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PROCESSES FOR CHLORINATION OF HYDROCARBONS

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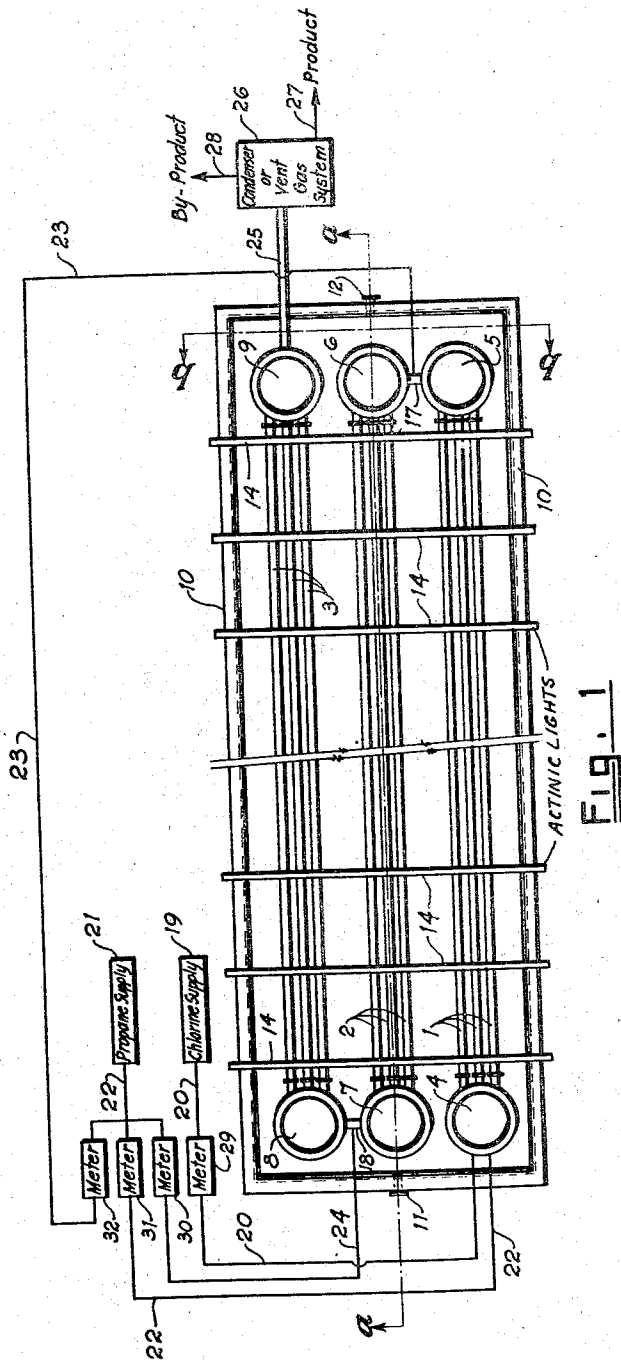


Fig. 1

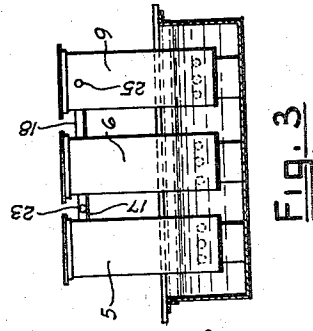


Fig. 3

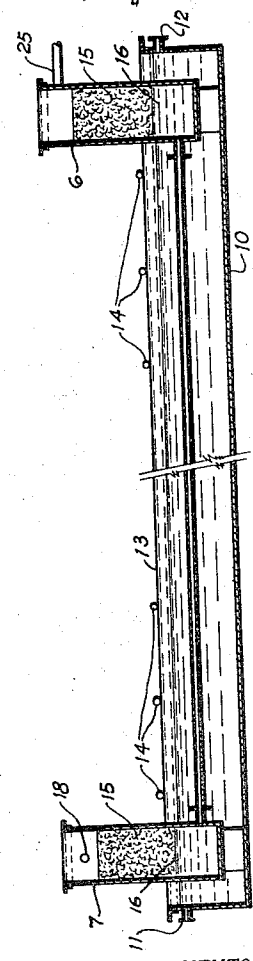


Fig. 2

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PROCESSES FOR CHLORINATION OF
HYDROCARBONS

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5 Claims. (Cl. 204-163)

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Our process relates more particularly to chlorination, in vapor phase, of paraffinic hydrocarbons which are too volatile to be chlorinated in liquid phase at feasible pressures, namely those of one to seven carbon atoms, and has for its object to secure a high velocity of reaction, while avoiding the decomposition and secondary reactions which have heretofore generally been characteristic of the vapor phase chlorination of such hydrocarbons.

If chlorine and vaporized hydrocarbons are brought together at room temperature in the dark, they do not react until the mixture is heated or exposed to actinic light. The reaction may then be explosive. In that case, secondary reaction products, such as chlorinated carbon ring compounds, e. g., hexachlorbenzene, may be formed, and more or less decomposition or carbonization may occur. It has heretofore been customary to add an inert diluent to the chlorine, or to introduce it at high velocity, or to bring the reagents together in the desired proportions and cause them to react beneath the surface of a bath of inert liquid or molten metal chlorides, or in very small tubes, or below 200° C., all of which devices introduce complication which it is desirable to avoid.

It is known that there are definite ranges of proportions within which mixtures of chlorine with such hydrocarbons react explosively and outside which the reaction is mild and readily controllable. The range of explosive reaction varies for different hydrocarbons. Thus, in the case of perfect mixtures of chlorine with methane, propane, normal butane, isobutane and heptane, for example, the mixtures which are liable to react explosively at atmospheric pressure are those containing 20 to 50 per cent, 8 to 42 per cent, 6.8 to 33 per cent, 5 to 40 per cent and 4.2 to 33 per cent of the hydrocarbon by volume, respectively. The straight chain hydrocarbons intermediate between those mentioned form a series of explosive mixtures, the upper and lower limits of which are intermediate between those given. The branched hydrocarbons form a slightly different series, as illustrated by isobutane.

In the vapor phase chlorination of hydrocarbons of the specified group, one way of avoiding violent reaction is therefore to control the composition of the mixture so that the proportion of hydrocarbon shall be above that which forms an explosive mixture with chlorine. In this case the hydrocarbon may be in excess of that which can be chlorinated, even to the monochloride, by the chlorine present in the mixture.

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The other way of avoiding violent reaction is to regulate the composition of the mixture so that the proportion of hydrocarbon shall be below that which forms an explosive mixture with chlorine. However, since there will then be a very great excess of chlorine, it is not possible to limit the chlorination to the monochloride or dichloride. Moreover, the product comes off mixed with the excess chlorine.

We have now found it possible to make up a mixture of one of the specified hydrocarbons with chlorine in which the proportion of hydrocarbon is above or below the predetermined explosive range, cause it to react, and then add whichever reagent is deficient, by carefully proportioned increments, until the desired end point is reached, the mixture being deactivated after each reaction and before addition of the next increment. Unless the mixture is deactivated, violent reaction is liable to occur at the moment of introduction of the next increment, even when the mixture resulting therefrom is theoretically outside the explosive range, owing to the fact that time is required for mixing, and explosive mixtures may form locally.

After the first reaction, the mixture is composed of residual reagents and products of reaction, some of which may be reactive with chlorine. These products absorb heat and lower the temperature of subsequent reactions, thus rendering the proportions less critical than during the initial reaction. Nevertheless, unless each increment is carefully proportioned to the reactive and non-reactive components of the mixture left by the preceding reaction, violent reaction may occur. The composition of the mixture after each reaction depends upon the proportions of the reagents used therein, and since these are variable within a considerable range, the composition of the resulting mixture is likewise quite variable. Hence the increment that may be safely used in a particular situation depends upon several factors and cannot be stated in simple terms or expressed by a graph of two co-ordinates. It must therefore be determined for each case, in accordance with the desired end point and other conditions, and can best be shown by examples.

When using heat to initiate the reaction, which in general involves heating to above 120° C., the reaction mixture may be deactivated between chlorination stages by cooling. When using light for activation we deactivate between stages by cooling below activating temperature and passing the reaction mixture over contact surfaces in a darkened zone. While the reaction mixture is

still in the deactivated state we add the new increment of reagent to it, so that the reagent may become thoroughly diffused throughout the mixture before reactivation.

The mixing of the reagents may be facilitated by passing the gases through an opaque container filled with Raschig rings, and when light is the activating agent the deactivation may be performed in similar apparatus.

Although the photochemical reaction starts at ordinary temperatures, it naturally proceeds more rapidly at higher temperatures, and notably so above 200° C. However, the temperature should not be allowed to reach a point at which decomposition begins to be appreciable. These considerations fix the optimum temperature range at 200° to 400° C. for both the thermal and photochemical reactions.

When the end product is to be the monochloride, it is necessary to avoid an excess of chlorine and preferable to start with a large excess of the hydrocarbon, adding chlorine by increments, with deactivation between, until the end point is reached. In this case the proportion of hydrocarbon is above the explosive range throughout the entire reaction. When the end product is to be the dichloride or trichloride, we may proceed as before up to the formation of the monochloride, or we may start with equal volumes of the gases and add chlorine by increments, with deactivation between, until the ratio of hydrocarbon to chlorine is 1 to 2 or 1 to 3, corresponding respectively to the dichloride and trichloride. In these proportions the mixture would of course be within the explosive range, if the reagents were brought together all at once.

When the proportion of hydrocarbon is above but close to the upper limit of the explosive range, and there is little or no excess of chlorine, a part of the hydrocarbon remains unreacted. The next increment of chlorine may then form with this residual hydrocarbon a mixture which would be in the explosive range in the absence of the products. However, as above stated, if the mixture is deactivated before the next increment so as to afford time for effective mixing before reactivation, and if the increment of chlorine is properly proportioned to the mixture as a whole, explosive reaction does not occur.

Fig. 1 is a plan view of a typical apparatus for carrying out our process.

Fig. 2 is a sectional elevation of the same, along the line a-a of Fig. 1.

Fig. 3 is a sectional elevation of the same, along the line b-b of Fig. 1.

Referring to the figures; 1, 2 and 3, are transparent reaction tubes, preferably of glass, in this case shown as sets of three parallel tubes, and 4, 5, 6, 7, 8 and 9, chambers for mixing the gases in darkness, and after the initial reaction, deactivating the mixture, preparatory to addition of an increment of one of the reagents. Tubes 1, 2 and 3, are immersed in water in tank 10, extending longitudinally thereof. Tank 10 is preferably open and quite shallow. Cooling water is introduced into tank 10 through pipe 11. After passing through the tank the water overflows through pipe 12. The height of pipe 12 determines the water level within the tank, which is preferably maintained so as to submerge the reaction tubes by only a few inches. Resting upon rim 13 of tank 10, and extending transversely thereof, is a series of tubular lights 14, preferably of the fluorescent type. The light from these reaches the reaction tubes through a

thin layer of cooling water, which should be clear and clean.

Reaction tubes 1 extend from chamber 4 to chamber 5. Similarly, reaction tubes 2 extend from chamber 6 to chamber 7, and reaction tubes 3 from chamber 8 to chamber 9. In Fig. 2 chambers 6 and 7 are shown in cross-section. By reference to this figure, it will be seen that these chambers are filled with contact material 15, supported by diaphragms 16. The reaction tubes are connected to the chambers below the diaphragms. Chambers 5 and 6 and 7 and 8 are cross-connected by pipes 17, 18 respectively, above the contact material. Chlorine is admitted to chamber 4 from source 19 through pipe 20. Hydrocarbon (e. g. propane) vapor is admitted to chamber 4 from source 21 through pipe 22. These gases intermingle in chamber 4 and flow downward through the contact material and into reaction tubes 1, where the reaction is initiated by exposure to actinic radiation from lights 14.

The rate of flow of reaction mixture through tubes 1, and of cooling water through tank 10, are regulated so that the temperature of the reaction mixture is kept between 200° and 400° C., and the reaction has gone as far as it will when the mixture reaches chamber 5. Passing upward through the contact material in chamber 5, the mixture is deactivated. As the deactivated mixture flows through pipe 17, an increment of whichever gas was originally deficient, in this case assumed to be propane, is added to it through pipe 23. This increment is thoroughly incorporated with the mixture in passing downward through the contact material in chamber 6. The augmented mixture having reacted while passing through reaction tubes 2, it is again deactivated while passing upward through the contact material in chamber 7 to pipe 18. Here a second increment of propane is added through pipe 24. This increment is thoroughly incorporated with the mixture in passing downward through the contact material in chamber 8. The augmented mixture reacts while passing through reaction tubes 3, and the final reaction product, possibly containing an excess of one of the reagents, is deactivated and cooled in chamber 9. The reaction product is conducted through pipe 25 to condenser 26 and condensed therein. The condensed product is withdrawn through pipe 27, and the by-product and any excess of chlorine may be withdrawn through pipe 28. After separation of the chlorine from the by-product hydrogen chloride, as by passing the mixture through water, the excess chlorine may then be recycled.

If it should be desired to carry the reaction further by heating the mixture to above 400° C., chamber 9, suitably modified, may be used for this purpose, instead of for cooling.

The flow of the gases through pipes 20, 22, 23 and 24 is controlled by flow meters indicated at 29, 30, 31 and 32 respectively.

It is to be understood that the use of triple parallel tubes is only a way of exposing more surface to the light in proportion to the cross-sectional area of the tubes, and optional. In small scale apparatus a single tube may be suitable; also, the mixing and deactivating chambers may be dispensed with, by simply backing sections of the tube where increments of reagents are to be introduced. It should also be understood that, instead of introducing the hydrocarbon by increments, when the monochloride is desired, it may be the chlorine that is introduced in this way. Also, instead of introducing one of

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the reagents by two increments, it may be added by three or more increments, in which case the reaction tube may be in four or more sections, joined by mixing and deactivating chambers.

Taking photochemical chlorination of propane for purpose of illustration as before:

Example I

Equal volumes of chlorine and propane are brought together at atmospheric pressure and room temperature in the dark, producing a mixture in which the propane is above the explosive range, and passed through a horizontal glass tube $\frac{1}{2}$ inch in diameter and 11 feet long, submerged a short distance beneath the surface of a body of water maintained at 95° C. in a tank, the tube being exposed to actinic light penetrating through the water. At a velocity of 6.2 feet per second or 12 liters per minute, the temperature rises to about 300° C. and falls again to 110° C., due to heat transfer to the wall, within the first 5 feet of tube. At this point 80 per cent of the propane is found to have been reacted and the product, which is mainly monochloropropane, is of high quality, i. e., colorless and free from decomposition and secondary reaction products. The next two feet of tube are shielded from the light. A second increment of chlorine equal in volume to the first is introduced at a point 6 feet from the start. Within the remaining 5 feet of tube, over 99 per cent of the chlorine reacts with the product of the preceding step. The product is mainly dichloropropane, colorless and free from decomposition and secondary reaction products, as before.

It should be noted that in this case after the first reaction there remains unreacted 20 per cent of the original volume of propane, which forms with the next increment of chlorine a mixture in which the propane is as 0.2 to 1 or 16.7 per cent of the total volume. This would be explosive if it were not for presence of the monochloropropane, which is also reactive with the chlorine, and the hydrogen chloride. The residual propane and the monochloropropane together amount to 1 volume, which forms with 1 volume of added chlorine, a 1 to 1 or 50 per cent mixture. This would be outside the explosive range, even without the diluting effect of the HCl formed, also amounting to 1 volume.

In the same way, another increment of chlorine may now be added, the dichloropropane of the first two reactions again forming with the third increment of chlorine a 1 to 1 mixture diluted with 2 volumes of HCl.

The trichloropropane resulting from the third chlorination step is of the same high quality, with respect to freedom from decomposition and secondary reaction products, as the product of the first chlorination, and the high yield of the first chlorination step is sustained throughout the succeeding stages.

It is impracticable to carry vapor phase chlorination of hydrocarbons much above the trichloride without the aid of external heat or pressure. However, the trichloropropane produced in this way may then be further chlorinated in liquid phase, or in vapor phase with heating, to tetrachloropropane, pentachloropropane, or hexachloropropane, in known manner. This further chlorination may be carried out with pyrolysis, so that the product will be a mixture of tetrachlorethylene and carbon tetrachloride.

When the vapor phase chlorination in accordance with our process is to be followed by fur-

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ther chlorination, it may be desirable to carry out the reaction so that there will remain a large excess of chlorine, i. e., to work in the range in which the proportion of hydrocarbon is below, instead of above, the explosive range. In the case of propane, this would be below 8 per cent propane by volume, corresponding to 1 volume of propane to $12\frac{1}{2}$ volumes of chlorine. This mixture reacts to form principally propane trichloride, and it is evident that after the reaction there will still remain $9\frac{1}{2}$ volumes of chlorine. In order to reduce this excess, we may therefore add more propane in one or more increments.

It should be noted that in this case the products of reaction are non-reactive with the next increment of reagent and have therefore only a diluting effect upon the next reaction. Therefore, if it were not for this diluting effect, the addition of a second increment of propane equal to the first would form with the residual chlorine a mixture that would be in the explosive range, if the original mixture were close to the lower limit. To avoid this, we may add the propane by diminishing increments, regulated so that the increment of propane is always below that which would form an explosive mixture with the residual chlorine in presence of the diluting gases; or, we may start with a still greater excess of chlorine and add the propane by equal increments, stopping when another increment would form an explosive mixture with the residual chlorine, in presence of the products.

Example II

One volume of propane is brought together with $12\frac{1}{2}$ volumes of chlorine in a mixing chamber consisting of a lead container filled with Raschig rings and passed at 9.2 to 43 feet per second through a horizontal glass tube 1 inch in diameter and 52 feet long. At distances of 16 and 32 feet from the initial end the tube is interrupted and the sections joined by mixers similar to the first. The tube is submerged a short distance beneath the surface of a body of water maintained at 80° to 90° C., and exposed to actinic light from four 40-watt mercury vapor lamps penetrating through the water. The second and third mixing chambers serve for deactivating and introduction of the increments of propane. For convenience, the tube is bent into six parallel sections. Since all the propane is reacted to the equivalent of trichloropropane, 3 volumes of chlorine are used up in the first reaction, leaving $9\frac{1}{2}$ volumes. In order to preserve the ratio of 1 volume of propane to $12\frac{1}{2}$ of chlorine, propane amounting to 0.76 of the original quantity is added at the second mixer and reacted with the mixture. Similarly, propane amounting to 0.58 of the original quantity is added at the third mixer. The resulting mixture contains 2.34 volumes of product, principally trichloropropane, 7.02 volumes of HCl and 5.48 volumes of chlorine. The excess chlorine in this mixture is then caused to react with the chloropropane by heating, in known manner, converting it to an equivalent amount of pentachloropropane, with a minor excess of chlorine.

Example III

One volume of propane is brought together with 25 volumes of chlorine. Propane is then added at the second and third mixers by increments, each equal to the original quantity. The mixture resulting from the reaction contains 3 volumes of product, principally trichloropropane,

9 volumes of HCl and 16 volumes of chlorine. The proportion of propane is therefore below the 1 to 12½ or 8 per cent explosive limit throughout the entire operation, even without the diluent effect of the products. This mixture is then further reacted, with pyrolysis, to tetrachlorethylene and carbon tetrachloride, in known manner.

It has been stated above that when the proportion of propane is above but close to the upper limit of the explosive range, a part of the propane remains unreacted. Thus when the reagents are in equimolecular proportions, as in Example I, only about 80 per cent of the propane reacts. The residual propane may then in theory form an explosive mixture with the next increment of chlorine. To make certain of avoiding this, we may add as the next increment chlorine in such amount that the chlorine will form with the residual propane a mixture in which the proportion of propane is below the explosive range. Thus a reaction in which the proportion of propane is above the explosive range is followed by a reaction in which the proportion of propane is below the explosive range.

Example IV

Equal volumes of chlorine and propane are mixed and caused to react as far as possible, as in Example I, 20 per cent of the original volume of propane remaining unreacted. After deactivation, 3 volumes of chlorine are added to the mixture. The propane remaining after the first reaction thus amounts to somewhat less than 6½ per cent of the mixture which it forms with the newly added chlorine. This is below the explosive range. The resulting product is principally trichloropropane, with 1 volume of excess chlorine, and of course 3 volumes of HCl.

It should be noted that in this case the total chlorine added is 4 volumes to 1 of propane, and if this were all added at one time the mixture would contain 20 per cent propane and would be in about the middle of the explosive range.

In the case of the higher boiling hydrocarbons, it is necessary to vaporize the hydrocarbon before introducing it into the reaction tube. Under these circumstances there is a tendency for the hydrocarbon to condense before reaching the zone of reaction. This fixes a practical limit, as to boiling point, of the hydrocarbons which can be chlorinated in accordance with our process, namely about 95° C., corresponding to heptane.

The above examples are all of continuous photochemical processes in which the gases are passed through transparent tubes, this being an excellent method of securing agitation, which is desirable in order that every part of the gas mixture may be brought into close proximity to the wall through which the light is received. The diameters and lengths of tube given in the examples are typical only and not critical.

In the foregoing discussion and examples atmospheric pressure has been indicated or implied. However, although pressure promotes the reaction, the conditions of reaction are not otherwise greatly modified by moderate pressures, and in some cases we may react chlorine with hydrocarbons by increments, separated by deactivation, in accordance with the above described process under moderate positive pressures. We do not therefore wish to be limited to reacting at atmospheric pressure.

We claim as our invention:

1. The process for photochemical vapor phase

chlorination of paraffinic hydrocarbons of three to seven carbon atoms to yield predominantly trichloride, substantially free from decomposition and secondary reaction products which comprises; (a) continuously forming, in darkness and at a temperature below 120° C., a mixture consisting substantially of gaseous chlorine and a vaporized hydrocarbon, in which the proportion of chlorine is above the range within which such mixtures, when activated, react violently; (b) causing the mixture to flow vigorously through a reaction zone irradiated by actinic light and simultaneously withdrawing heat to limit the temperature rise during the ensuing reaction to a maximum between 200° and 400° C., and yield chiefly the trichloride; (c) continuously deactivating the reaction mixture by causing it to flow through a darkened zone, and there cooling it to below 120° C.; (d) continuously adding to the stream of deactivated mixture more of the hydrocarbon, in amount resulting in a mixture with the residual chlorine in which the proportion of chlorine is still above the range of violent reaction; and (e) treating the augmented mixture in accordance with step (b), to yield more of the trichloride.

2. The process for photochemical vapor phase chlorination of paraffinic hydrocarbons of three to seven carbon atoms to yield predominantly trichloride, substantially free from decomposition and secondary reaction products which comprises: (a) continuously forming, in darkness and at a temperature below 120° C., a mixture consisting substantially of gaseous chlorine and the vaporized hydrocarbon, in which the proportion of chlorine is above the range within which such mixtures, when activated, react violently; (b) causing the mixture to flow vigorously through a transparent-walled elongated conduit immersed in a body of cooling liquid and exposed to actinic light penetrating through the surface of the liquid and simultaneously limiting the temperature rise of the reaction mixture during the ensuing reaction to a maximum between 200° and 400° C., by heat transfer to said liquid, and yield chiefly the trichloride; (c) continuously deactivating the reacted mixture by causing it to flow through a darkened chamber and there cooling it to below 120° C.; (d) continuously adding to the stream of deactivated mixture more of the hydrocarbon, in amount resulting in a mixture with the residual chlorine in which the proportion of chlorine is still above the range of violent reactions; (e) treating the augmented mixture in accordance with step (b), to yield more of the trichloride.

3. The process for photochemical vapor phase chlorination of propane to yield predominantly trichloride, substantially free from decomposition and secondary reaction products which comprises; (a) continuously forming in darkness and at a temperature below 120° C., a mixture consisting substantially of gaseous chlorine and vaporized propane, in which the propane is less than 8 per cent by volume; (b) causing the mixture to flow vigorously through a reaction zone irradiated by actinic light and simultaneously withdrawing heat to limit the temperature rise during the ensuing reaction to a maximum between 200° and 400° C., and yield chiefly the trichloride; (c) continuously deactivating the reacted mixture by causing it to flow through a darkened zone and there cooling it to below 120° C.; (d) continuously adding to the deactivated mixture more propane, in amount resulting in

a mixture with the residual chlorine in which the proportion of propane is still less than 8 per cent by volume; and (e) treating the augmented mixture in accordance with step (b), to yield more of the trichloride.

4. The process for photochemical vapor phase chlorination of butane to yield predominantly trichloride, substantially free from decomposition and secondary reaction products which comprises (a) continuously forming in darkness and at a temperature below 120° C., a mixture consisting substantially of gaseous chlorine and vaporized butane in which the butane is less than 6.8 per cent by volume; (b) causing the mixture to flow vigorously through a reaction zone irradiated by actinic light and simultaneously withdrawing heat to limit the temperature rise during the ensuing reaction to a maximum between 200° and 400° C., and yield chiefly the trichloride; (c) continuously deactivating the reacted mixture by causing it to flow through a darkened zone and there cooling it to below 120° C.; (d) continuously adding to the deactivated mixture more butane, in amount resulting in a mixture with the residual chlorine in which the proportion of butane is still less than 6.8 per cent by volume; and (e) treating the augmented mixture in accordance with step (b), to yield more of the trichloride.

5. The process for photochemical vapor phase chlorination of heptane to yield predominantly trichloride, substantially free from decomposition and secondary reaction products which comprises (a) continuously forming, in darkness and at a temperature below 120° C., a mixture consisting substantially of gaseous chlorine and vaporized heptane, in which the heptane is less than 4.2 per cent by volume; (b) causing the mixture to flow vigorously through a reaction zone irradiated by actinic light and simultaneously withdrawing

heat to limit the temperature rise during the ensuing reaction to a maximum between the 200° and 400° C., and yield chiefly the trichloride; (c) continuously deactivating the reaction mixture by causing it to flow through a darkened zone and there cooling it to below 120° C.; (d) continuously adding to the deactivated mixture more heptane, in amount resulting in a mixture with the residual chlorine in which the proportion of heptane is still less than 4.2 per cent by volume; and (e) treating the augmented mixture in accordance with step (b), to yield more of the trichloride.

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