May 14, 1940. H. BENDER 2,200,254

CHLORINATION

Original Filed June 1, 1937 2 Sheets-Sheet 1

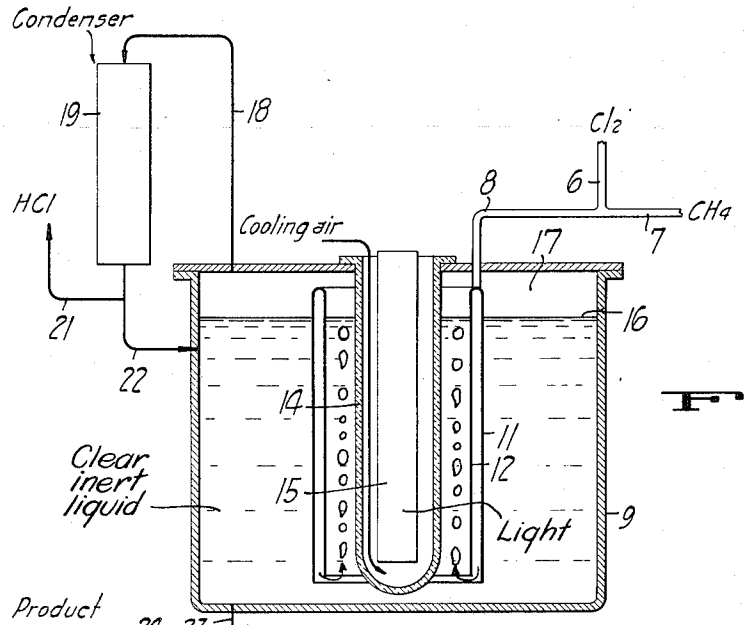


FIG. 1

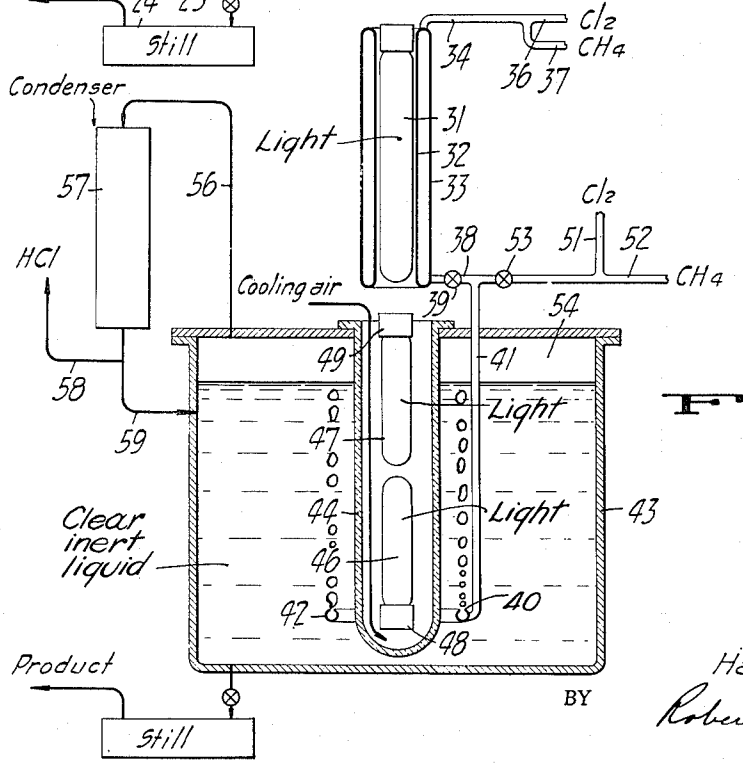


FIG. 2

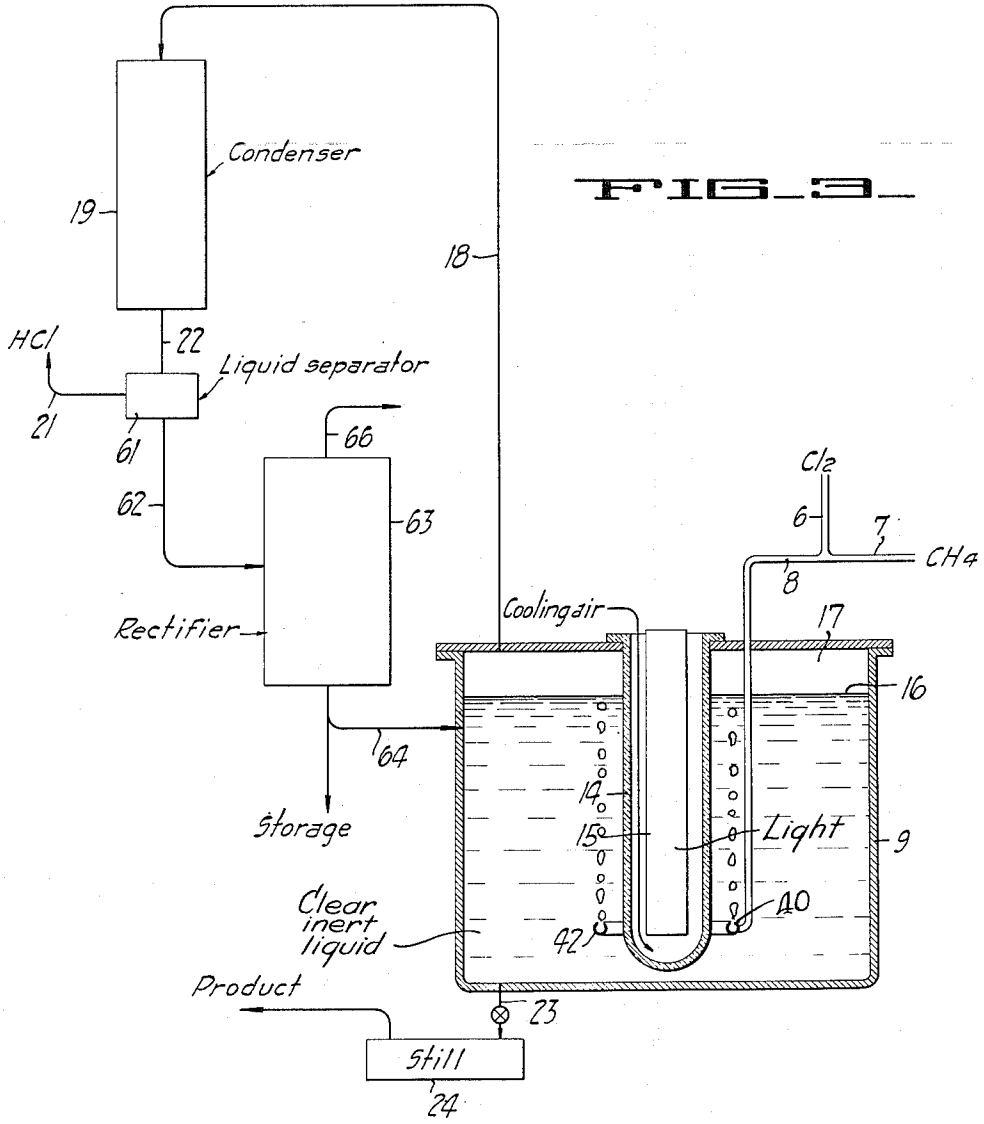
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FIG. 3.



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UNITED STATES PATENT OFFICE

2,200,254

CHLORINATION

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Application June 1, 1937, Serial No. 145,734
Renewed July 8, 1939

14 Claims. (Cl. 260—661)

This invention relates to the chlorination of saturated aliphatic hydrocarbons by substitution and, more particularly, to a process enabling the chlorination operation to be carried out without fear of explosion or ignition.

Ellis in his work, The Chemistry of Petroleum Derivatives, the Chemical Catalog Company, 1934, states at page 686 that "Because of the very highly exothermic nature of the chlorination reactions, the successful control of the process is often a matter of difficulty even on a laboratory scale. Furthermore, there is always a danger of chlorination proceeding extremely violently and even with explosive force. When this occurs high reaction temperatures are attained and the main products are carbon and hydrogen chloride formed according to the reaction:

$$CH_4+2Cl_2\rightarrow C+4HCl$$"

It has been my observation that successful control of the methane chlorination reaction is extremely difficult, and that an operation or process which might be successfully controlled in a laboratory, for example that disclosed in U. S. Bureau of Mines Technical Paper No. 225, 1921, could not be practiced on a plant scale.

One of the difficulties in carrying on the chlorination reaction with hydrocarbons is that ignition takes place. The chlorination of methane is apparently a chain reaction, and once chlorination is started it tends to continue. This is because at the temperatures usually employed in the chlorination the hydrocarbon, methane for example, is unstable, and the tendency for the hydrocarbon is to decompose to an equilibrium mixture of the hydrocarbon, carbon and hydrogen, the latter in the presence of chlorine reacting to form hydrochloric acid.

In Patent No. 1,717,136 of June 11, 1929, Ayres has stated that ignition could be suppressed and eliminated if the rate of flow of the hydrocarbon vapor was sufficiently high at the point at which the chlorine was introduced and Ayres further specified that this velocity should be in excess of one half of that required for distinct turbulent flow of the mixture. I have found that it is unnecessary to observe the teaching of Ayres, and that in fact ignition of the mixture can be prevented independently of the flow velocity, and I have successfully suppressed ignition even though the flow rate was very low, far less than the supposedly critical one half of turbulent flow, or the mixture was stationary. Thus, my invention enables the hydrocarbon to be chlorinated successfully and at the same time the undesirable decomposition reactions of the hydrocarbon are obviated during the entire course of the reaction irrespective of the flow rate.

The question of ignition is important not only at the time the chlorine is brought into contact with the hydrocarbon, but also during the entire course of the chlorination reaction. There is little point in preventing the ignition of the hydrocarbon at the time the chlorine is introduced into the hydrocarbon if subsequently, during the reacting of the hydrocarbon and chlorine, ignition can occur. The present invention enables the chlorine-hydrocarbon mixture to be not only constructed but reacted while ignition is obviated during the entire time that chlorine is in contact with the hydrocarbon at a reacting temperature and when ignition normally occurs unless this invention is practiced.

It is the discovery of the present invention that the suppression of undesirable decomposition reactions can be successfully effected if the walls confining the chlorine-hydrocarbon mixture are so close together that reacting molecules cannot travel any great distance before contacting the walls of the vessel confining the mixture. For example, in chlorinating methane in the presence of light, the methane being mixed with a stochiometrical quantity of chlorine sufficient to produce carbon tetrachloride, I have been able to react the chlorine with methane successfully at about atmospheric pressure without any ignition while exposing the mixture to a light source having four times the intensity of sunlight, if the walls of the vessel confining the mixture were not over 5 mm. apart. The reaction took place independently of the velocity through the vessel and independently of the velocity past the light, velocity being an insignificant factor. The outer walls of the vessel were cooled in a water bath so that they were maintained cold.

The same consideration applies to thermal chlorination of methane. For example, I am able to mix methane and chlorine successfully without regard to the velocity of either of the components and to avoid ignition, even at the point of introduction of the chlorine into the methane, irrespective of the ratio of the chlorine to the methane, so long as the walls of the vessel confining the mixture are sufficiently close together that the chain reaction is suppressed and ignition, if it ever occurs, is instantly suppressed.

It is to be remarked that the closeness of the walls is really the factor effecting the ignition suppression and that velocity has in fact nothing to do with it because I have worked with veloci-

ties extending the full range, that is, from substantially still bodies of gas to gas flowing under conditions of turbulent flow. Flow rate does not affect the ignition.

In the thermal chlorination of methane, the same teaching applies. Thus, if a chlorine-methane mixture be formed for subsequent reaction in a reactor in which the substitution is effected by thermal means, for example, exposure to a temperature of 360° C., I have found that the reaction can be made to go on smoothly and without the undesirable decomposition or ignition occurring if the wall spaces are closely adjacent, at least during the initial portion of the reaction, so that the reaction proceeds smoothly and without any decomposition to form carbon and hydrochloric acid. For example, I have determined that the walls of a reactor into which a cold (30° C.) chlorine-methane mixture was introduced, the walls being maintained at a temperature 360° C., should be only about $\frac{1}{32}$ of an inch apart at least during the initial length of the reactor, so that the chain decomposition reaction be suppressed and the highly exothermic chlorination reaction started out smoothly. Once the reacting materials have become diluted with a partially chlorinated material, these afford buffers for the reactants and prevent such a degree of activity that the decomposition reaction occurs to the suppression of the others. The walls of a reactor for the chlorination of methane can be made of glass, graphite, "Carborundum," and the like materials having little if any catalytic effect upon the reaction and having substantially no absorbent capacities for either the methane or any of the other reactants or constituents.

In carrying out the photochemical chlorination, I have been able to successfully chlorinate methane and other hydrocarbons even though the light was very intense. For example, in the chlorination of methane, I have found that radiation band between 3000–4400 Å., even when present in an intensity four times greater than that with which it is present in noon sunlight, activates the reaction to proceed smoothly, evenly and without undesirable decomposition reactions, if the walls of the confining vessel, in this case glass, are not over 5 mm. apart. The walls of the confining vessel should usually be cold. That is, they should not be raised to a temperature sufficiently high that the temperature in and of itself can effect thermal chlorination.

I have found that increasing the light intensity above four times that of noon sunlight is ineffective. Increasing the light intensity beyond a certain point is wasted effort. By raising the pressure, however, the light intensity can be increased effectively and the reaction rate increased. For example, I have increased the reaction rate between chlorine in methane to produce carbon tetrachloride, using a light intensity of eight times (3000–4400 Å.) that of strong sunlight by increasing the pressure to 30 pounds absolute.

The previously discussed distances are at pressures close to atmospheric. As the pressure is raised the distance becomes less. For example, if the pressure be increased to about two atmospheres the distance between the surfaces must be decreased. I have found that a distance of 3 mm. will suffice to suppress ignition under approximately two and a half atmospheres absolute pressure. This is indicative of the distance variation with pressure of the suppressing walls. With pressures lower than atmospheric, that is, less than one atmosphere absolute, the distance between the walls can of course be made greater. Roughly, it will be found that the pressure can be varied according to the square of the distance between the walls, within the limits previously indicated. Operation at pressures less than atmospheric are not preferred because this means a lower total through put, increased apparatus size, and a greater investment in apparatus.

This variation can be expressed by the equation $Pd^2=375$ where P is the absolute pressure in pounds per square inch and d is the distance in millimeters between the surfaces. The distance d at the point of release or exposure to intense irradiation should not exceed and should preferably be slightly less than that required to satisfy this expression, for the absolute pressure employed.

In producing carbon tetrachloride I have found it advantageous to use a combined vapor and liquid phase process. That is, a portion of the process reaction is conducted initially in the vapor phase while the final reaction is largely conducted in the liquid phase. This manner of operation I have secured in different ways, and I have successfully reacted the chlorine-methane mixture initially in the vapor phase and then injected this into a body of irradiated carbon tetrachloride or other suitable material.

I have found that various apparatus arrangements can be satisfactorily used, and hereinafter these will be disclosed in conjunction with the preferred process.

It is generally the broad object of the present invention to provide a novel process for the production of carbon tetrachloride by the direct reaction of methane and chlorine to produce the carbon tetrachloride, the reaction being activated only by light or a light band, the use of a catalyst or heat being excluded.

It is another object of the invention to provide a novel process for carrying out the reaction of chlorine and methane to form carbon tetrachloride.

In addition to the foregoing objects, the invention includes numerous others as well as other features of advantage, some of which, together with the foregoing, will be readily apparent to those skilled in the art upon a reading of the detailed processes of my invention and the apparatus for conducting these, as set forth hereinafter.

In the drawings accompanying and forming a part of this specification, Figure 1 is a diagrammatic illustration of an apparatus set up for conducting a process in accordance with my invention.

Figure 2 is another diagrammatic illustration of an apparatus set up for conducting the present invention.

Figure 3 is another diagrammatic illustration of an apparatus set up for conducting the present invention, particularly as related to the partial chlorination of methane.

Referring particularly to Figure 1, I have found it advantageous to use a combined vapor and liquid phase process in the production of carbon tetrachloride. This is secured by injecting a preformed chlorine-methane mixture, in the desired stochiometric ratio, into a vessel filled with carbon tetrachloride. As appears in Figure 1, chlorine from line 6 is mixed with methane from line 7. The following reaction is typical of the result achieved:

$$CH_4+4Cl_2\rightarrow CCl_4+4HCl$$

Tubes 6 and 7 are connected to a pipe 8. The internal diameter of these is such that free ignition does not occur. Usually no difficulty is encountered on this score if the chlorine and methane are cold, that is, at about room temperature.

Pipe 8 leads into a vessel 9 wherein the reaction is to be conducted. The pipe is connected to that space existing between an outer glass shell 11 and an inner glass shell 12. These shells are spaced apart, usually a distance of between 3 and 5 mm. The inner shell is somewhat shorter than the outer shell so that gas bubbles released from between the shells will pass up on the inside of shell 12, receive light passed through lightwell 14 from light source 15. The inner shell 12 and the lightwell are made as close to the diameter of the light 15 as is possible. For other things being equal, the effect of the light upon the reaction varies inversely as the square of the distance, and it is therefore desirable to have as little distance as possible between the light source and the reacting material.

As the mixture passes between the glass walls 11 and 12 it reacts to form carbon tetrachloride, partially chlorinated methane, some unreacting materials being present. Since the materials passing between the walls 11 and 12 are discharged directly into the liquid carbon tetrachloride, they mix with the carbon tetrachloride, bubbles of unreacted material rising through the liquid mass, and undergo, within each bubble, a local vapor phase chlorination for each bubble contains reactible chlorine and methane.

It is important that the point of release of the bubbles into the liquid carbon tetrachloride be in an effective region of the light source. This is contrary to the Brooks et al. Patent 1,191,916 of July 18, 1916, which teaches that the chlorine should be permitted to rise toward the light source after being introduced in a relatively poorly irradiated portion of the liquid body. Chlorine, being more soluble in carbon tetrachloride than methane, dissolves in the carbon tetrachloride liquid body in a relatively short time. It is therefore desirable that each body of the gas as it is released into the liquid body be subject to activation by the light source so that reaction goes on while available chlorine is present. The partially chlorinated methanes, as methyl chloride, dissolve in the carbon tetrachloride, being more soluble therein than methane. These react with dissolved chlorine in the liquid body to form carbon tetrachloride which is added directly to the liquid phase.

The process disclosed has a relatively high efficiency because light which is not effective to activate the materials undergoing reaction is effective upon the liquid body, irradiating it so that liquid phase reactions go on therein.

In the drawings I have indicated the liquid level as being maintained at about 16 so that a vapor space 17 is provided. This is not essential, but I have found it advantageous because it permits of further reaction in the vapor phase, one in which the material is retained for a relatively great length of time as compared to the length of time that the chlorine and methane have to react while passing between walls 11 and 12 or are rising in the form of bubbles past the light source. For example, in one apparatus the length of the bubble path was 14 inches, while the retention time in the vapor space 17 was several hundred times as long as that time required for a bubble of chlorine and methane to traverse the bubble path.

Approximately half a second was required for the chlorine methane bubbles to rise past the light. The retention time in the vapor space was regulated so that the vapor volume was only replaced every fifteen or twenty minutes, the unreacted materials in the vapor phase thus having three or four hundred times as long to react in the vapor space as they had while present as bubbles. By permitting the vapor space to exist over a body of carbon tetrachloride, by maintaining the body of carbon tetrachloride at a suitable temperature, the partial pressure of carbon tetrachloride in the vapor phase can be maintained so high that there is no danger of explosion if the light should be suddenly turned on and off, something which could readily occur upon current failure.

The body of carbon tetrachloride in vessel 9 is maintained warm, usually a temperature of about 60° C. although temperature does not appear to have any great effect upon the reaction. At this temperature, the products are vaporized and pass off through line 18 into the condenser 19. This condenser liquefies substantially all of the vaporized products except hydrochloric acid, which is permitted to pass off through line 21, the liquefied products being separated and returned through line 22 into the tank 9. By passing the vapors in at the upper end of the condenser, and by positioning the condenser in a vertical position, the condenser in effect acts as a rectification unit and effects a thorough separation of the hydrochloric acid.

The liquefied products in the tank 9 are drawn off through line 23 into a still 24 to be refined to provide the final carbon tetrachloride as a major product.

I have heretofore mentioned that the liquid in vessel 9 is carbon tetrachloride. Any other inert liquid can be used, but since the carbon tetrachloride will accumulate therein it is the most convenient liquid to use as the liquid body in which to conduct the liquid phase chlorination reaction. However, any other inert material can be used, such as water or another material which will not react with materials present or which, if it does react, is not objectionable.

In Figure 2, I have shown another form of apparatus in which the reactions are conducted separately. In this, a light source is provided by light 31. A glass walled vessel is positioned closely adjacent the lamp, the vessel being provided by walls 32 and 33. These walls are joined together and are closely placed, between 3 and 5 mm. A preformed chlorine-methane mixture is introduced through line 34 from lines 36 and 37. The gaseous mixture is passed between the walls, reacting at least partially therein. The light may be suddenly turned off or turned on in the presence of the mixture and an explosion or ignition does not occur if the walls are sufficiently close together to suppress the ignition or explosion, as has been previously discussed at some length heretofore.

An outlet pipe 38, including a valve 39 therein, extends to inlet pipe 41. This pipe is connected to a header ring 42 positioned near the bottom of a vessel 43. A well 44 is provided in the vessel and within this well are positioned lamps 46 and 47. These lamps are conveniently of the 400 watt G. E. H-1 lamps, of high intensity and having glass bulbs. The lamps are positioned to secure a maximum length of radiation path,

the lamps being positioned with retaining socket 48 for lamp 46 at the bottom of the well and socket 49 for lamp 47 being positioned at the top of the well so that the ends of the lamps are closely adjacent. The glass well is made as small as possible in internal diameter, while the header ring is also placed as close to the well as is consistent with good mechanical practice. Since the effectiveness of the light varies inversely as the square of the distance from the light, the reason for this is apparent.

The partially chlorinated materials are introduced through pipe 41 and are released through apertures 40 in the header ring 42 to rise past the light source and be effectively chlorinated. In dealing with such light sources as that previously mentioned, it is to be pointed out that the point of release of the material to be chlorinated must be in the zone of effective light radiation. Thus, for example, I find that if the material to be chlorinated is released in a zone where the light is relatively of low intensity, and if the chlorinated products then rise into a zone where the light is intense, little if any chlorination occurs, and the effectiveness of the operation is low. I have determined that the products to be chlorinated must be initially released into the liquid body in the region where the intensity of the light is relatively high, and preferably at a maximum. Apparently this is due to chlorine extraction from the material by the solvent action of the body of liquid material. In the case of the lamps discussed, I have found that the header ring should not be over two inches below the lowest point of the pencil of light in the lamp, because if this occurs, then effective chlorination does not occur at a rate comparable to that secured if the chlorine and methane, for example, are released at a level within the pencil of light. The header ring should preferably not be above the bottom level of the pencil of light because if it is, then the effective length of the light is being lost and is not utilized to maximum advantage.

Instead of first chlorinating the materials in the vessel provided by walls 32 and 33, valve 39 can be closed and chlorine and methane, in premixture, can be introduced from line 51 and 52 directly into the header pipe 49 past valve 53.

The vapor space indicated at 54 is also preferably provided in the tank 43 to permit cleaning up of the extra gas in the vapor. The retention time in this vapor space is preferably adjusted so that it can be coordinated with the operation in the liquid phase. The retention time for any particular piece of apparatus will of course vary, depending upon the percentage of the materials delivered to it. In any event, it can be made considerable and a considerable volume of vapor can be present as long as the carbon tetrachloride is relatively warm and a sufficient concentration thereof is maintained to insure that partial vapor pressure is so high that explosion will not occur. Vaporized materials are passed out of tank 43 and the vapor space 54 thereof through line 56 into the top of a condenser 57. This condenser is maintained at a suitable temperature so that all products passed out are liquefied with the exception of substantially only hydrochloric acid which is removed through line 58 in the bottom of the condenser, liquefied materials being returned through line 59 to the liquid.

The invention is of course applicable to the chlorination of other saturated hydrocarbons, particularly the first six members of the paraffine series, including methane, ethane, propane, butane, pentane and hexane, and these, whether they be present as single gaseous components or mixed together in the form of mixed vapors such as that of a casinghead gasoline.

In Figure 3 I have indicated an apparatus closely resembling that in Figure 1 (the same numerals being applied to the common parts) except that a header 61 is employed to release the chlorine-methane mixture from line 8. This apparatus assembly is particularly intended for use when it is desired to produce partially chlorinated methane, methyl chloride, dichloromethane, or chloroform. I have found that partially chlorinated methane can be manufactured successfully using actinic light if the chlorine-methane ratio is adjusted and, preferably, if some other factors affecting the reaction are taken into consideration. I have observed that to produce carbon tetrachloride it is preferable that the chlorine be in excess of a methane-chlorine ratio of 1 to 2. I have also observed that if this ratio be lowered so that it is less, and if in fact, excess methane is present over that stochiometrically required to react with the chlorine, then the production of partially chlorinated methane is favored. For example, in the operation of the apparatus shown in Figure 1, I have found a 2.6% chloroform content in the liquid returned through line 22, with a methane-chlorine ratio of 1 to 2. When this ratio is reduced to equal volume, or a ratio of 1 to 1, the chloroform content increases to 7%, while if the ratio is further reduced, and the excess of methane increased until the volume ratio is 2 to 1, the chloroform content increases to 15%. The percentage of dichloromethane is similarly increased.

The apparatus shown in Figure 3 is particularly useful in securing the partially chlorinated methane produced. As appears in Figure 3, the material from condensers 19 is passed through a liquid-gas separator indicated at 61 and connecting lines 22 and 21. This separator delivers uncondensed hydrochloric acid, methane and chlorine to line 21. The liquid fraction passes through line 62 into a rectification column indicated at 63. The carbon tetrachloride is drawn off through line 64 and can be returned either to vessel 9 or sent to storage. At the top of the rectification column the partially chlorinated methane content is removed through line 66. This content comprises the methyl chloride, dichloromethane and chloroform manufactured.

It is preferred that the temperature in tank 9 be kept relatively high, because it has been my observation that the chlorination which is going on in the tank can be considered as occurring in three different ways. First, the gas phase reaction evidenced by chlorination of the methane in the bubbles released from the header ring. Second, a liquid phase chlorination reaction of partially chlorinated material which occurs throughout the liquid. Partially chlorinated materials are contained in and constitute largely the reflux return through line 22. Third, the chlorination of the methane which has become dissolved in the inert liquid in the vessel 9. Once chlorination of the methane has commenced, it is thereafter relatively easy to chlorinate. The temperature is kept relatively high, of the order of 50° C. or higher. Cooling means can be provided if under specific operating conditions this is found necessary.

I claim:

1. In the chlorination of saturated aliphatic hydrocarbons of less than seven carbon atoms in the vapor phase the step of subjecting a chlorine and hydrocarbon mixture at about atmospheric pressure to light promoting said reaction while confining said mixture between surfaces not over 5 mm. apart.

2. In the chlorination of saturated aliphatic hydrocarbons of less than seven carbon atoms in the vapor phase the step of subjecting a chlorine and hydrocarbon mixture at about atmospheric pressure to actinic light while confining said mixture with smooth, substantially non-catalytic surfaces not over 5 mm. apart, while maintaining said surfaces at a temperature below that at which appreciable thermal chlorination of said hydrocarbon occurs.

3. In the chlorination of saturated aliphatic hydrocarbons of less than seven carbon atoms in the vapor phase, the step of reacting chlorine and the hydrocarbon at about atmospheric pressure under the influence of light while confining the mixture between smooth, substantially non-catalytic surfaces not over 5 mm. apart.

4. In the chlorination of saturated aliphatic hydrocarbons of less than seven carbon atoms in the vapor phase, the step of releasing chlorine and the hydrocarbon in unreacted form into a zone of light promoting reaction of said chlorine and said hydrocarbon while confining the mixture between surfaces so closely adjacent that said surfaces suppress and prevent ignition at the point of said release at the temperature, pressure and light intensity existing at said point, said temperature and pressure being such that normally the chlorine reacts with the hydrocarbon so rapidly as to form free carbon which deposits on said surfaces, the distance in millimeters between said surfaces, under the pressure of operation, not exceeding that required by the equation $Pd^2=375$ where P is the absolute pressure in pounds per square inch and d is the distance in millimeters between said surfaces at the point of release.

5. In the chlorination of methane, the step of subjecting a methane-chlorine mixture to electromagnetic radiations containing a preponderant quantity of rays of wavelength 3000–4400 Å, while confining said mixture at least initially between smooth and substantially non-catalytic surfaces about 5 mm. apart, at not over atmospheric pressure.

6. In the chlorination of saturated aliphatic hydrocarbons of less than seven carbon atoms with elemental chlorine, the step of subjecting a mixture of chlorine and said hydrocarbon in the vapor phase to a reaction promoter e. g. light whereby said mixture reacts to produce HCl and chlorinated hydrocarbon while suppressing C formation substantially entirely by confining said mixture between closely adjacent smooth and substantially non-catalytic surfaces, the distance in millimeters between said surfaces, under the pressure of operation, not exceeding that required by the equation $Pd^2=375$ where P is the absolute pressure in pounds per square inch and d the distance in millimeters between said surfaces.

7. In the chlorination of saturated aliphatic hydrocarbons of less than seven carbon atoms with elemental chlorine, the step of subjecting a mixture of chlorine and said hydrocarbon in the vapor phase to a reaction promoter e. g. light whereby said mixture reacts to produce HCl and chlorinated hydrocarbon while suppressing C formation substantially entirely by confining said mixture between smooth and substantially non-catalytic surfaces 5 mm. apart while maintaining a pressure of not over 15 pounds per square inch absolute.

8. In the chlorination of saturated aliphatic hydrocarbons of less than seven carbon atoms with elemental chlorine, the step of subjecting a mixture of chlorine and said hydrocarbon in the vapor phase to a reaction promoter e. g. light whereby said mixture reacts to produce HCl and chlorinated hydrocarbon while suppressing C formation substantially entirely by confining said mixture between smooth and substantially non-catalytic surfaces not over about 3 mm. apart while maintaining a pressure of 37.5 pounds per square inch absolute.

9. In the production of carbon tetrachloride, subjecting a chlorine-methane mixture between smooth, substantially non-catalytic surfaces from 3 to 5 m. m. apart to vapor phase reaction in the presence of an effective light band from a light source, to react said mixture at least partially, and discharging said reacted mixture in a substantially inert transparent liquid body to react said mixture further in the presence of an effective light band effective to catalyze said reaction, said discharge being at substantially a point of maximum effectiveness of said light band.

10. In the production of carbon tetrachloride, subjecting a mixture of chlorine and methane between smooth, substantially non-catalytic surfaces from 3 to 5 mm. apart to light in the vapor phase to chlorinate at least partially said methane and discharging said mixture after vapor phase light chlorination into an irradiated carbon tetrachloride body at a point of relatively intense irradiation.

11. In the production of carbon tetrachloride from chlorine and methane, continuously exposing between smooth, substantially non-catalytic surfaces from 3 to 5 mm. apart a preformed gaseous mixture of chlorine and methane to light, at a temperature below that at which methane chlorinates thermally, to form carbon tetrachloride.

12. Continuously reacting between smooth, substantially non-catalytic surfaces from 3 to 5 mm. apart a preformed gaseous chlorine-methane mixture at a temperature below 250° C., and in the presence of light effective to initiate and continue said reaction at said temperature.

13. A continuous process for the production of carbon tetrachloride directly from chlorine and methane in the gas phase at temperatures below that at which methane chlorinates due to heat, said process including the steps of continuously passing between smooth, substantially non-catalytic surfaces from 3 to 5 mm. apart a stream of intimate mixture of chlorine and methane past a light effective to initiate and continue reaction of said chlorine and methane to substantially only carbon tetrachloride at said temperature.

14. A process for the production of partially chlorinated methanes from methane and chlorine comprising subjecting between smooth, substantially non-catalytic surfaces from 3 to 5 mm. apart a chlorine and methane mixture containing methane in excess of that required to produce carbon tetrachloride stochiometrically to the action of light to produce a reaction product containing an appreciable volume of partially chlorinated methane.

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