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CHLORINATION PROCESS AND PRODUCT THEREOF

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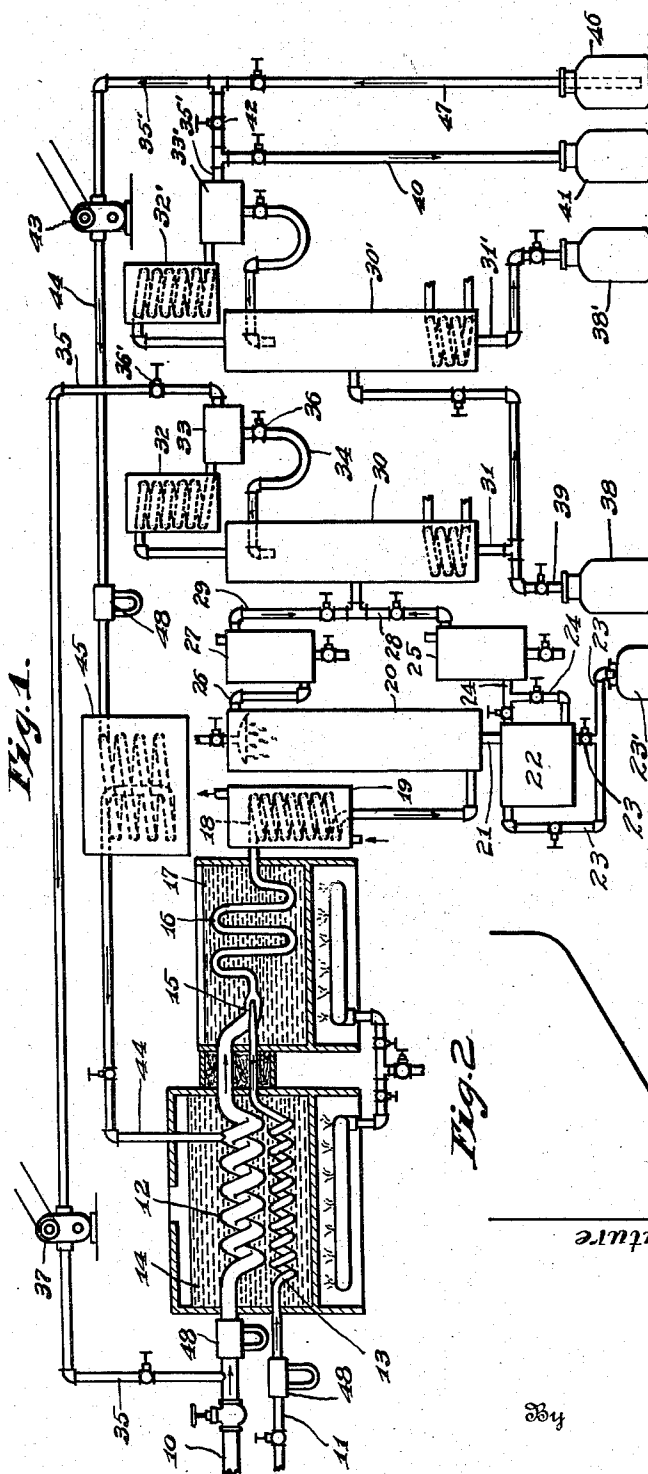


Fig. 2

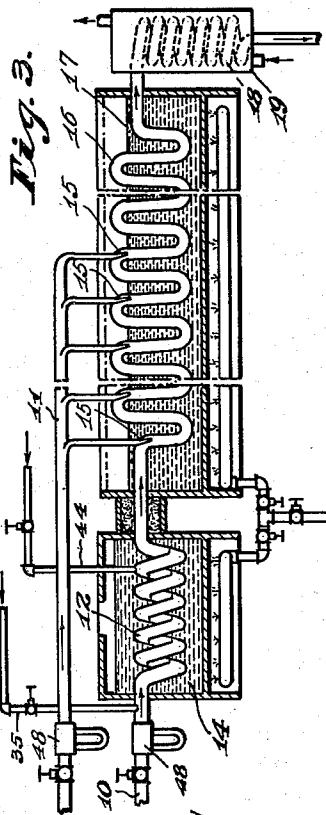
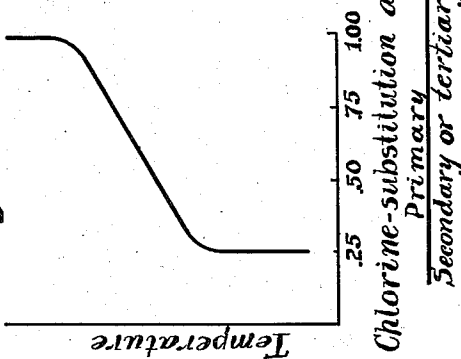


Fig. 3

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2,004,072

CHLORINATION PROCESS AND PRODUCT THEREOF

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Application February 1, 1932, Serial No. 590,046

35 Claims. (Cl. 260—162)

This invention relates to a process for chlorinating hydrocarbons and/or their partially chlorinated derivatives, in the gaseous phase; and to new products obtained by that process.

A primary object of our invention is to chlorinate hydrocarbons and/or their partially chlorinated derivatives, with safety and at low cost.

A further primary object is to limit the chlorination reaction to a desired range of temperatures, and to avoid its occurrence while the materials to be chlorinated are being heated to that range of temperatures.

Another primary object of our invention is to increase the proportion of chlorination in the primary position as compared to that in the secondary and/or tertiary positions, as contrasted with other methods.

A further primary object is to make safely possible a polychlorination in a single operation without the need of intermediate cooling below reaction temperature.

Another primary object is to shorten the period during which the chlorinated products are in the high-temperature zone, and thus to decrease the amount of decomposition of such chlorinated products.

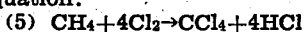
A further and highly important object is to obtain a new chlorinated product, 1,3-dichloro-2-methylpropane, desirably substantially free from isomers; and also to obtain a new chlorinated mixture, consisting substantially of 1,3-dichloro-2-methylpropane and 1,2-dichloro-2-methylpropane with the former in preponderating amount.

In carrying out our invention, fundamentally, we heat the hydrocarbon and/or partially chlorinated derivatives thereof to a desired reaction temperature; and then, and not until then, introduce the chlorine. Further, we introduce the chlorine at high velocity, to avoid flame; and may do so at a plurality of separated points along the reaction tube while the material being chlorinated is maintained constantly within the desired range of reaction temperatures.

It is well known that when certain hydrocarbons—for instance, the paraffins, the naphthenes, and the aromatics—react with chlorine, there may be a series of substitution reactions, chlorine being substituted for hydrogen, in the manner exemplified in the following series starting with methane.

- (1) $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$
- (2) $\text{CH}_3\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \text{HCl}$
- (3) $\text{CH}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow \text{CHCl}_3 + \text{HCl}$
- (4) $\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}$

These reactions may be summarized in a single equation:

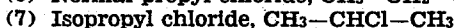
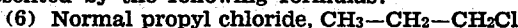


Such a series of reactions cannot in practice be effected with safety by simply grossly mixing and heating the reactants in the proportions indicated by the equation, because an explosive mixture is produced. But by admitting the chlorine at high speed, from any suitable number of jets along the reaction tube, into the already heated material to be chlorinated, any desired degree of chlorination may be effected with safety in a single operation.

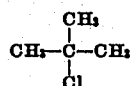
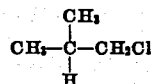
With some hydrocarbons, notably ethane and methane, only primary chlorosubstitution products are possible. That is, chlorine can attach itself only to carbon atoms which are in turn attached to not more than one carbon atom. Thus the only monochlorosubstitution products obtainable from ethane and methane are primary alkyl chlorides.

With most higher hydrocarbons, however, there is a possibility of substitution by chlorine in two or more positions.

Thus propane may form two monosubstitution products when it is chlorinated. These are the primary chloride, called normal propyl chloride or 1-chloropropane; and the secondary chloride, called iso-propyl chloride or 2-chloropropane. These two monochlorides of propane may be represented by the following formulas:



Similarly, isobutane may form two isomers when monochlorinated. These are the primary chloride, called isobutyl chloride or 1-chloro-2-methylpropane; and the tertiary chloride, called tertiary butyl chloride or 2-chloro-2-methylpropane. The structures of these two monochlorides of isobutane are shown by the following formulas:



It has long been accepted among chemists that when chlorine is allowed to react with hydrocarbons, such for instance as propane and isobutane,

which permit the formation of isomers, the substitution by chlorine shows a marked preference for the secondary and tertiary positions rather than for the primary positions, and for tertiary positions rather than for secondary positions. This is in fact the case with all prior processes of which we are aware, and has been confirmed in all prior cases carefully studied.

This preference is usually an unfortunate one, from several standpoints, which need not be discussed in detail here.

Our invention enables us to greatly reduce this tendency of the chlorine to substitute in the secondary and tertiary positions at a greater rate than in the primary positions. Thus we are able to increase greatly the yields of the desirable primary substitution products, and to lessen the yields of the more unstable and usually less desirable secondary and tertiary substitution products.

This can best be made clear in connection with a specific example; for which we have selected isobutane.

Isobutane has previously been chlorinated at or near room temperature by Butlerow, (*Annalen der Chemie* 144, 17,) and the only monochloro-substitution product reported was tertiary butyl chloride. If any isobutyl chloride was formed, as from our repetition of his work we think is probable, it apparently escaped Butlerow's notice.

It has also been proposed to chlorinate certain hydrocarbons by mixing chlorine with the hydrocarbon while the latter is relatively cold, or only slightly above the boiling point, and then heating the mixture. This is described in the Ayres U. S. Patent No. 1,741,393. Ayres does not specifically report the use of his method to chlorinate isobutane; but we have tried it on isobutane, and have found that while a considerable amount of isobutyl chloride was obtained, there was still a marked preference, about 4 to 1, for the chlorine substitution in the tertiary position. That is, since there are nine primary hydrogen atoms and one tertiary hydrogen atom in the isobutane molecule, a chlorination in which the entering chlorine showed no preference for position should result in a yield of 90% isobutyl chloride and only 10% tertiary butyl chloride; whereas our best actual results by the Ayres method were about 30% tertiary butyl chloride and about 70% isobutyl chloride, or less than 8% substitution for each of the nine primary hydrogens as against 30% for the single tertiary hydrogen. We have been unable by the Ayres method to obtain a chlorination in which this marked preference for the tertiary position over the primary positions was avoided, or even materially lessened over this four-fold preference indicated; although many trials have been made at various temperatures.

We believe this is due to a fundamental characteristic of the Ayres process. This is, that the Ayres process consists in mixing the hydrocarbon vapors and chlorine at temperatures below that at which the chlorination reaction proceeds with noticeable velocity in the absence of light, and subsequently heating the mixed gases to reaction temperature. Since chlorination of isobutane in the Ayres process begins at about 200° C., and proceeds with increasing velocity as the temperature rises to the temperature he names of 600° F. or 700° F. (about 315° C. to 370° C.), it is obvious that it is impossible in that process to cause all the reaction to take place at any specific temperature, and that all the reaction which oc-

curs takes place at a temperature no higher than the maximum Ayres mentions. No matter how quickly the gases are heated in the Ayres process, the reaction is so rapid that most of the chlorination takes place at temperatures below the maximum temperature reached, even if the final temperature be raised far beyond that named by Ayres.

We have found that the chlorination within the range of temperatures named by Ayres is highly favorable to preferential chlorination in the secondary and tertiary positions, and that to avoid or minimize that preferential chlorination it is necessary to carry on the whole reaction at a higher temperature.

There are other prior processes of chlorinating, involving the use of light and of catalysts; but they also favor the production of secondary and tertiary chlorides rather than of primary chlorides, and in general do so more greatly than does the Ayres process.

Instead of mixing the hydrocarbon and chlorine while relatively cold, and then heating the mixture as Ayres does, our invention contemplates preliminarily heating the hydrocarbon, and if desired the chlorine also, to a desired high reaction temperature, and then mixing them at that temperature at high velocity to cause turbulent flow. In this way we carry out the whole reaction above a definite high temperature, instead of during a rise of temperature over a considerable range. Ayres mixes, and then heats to reaction temperature. We heat to reaction temperature, and then mix.

The optimum temperature for the reaction varies with different hydrocarbons; but by heating to reaction temperature before mixing we are able to prevent reaction at the lower temperatures; which Ayres can not avoid. We confine the reaction to a desired optimum range of temperatures, in which we find that the preference for chlorine substitution in the secondary and/or tertiary positions instead of in the primary positions is markedly reduced.

In general, the optimum temperature lies between 250° C. and 700° C. If the temperature is too low, not only is too large a proportion of secondary and/or tertiary substitution products obtained, but the apparatus must be too large on account of the slowness of the reaction. For both reasons, the temperature should be high enough to cause the chlorination reaction to be at least 90% complete within one minute, in the absence of light and of a chlorination catalyst. If the temperature is too high it becomes increasingly difficult to avoid a considerable pyrolysis of the chlorination products and even of the hydrocarbon being chlorinated. This pyrolysis may, of course, be greatly reduced by allowing the hydrocarbon and particularly the chlorinated products to remain in the heated zone for only a very short time. Since the rate of chlorination increases rapidly with rising temperature, and at all temperatures within the range specified is much more rapid than the pyrolysis, there is no definite upper limit to the temperatures which might be used. If it were possible to heat the reactants and cool the reaction products with sufficient rapidity it would be possible to chlorinate at temperatures even above 700° C. without any considerable pyrolysis. As a practical matter, however, it becomes more and more difficult to suppress pyrolysis and the formation of free carbon as the temperature proceeds above 550°-700° C., and we therefore consider the optimum reaction temperature for our

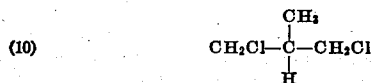
purposes to be usually the highest temperature at which chlorination proceeds substantially without pyrolysis. For the monochlorination of isobutane this optimum temperature is not above 600° C.

The use of a high velocity and of turbulent flow is to prevent the occurrence of flame and its concomitant production of free carbon, and to make higher working temperatures usable. The high velocity enables the gases to enter at a speed in excess of the speed of flame propagation, and the turbulent flow produces an intimate mixing which enables the reactants to become uniformly dispersed in each other before any considerable amount of chlorination takes place; this avoids the formation of undue amounts of highly chlorinated products, which are formed if the reaction occurs in the presence of a local excess of chlorine.

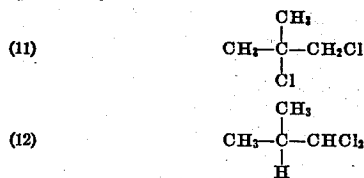
In the chlorination process, polychlorinated products are obtainable as well as monochlorinated products. By providing sufficient chlorine, at one or more jets, and re-cycling the monochlorides, the proportion of dichlorides to monochlorides obtained may be increased.

By our process of limiting the reaction to a temperature above a predetermined minimum, of 250° C. and higher, we are able to reduce the preference of the chlorine for the secondary and/or tertiary positions in the dichlorination step as well as in the monochlorination step.

Thus in operating our process upon isobutane, we obtain as the principal dichlorination product a new compound, 1,3-dichloro-2-methylpropane, which may be represented by the following formula:



As first formed in our process, this 1,3-dichloro-2-methylpropane occurs mixed with other chlorinated products, mainly 1,2-dichloro-2-methylpropane and probably with small amounts of 1,1-dichloro-2-methylpropane and of more highly chlorinated products as well as monochlorides. The 1,2-dichloro-2-methylpropane and the 1,1-dichloro-2-methylpropane are represented by the following Formulas 10 and 11 respectively:



However, the 1,3-dichloro-2-methylpropane is present in about three times the amount of the 1,2-dichloro-2-methylpropane; which shows further that our process promotes primary substitution. So far as the literature records, we believe, no chlorination of isobutane to yield 1,3-dichloro-2-methylpropane has ever previously been done; and prior processes which produce dichlorides of isobutane have yielded only 1,2-dichloro-2-methylpropane; so that 1,3-dichloro-2-methylpropane is new with us, both alone when substantially free from isomers, and when copresent with but preponderating in amount over 1,2-dichloro-2-methylpropane and other chlorinated products.

In obtaining the dichlorination of isobutane by our process, as in obtaining the monochlorina-

tion thereof, the optimum reaction temperature for the chlorination is the highest temperature at which chlorination proceeds substantially without pyrolysis. For the dichlorination, this does not exceed 600° C., and is desirably lower than that, or approximately 450-500° C.

The group of dichlorides may easily be separated from the more highly chlorinated products, and the various dichlorides may if desired be separated from one another and from all the co-produced chlorinated products, by rectification in the usual way, employing either continuous or batch apparatus. The separation of 1,3-dichloro-2-methylpropane is quite easily accomplished; for its boiling point is 136.4° C., while the other two dichlorides boil between 103° and 108° C.

The new product 1,3-dichloro-2-methylpropane is a clear, colorless liquid, and has a density of

$$1.131 \frac{\text{g.}}{\text{cc.}}$$

at 20° C. It volatilizes quite rapidly and completely at normal temperatures and pressures. This new product, desirably either in substantially isolated form or when mixed with only the other dichlorides, is found to have various uses. It is especially useful as a cleaner, for cleaning clothes and fabrics; for it has more desirable solvent properties for certain types of dirt than has carbon tetrachloride, now quite commonly used for that purpose, and while it is capable of producing a momentary flash at 111° F. or higher it is substantially non-inflammable at room temperature and any such flash produced even at 111° F. is merely momentary and extinguishes itself.

We are aware of the paper by Kleinfeller in *Berichte der Deutschen Chemischen Gesellschaft*, Volume 62, (1929,) pages 1582-1597; in which a substance called 3-chloro-2-chloromethylpropane is said to have been obtained by him. Although the name "3-chloro-2-chloromethylpropane" seems to imply a structure like that of our 1,3-dichloro-2-methylpropane, the Kleinfeller product is evidently not our product, because it has different properties from ours. He says his substance is a colorless and odorless oil which at 10 mm. pressure boils at 45° C.; which, according to the International Critical Tables, Volume III, page 246, means a boiling point of about 160° C. at atmospheric pressure. Our 1,3-dichloro-2-methylpropane, on the other hand, is not an oil; has a definite odor similar to but not so pronounced as that of carbon tetrachloride; and boils at about 136.4° C. at atmospheric pressure, and at about 21° to 25° C. at 10 mm. pressure.

The accompanying drawing shows one illustrative apparatus suitable for carrying out our process, and a modification thereof, and also shows a curve indicating the general nature of the relation to reaction temperature of the ratio in chlorine-substitution activity of the primary to the secondary and/or tertiary positions.

In such drawing: Fig. 1 is a diagrammatic view of such an apparatus; Fig. 2 is such a curve; and Fig. 3 is a partial diagram showing a modification of the apparatus of Fig. 1.

The hydrocarbon to be chlorinated is supplied by a pipe 10, and the chlorine by a pipe 11. The hydrocarbon may be diluted with an inert diluent, such as nitrogen, if desired; but that is a matter of preference, for individual cases. If such an

inert diluent is used, it does not enter into the chemical reactions; but it does exert an effect on physical conditions, as by its capacity to absorb heat. The proportions of hydrocarbon and chlorine vary with the molecular weight of the hydrocarbon and the amount of chlorination desired.

The hydrocarbon-supply pipe 10 leads to a suitable coil 12 in a suitable heating device 14, such as an ordinary bath of molten salts; in which the hydrocarbon is heated to the desired reaction temperature, which is always above 250° C. The chlorine-supply pipe 11 may lead to a coil 13 in the heating device 14, as is shown in Fig. 1, if it is desired to heat preliminarily the chlorine as well as the hydrocarbon; but the chlorine-heating coil 13 may be omitted, as is illustrated in Fig. 3.

The heated hydrocarbon, and the chlorine heated or unheated as the case may be, pass separately to a reaction passage 16, and with the hydrocarbon (at least) still at the desired reaction temperature the chlorine is injected into it at high velocity, greater than the speed of flame propagation of the chlorine-hydrocarbon reaction, and usually of the order of a hundred miles a minute. The chlorine supply is under sufficient pressure to produce this speed. The chlorine is thus injected by one or more mixing jets 15, one being shown in Fig. 1 and a plurality in Fig. 3. When there are a plurality of such jets 15, they are desirably arranged at different points along the reaction tube 16, as is clear from Fig. 3, so that the reaction of the chlorine injected at one jet may be completed or nearly so, and the heat of reaction largely absorbed by a surrounding bath 17, before the chlorine from the next jet is introduced. The reaction passage 16 is desirably a crooked one, to create at and after each chlorine injection an immediate turbulence that produces intimate dispersion of the hydrocarbon and the chlorine in each other before any considerable chlorination has occurred, so that flame is effectively prevented and the formation of free carbon lessened and practically avoided. This makes the high reaction temperature practicable. The chlorination all occurs in the passage 16. If a high yield of primary chlorides as against isomeric secondary and/or tertiary chlorides is desired, the reaction passage 16 is maintained wholly above the predetermined minimum temperature, so that there will be no opportunity for reaction below that temperature. On the other hand, where that is not desired or necessary, as in chlorinating methane or ethane, the reaction tube 16 may be permitted to be at a lower temperature at the various jets 15, in order better to dispose of the heat developed in the chlorination, and the heating coils 12 and 13 may be dispensed with. At the temperatures used, the reaction ordinarily goes to completion in a fraction of a second.

The reaction passage 16 is desirably in a suitable heat-absorbing device 17, such as an ordinary open bath of molten salts; which serves to prevent too great a rise in temperature due to the heat developed by the exothermic chlorination reaction, and to absorb the heat of reaction occurring between adjacent chlorine-injecting jets 15 when there are more than one. The level of the molten salts may be sufficiently high to cover the whole reaction tube, or may be low enough so that the reaction tube is exposed at and near the jets 15.

The reaction products, with any unreacted

hydrocarbon, pass from the coil 16 immediately to the worm 18 of a cooler 19, by which they are quickly cooled to a temperature in the neighborhood of room temperature. These cooling actions lessen pyrolysis.

The parts 12, 13, 15, 16, and 18 should be of material which will not react with or catalyze the decomposition of the fluids passing through them, and are desirably of silica. No chlorination catalyst is present.

From the worm 18 the reaction products pass to the bottom of a water-scrubber 20, of any conventional form; in which the water takes up the HCl present. This hydrochloric acid, and any condensed organic vapors, pass out from the bottom of the water-scrubber 20 by a pipe 21 to a separator 22; whence the hydrochloric acid is drawn off at one level, desirably into a container 23' for sale as a by-product, and the organic liquids are drawn off at another level and pass to an alkali scrubber 25. The levels at which the hydrochloric acid and the organic liquids are drawn off respectively depends on which has the greater density, and so suitably valved pipes 23 and 24 are provided by which either liquid may be drawn off at a lower level and either at a higher level. Any vapors which rise in the water-scrubber 20 pass off at the top through a pipe 26 to an alkali scrubber 27. These alkali scrubbers are provided out of abundant caution, to ensure the removal of all HCl.

Valved pipes 28 and 29 from the outlets of the two alkali scrubbers join each other, and lead to a rectifying column 30, of any suitable type, the temperatures in which are so controlled that the chlorinated hydrocarbons are condensed and pass as liquid to the bottom of the column, whence they may be drawn off through a pipe 31.

The unreacted hydrocarbon passes out at the top of the rectifying column 30, and is divided in conventional manner by a dephlegmator 32 and a weir-box 33 into reflux and take-off portions which pass respectively by a valved reflux pipe 34 back to the rectifying column 30 and into a valved take-off pipe 35. The ratio between reflux and take-off may be controlled by the valves 36 and 36' in these two pipes.

The take-off pipe 35 leads through a recycling pump 37 back to the hydrocarbon-supply pipe 10; so that the unreacted hydrocarbon may be recycled, to cause its chlorination.

The chlorinated hydrocarbons drawn off by the pipe 31 may be supplied to a suitable storage receptacle 38 if desired, through a valved outlet 39. However, these chlorinated hydrocarbons are a mixture, and it is usually desirable to separate some of them from others. To this end, they may be passed through any desired number of rectifying columns, to get any desired separation. The drawing shows one such additional rectifying column 30', as for separating the monochlorides from the polychlorides. If that is the separation desired, the temperatures in the rectifying column 30' are so controlled that the polychlorides are condensed and pass off at the bottom by a valved pipe 31' into a suitable storage receptacle 38'; which thus receives the dichlorides of isobutane already described if isobutane is the hydrocarbon being treated. These polychlorides may be separated from one another by rectification in known manner.

The more volatile monochlorides pass off at the top of the rectifying column 30', and are divided by a dephlegmator 32' and a weir-box 33' into reflux and take-off portions in a manner similar

to the division of the unreacted hydrocarbon already described.

The take-off portion goes into a pipe 35'. This may discharge, by a valved outlet 40, into a storage receptacle 41, if monochlorides are desired. These monochlorides may be separated from one another, if desired, by suitable rectification in a known manner. Primary monochlorides may thus be obtained in larger proportion than by previous methods.

If the monochlorides are not desired, the pipe 35' may lead, through a valve 42, to a recycling pump 43, which discharges by a pipe 44 and through a vaporizer 45 into the heating coil 12, desirably at a point near the outlet of the latter to minimize time for decomposition to occur. The monochlorides pass through the apparatus with the hydrocarbon, and are further chlorinated; and the polychlorides obtained are collected in the receptacle 38'.

If it is desired to recycle only one of the monochlorides, a container 46 holding the one which it is desired to recycle may be connected to the inlet of the pump 43, by way of a valved pipe 47.

We desirably provide flow-meters 48 in the pipes 10, 11, and 44, to give information which facilitates the control of the quantities of reactants supplied.

Our process may be used for chlorinating various hydrocarbons of the paraffin, aromatic, and naphthene series, where the chlorination is by substitution. Among the aromatics which may thus be chlorinated we may mention toluene; and among the naphthenes, cyclohexane. Among the paraffins it is of especial advantage with hydrocarbons having a number of carbon atoms between 3 and 5 inclusive, and especially n-butane and isobutane. It is of advantage in reducing the amount of decomposition products formed, not only in the chlorination of hydrocarbons which have secondary and/or tertiary carbon atoms as well as primary carbon atoms, but also in many cases in the chlorination of hydrocarbons which have only primary carbon atoms or only secondary carbon atoms; since the prevention of the chlorination reaction during the time the reactants are being raised to the desired high temperature, by deferring the mixing of the reactants until that temperature has been attained, makes possible the reduction of the time during which chlorinated products are in the heated zone. However, our process is of especial advantage in the chlorination of hydrocarbons which have carbon atoms other than primary ones, in that it reduces the usual preference for chlorination in the secondary and/or tertiary positions.

In operation, the temperatures of the baths 14 and 17 are set as desired; the former to heat the hydrocarbon, the chlorine if desired, and any recycled chlorides, to the desired reaction temperature, which is considerably above the vaporization point of the hydrocarbon, and the latter to absorb the heat which is generated by the chlorination reaction and prevent the temperature from rising too high at such chlorination.

The optimum chlorination temperature, which may vary for different hydrocarbons and with the details of the particular apparatus used, is the highest temperature at which the chlorination can be carried out while substantially avoiding pyrolysis. For isobutane it is not above 600° C., and for dichlorination especially it is desirably in the range from 450-500° C. The curve shown in Fig. 2 is a typical one showing the ratio of primary

chlorine substitution activity to secondary or tertiary chlorine substitution activity as measured by the composition of the monochloride mixture obtained.

If isobutane is the hydrocarbon to be chlorinated, the molten-salt bath 14 is maintained at such a temperature, in any case not higher than 600° C., that the isobutane and the chlorine reach the mixing jet 15 at a temperature above 250° C. and not above 600° C., and especially in the dichlorination procedure so that any already chlorinated products of isobutane desirably do not exceed the temperature range of 450-500° C. Similarly, the temperature of the bath 17 is maintained less than 600° C. so that it will prevent the temperature of the mixing gases at the jet 15 and in the tortuous passage 16 from greatly exceeding the temperature of 600° C.

When dichlorides are obtained from isobutane by our process, there is a preponderance of 1,3-dichloro-2-methylpropane, usually about 70% of the whole; mixed with a smaller amount of other polychlorides, mainly 1,2-dichloro-2-methylpropane.

If the hydrocarbon to be chlorinated has only one kind of carbon atoms, such as primary carbon atoms in the case of methane, it becomes safely possible to get a high degree of chlorination by the use of multiple chlorine-injecting jets 15 (Fig. 3); even if the temperature of the reaction tube at the jets is allowed to be below the maximum desirable for the reaction, and if the heating coils 12 and 13 are not used. In this way, for instance, we may get in our apparatus a preponderance of any desired ones of the chlorination products of Equations 1 to 4. Such chlorinated products may be separated from one another by rectification.

We claim as our invention:

1. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in separately preheating chlorine and the material to be chlorinated to a predetermined reaction temperature materially above the boiling point of the hydrocarbon, and then mixing the heated material to be chlorinated with the heated chlorine, at a velocity in excess of that of flame propagation under the conditions existing, to effect the chlorination.

2. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin and naphthene series and their partially chlorinated derivatives, which consists in preheating the material to be chlorinated, at a rate which substantially avoids cracking it, to a predetermined reaction temperature at which such material is in the vapor or gaseous phase and at which chlorine substitution can be produced rapidly in the absence of light and of a catalyst; and then promptly injecting chlorine which until then is substantially undiluted with the material being chlorinated into such heated material, at a velocity in excess of that of flame propagation under the conditions existing, to effect such chlorine substitution.

3. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in separately preheating chlorine and the material to be chlorinated to a temperature approximating the optimum reaction temperature and at which both reactants are in the vapor or gase-

ous phase, and then mixing the heated material to be chlorinated with the heated chlorine, in the absence of light and of a chlorination catalyst, to effect the chlorination.

4. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in preheating the material to be chlorinated, at a rate which substantially avoids cracking it, to a temperature approximating the optimum reaction temperature, and then promptly mixing the heated material to be chlorinated with chlorine, at a velocity in excess of that of flame propagation under the conditions existing, to effect the chlorination.

5. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in separately preheating chlorine and the material to be chlorinated to a predetermined reaction temperature at which such material to be chlorinated is in the vapor or gaseous phase and at which chlorine substitution can be produced rapidly in the absence of light and of a catalyst; and then promptly mixing the heated material to be chlorinated with the heated chlorine, at a velocity in excess of that of flame propagation under the conditions existing, to effect such chlorine substitution.

6. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin and naphthene series and their partially chlorinated derivatives, which consists in preheating the material to be chlorinated, at a rate which substantially avoids cracking it, to a predetermined reaction temperature at which such material is in the vapor or gaseous phase and at which chlorine substitution can be produced rapidly in the absence of light and of a catalyst; and then promptly mixing such heated material with chlorine which until then is substantially undiluted with the material being chlorinated, at a velocity in excess of that of flame propagation, to effect such chlorine substitution.

7. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in separately preheating chlorine and the material to be chlorinated to a predetermined reaction temperature materially above the boiling point of the hydrocarbon, and then mixing the heated material to be chlorinated with the heated chlorine, at a velocity in excess of that of flame propagation under the conditions existing, to effect the chlorination, and cooling the gases during and immediately following mixing.

8. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin and naphthene series and their partially chlorinated derivatives, which consists in preheating the material to be chlorinated, at a rate which substantially avoids cracking it, to a predetermined reaction temperature at which such material is in the vapor or gaseous phase and at which chlorine substitution can be produced rapidly in the absence of light and of a catalyst; and then promptly mixing such heated material with chlorine which until then is substantially undiluted with the material being chlorinated, at a velocity in excess of that of flame propagation, to effect such chlorine substitution, and cooling the gases during and immediately following mixing.

9. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in separately preheating chlorine and the material to be chlorinated to a predetermined reaction temperature materially above the boiling point of the hydrocarbon, and then mixing the heated material to be chlorinated with the heated chlorine, at a velocity in excess of that of flame propagation under the conditions existing, to effect the chlorination, separating the reaction products by condensation and rectification, and recycling material still requiring chlorination.

10. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin and naphthene series and their partially chlorinated derivatives, which consists in preheating the material to be chlorinated, at a rate which substantially avoids cracking it, to a predetermined reaction temperature at which such material is in the vapor or gaseous phase and at which chlorine substitution can be produced rapidly in the absence of light and of a catalyst; and then promptly mixing such heated material with chlorine which until then is substantially undiluted with the material being chlorinated, at a velocity in excess of that of flame propagation, to effect such chlorine substitution, separating the reaction products by condensation and rectification, and recycling material still requiring chlorination.

11. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in producing a substitution reaction between such material to be chlorinated and chlorine wholly at a temperature above 250° C. and in a period of time which gives little cracking of the starting material.

12. The process of chlorinating compounds of the class consisting of hydrocarbons having from 3 to 5 carbon atoms and of the paraffin and naphthene series and their partially chlorinated derivatives, which consists in producing a substitution reaction between such material to be chlorinated and chlorine wholly at a temperature far above the boiling point of the material to be chlorinated and in a period of time which gives little cracking of the starting material.

13. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in producing a substitution reaction between such material to be chlorinated and chlorine wholly at a temperature between 250° C. and 700° C.

14. The process of chlorinating compounds of the class consisting of paraffin and naphthene hydrocarbons having primary and other carbon atoms and aromatic hydrocarbons having side chains which contain carbon atoms other than primary ones, and their partially chlorinated derivatives, which consists in producing a reaction in the vapor or gaseous phase between the material to be chlorinated and chlorine wholly at a temperature in the neighborhood of the optimum temperature for producing maximum primary chlorination.

15. A new composition of matter, consisting essentially of 1,3-dichloro-2-methylpropane which at atmospheric pressure boils at about 136.4° C. and at 10 mm. pressure boils at about 21 to 25° C.

16. A new composition of matter, consisting

essentially of a mixture of 1,3-dichloro-2-methylpropane which at atmospheric pressure boils at about 136.4° C. and at 10 mm. pressure boils at about 21 to 25° C.; and 1,2-dichloro-2-methylpropane with the former in preponderating amount.

17. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in injecting chlorine at a speed exceeding that of flame-propagation of the reaction into a stream of the material to be chlorinated with the latter preheated above 250° C. and relatively free from decomposition products.

18. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in injecting chlorine at a speed exceeding that of flame-propagation of the reaction into the material to be chlorinated with the latter preheated above 250° C. and relatively free from decomposition products.

19. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in injecting chlorine at a speed exceeding that of flame-propagation of the reaction into a stream of the material to be chlorinated which is relatively free from decomposition products and which is at a temperature where it will react with chlorine to 90% completion within one minute in the absence of light and of a chlorination catalyst.

20. The process of chlorinating compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in injecting chlorine at a speed exceeding that of flame-propagation of the reaction into the material to be chlorinated which is relatively free from decomposition products and which is at a temperature where it will react with chlorine to 90% completion within one minute in the absence of light and of a chlorination catalyst.

21. The process of substituting chlorine atoms for hydrogen atoms in compounds of the class consisting of hydrocarbons of the paraffin and naphthene series and their partially chlorinated derivatives, which consists in injecting chlorine into a stream of the material to be chlorinated which is at a temperature above 250° C., at a plurality of separated jets along said stream.

22. The process of substituting chlorine atoms for hydrogen atoms in compounds of the class consisting of hydrocarbons of the paraffin, naphthene, and aromatic series and their partially chlorinated derivatives, which consists in injecting chlorine at high speed into a high-speed stream of the material to be chlorinated at a plurality of separated jets along said stream, and removing heat from the stream between adjacent jets.

23. The process of chlorinating methane, which consists in injecting into a stream of methane while it is at a temperature sufficiently high for rapid reaction a plurality of jets of chlorine at separated points along such stream under conditions which cause chlorine substitution between the jet-points.

24. The process of chlorinating toluene, which consists in injecting a jet of chlorine into a stream of toluene preheated above 250° C.

25. The process of chlorinating a paraffin hydrocarbon having from 3 to 5 carbon atoms, which consists in injecting a jet of chlorine into a stream of such paraffin hydrocarbon preheated materially above its boiling point.

26. The process of chlorinating isobutane, which consists in injecting a jet of chlorine into a stream of isobutane preheated materially above its boiling point.

27. The process of polychlorinating isobutane, which consists in injecting a jet of chlorine into a stream of isobutane at a temperature of at least 250° C., to produce monochlorides of isobutane, and then chlorinating such monochlorides of isobutane by reaction with chlorine at a temperature of at least 250° C. to produce polychlorides of isobutane.

28. The process of producing polychlorides of isobutane, which consists in chlorinating a monochloride of isobutane at a temperature above 250° C.

29. The process of polychlorinating isobutane, which consists in injecting a jet of chlorine into a stream of isobutane at a temperature of at least 250° C., to produce a mixture of chlorides including isobutyl chloride, and chlorinating such isobutyl chloride by reaction with chlorine at a temperature of at least 250° C. to produce polychlorides of isobutane.

30. The process of producing polychlorides of isobutane, which consists in chlorinating isobutyl chloride by heating it to a temperature between 250° C. and 600° C. and then exposing it to the action of chlorine.

31. The process of producing polychlorides of isobutane, which consists in exposing isobutyl chloride to the action of chlorine at a temperature above 250° C.

32. The process of polychlorinating isobutane, which consists in exposing isobutane to chlorine at a temperature above 250° C., to produce isobutane-monochlorides, and exposing an isobutane-monochloride to additional chlorine at a temperature above 250° C. to produce isobutane-polychlorides, including dichlorides, and separating the dichlorides so obtained from co-present material.

33. The process of producing 1,3-dichloro-2-methylpropane, which consists in chlorinating isobutane by exposing it to the action of chlorine at a temperature above 250° C. to produce a mixture of chlorides thereof, and fractionating such mixture to obtain therefrom a fraction rich in 1,3-dichloro-2-methylpropane.

34. A new composition of matter, consisting of a mixture of 1,3-dichloro-2-methylpropane which at atmospheric pressure boils at about 136.4° C. and at 10 mm. pressure boils at about 21 to 25° C.; and other chlorides of isobutane.

35. A new composition of matter, consisting of a mixture of 1,3-dichloro-2-methylpropane which at atmospheric pressure boils at about 136.4° C. and at 10 mm. pressure boils at about 21 to 25° C.; and other di-chlorides of isobutane.

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