing stream of chlorine gas under conditions including irradiation by actinic light rays until the rate of acceptance of chlorine by the hydrocarbon mixture has substantially decreased, removing the resulting partially chlorinated hydrocarbon mixture from contact with free chlorine, then flowing the resulting partially chlorinated hydrocarbon mixture through an amount of an adsorbent in active condition thereby removing from said resulting partially chlorinated hydrocarbon mixture more easily adsorbed bodies formed in said chlorination to produce a treated mixture, flowing the treated mixture into a second chlorination zone, flowing said mixture downwardly in liquid phase in intimate admixture with an upwardly flowing stream of chlorine gas in said second chlorination zone under conditions including irradiation by actinic light rays to accomplish additional chlorination, fractionating the resulting chlorinated product into a heavily chlorinated fraction and a less-heavily chlorinated fraction, and returning the less-heavily chlorinated fraction to intimate contact with chlorine in the second chlorination zone.

6. A process in accordance with claim 5 in which a temperature gradient is maintained over the first and second chlorination zones, the temperature at the top of each of said zones being lower than temperature at the bottom of each of said zones.

7. A process in accordance with claim 5 in which the hydrocarbon mixture is a light liquid petroleum fraction.

8. The process of chlorinating a liquid petroleum fraction to a high chlorine content which comprises reacting the petroleum fraction in liquid phase with chlorine under irradiation by actinic light rays at a temperature within the range of about 80° to about 110° C. until the rate of acceptance of chlorine by the petroleum fraction has substantially decreased, removing the resulting chlorinated petroleum fraction from contact with free chlorine, then flowing the resulting chlorinated petroleum fraction through an amount of an adsorbent in active condition thereby removing from said resulting chlorinated petroleum fraction more easily adsorbed bodies formed in said chlorination, and then admixing the treated product free from said more easily adsorbed bodies with chlorine under irradiation by actinic light rays at a temperature of about 110° to about 170° C. to accomplish additional chlorination.

9. The process of chlorinating a hydrocarbon mixture to a high chlorine content which comprises, in a first chlorination zone, continuously flowing the mixture downwardly in liquid phase in intimate admixture with an upwardly flowing stream of chlorine gas under conditions including irradiation by actinic light rays to accomplish substantial but incomplete chlorination, flowing the resulting partially chlorinated hydrocarbon mixture from the bottom of said first chlorination zone through the first of two adsorption zones containing a solid adsorbent in active condition thereby removing from said resulting partially chlorinated hydrocarbon mixture more easily adsorbed bodies formed in said chlorination to produce a treated mixture, flowing the treated mixture into a second chlorination zone, flowing said mixture downwardly in liquid phase in intimate admixture with an upwardly flowing stream of chlorine gas in said second chlorination zone under conditions including irradiation by actinic light rays to accomplish additional chlorination, continuing flowing the partially chlorinated hydrocarbon mixture from said first chlorination zone through said adsorption zone until the adsorbent becomes inactive due to adsorption of the more easily adsorbed bodies formed in the chlorination in said first chlorination zone, then flowing the partially chlorinated hydrocarbon mixture from the bottom of said first chlorination zone through the second adsorption zone containing a solid adsorbent in active condition, and regenerating the inactive solid adsorbent in the first adsorption zone.

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