July 16, 1968 H. M. FOX ETAL 3,393,249

PROCESS AND APPARATUS FOR PRODUCTION OF ALKYLATE

Filed Nov. 1, 1963 2 Sheets-Sheet 1

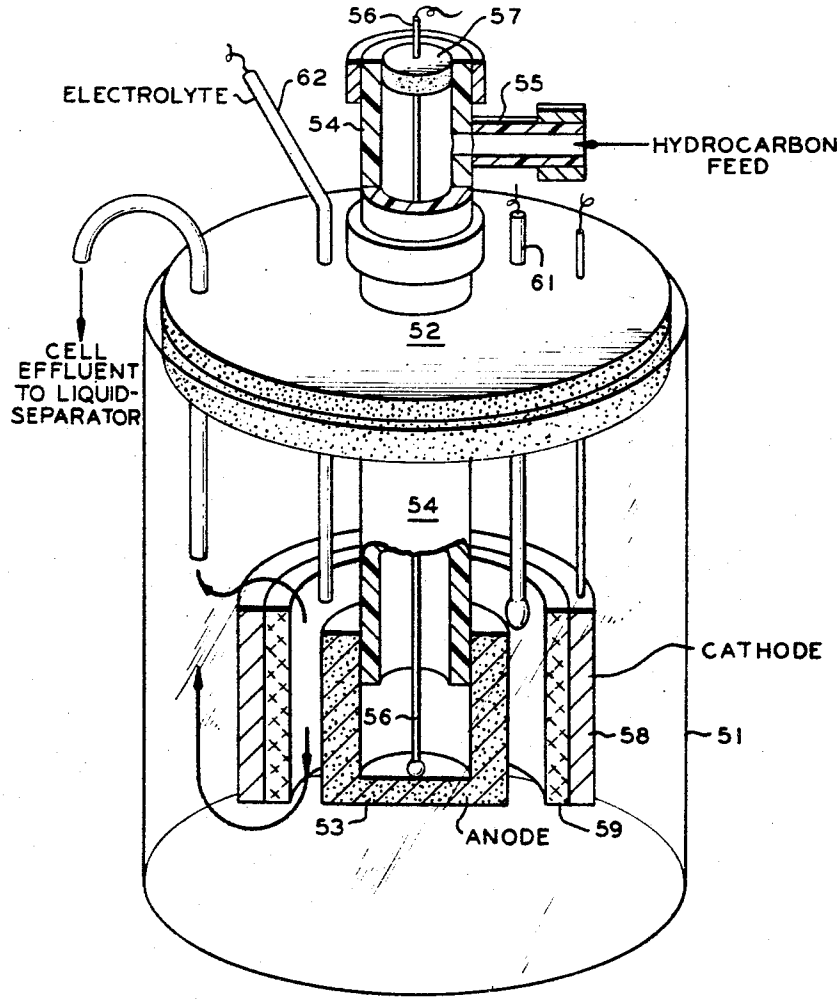


FIG. 3

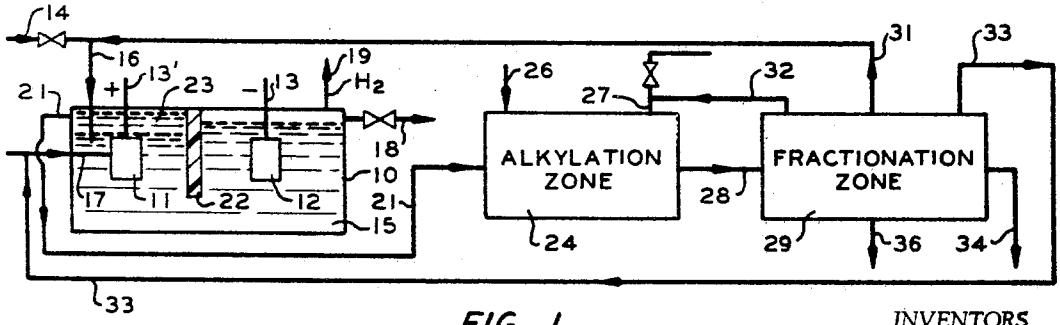


FIG. 1

INVENTORS
H.M. FOX
F.N. RUEHLEN

BY Young and Quigg

ATTORNEYS

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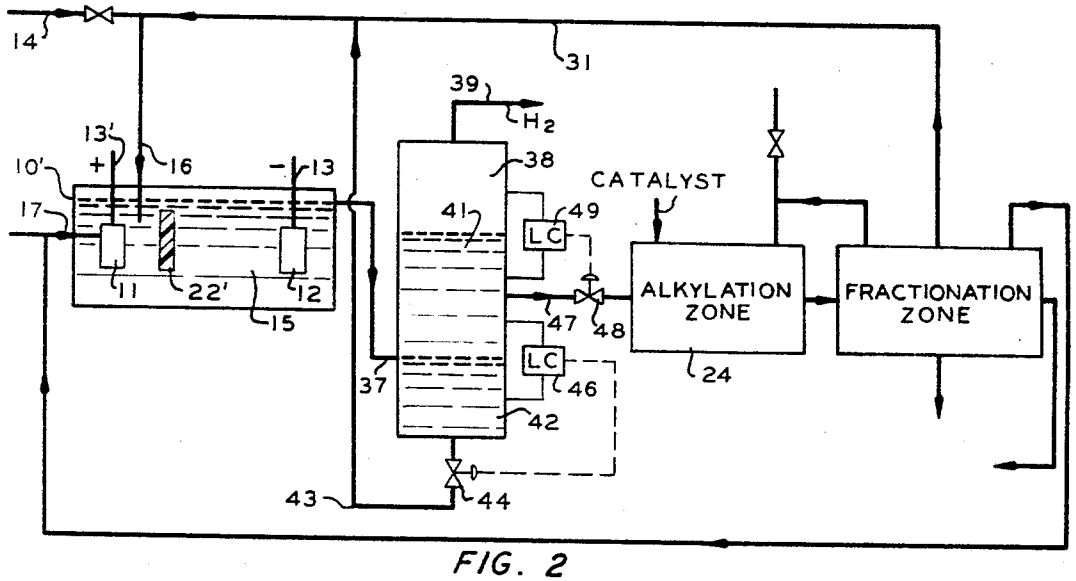


FIG. 2

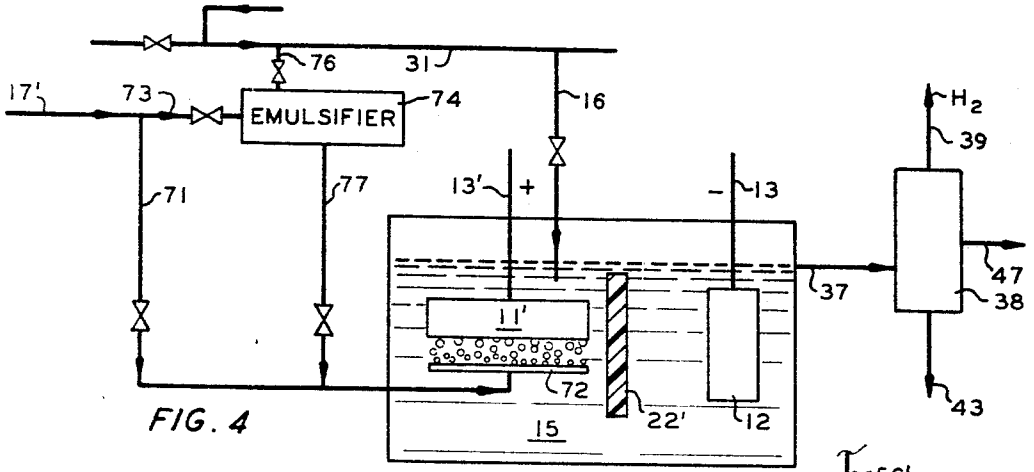


FIG. 4

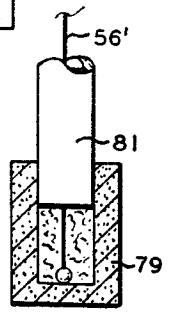


FIG. 6

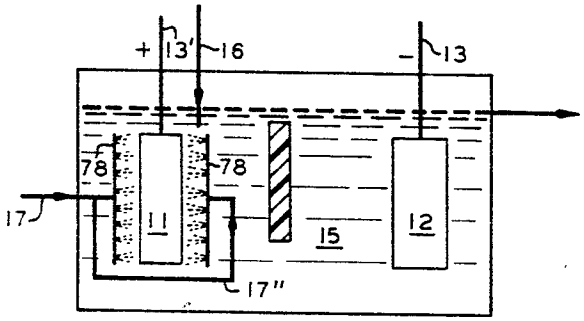


FIG. 5

INVENTORS
H.M. FOX
F.N. RUEHLEN

BY Young and Quigg

ATTORNEYS

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PROCESS AND APPARATUS FOR PRODUCTION OF ALKYLATE

Homer M. Fox and Forrest N. Ruehlen, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

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19 Claims. (Cl. 260—671)

ABSTRACT OF THE DISCLOSURE

Halogenation of a hydrocarbon by reacting said hydrocarbon with a halogen evolved at the active surface of an anode in an electrolytic cell during electrolysis of a halide containing electrolyte in the presence of a promoter for the reaction. In a combination of said halogenation process with an alkylation process, alkyl halides from the halogenation process are used as alkylating agents to alkylate an alkylatable hydrocarbon, hydrogen halide liberated during the alkylation reaction is recovered from the product alkylate stream and passed to the electrolytic cell in the halogenation step to supply halogen for the electrolyte therein.

This application relates to a process and an apparatus for the production of alkylates. In one aspect this invention relates to an integrated halogenation-alkylation process for the production of alkylates. In another aspect this invention relates to apparatus which can be employed for carrying out said integrated halogenation-alkylation process.

Various processes for the alkylation of alkylatable hydrocarbons utilizing a variety of alkylating agents are well known in the art. For example, olefins such as ethylene, isobutylene, etc. are well known as alkylating agents for various types of hydrocarbons such as isobutane and benzene. Alkyl halides or halogenated hydrocarbons are another well known class of alkylating agents which can be utilized for alkylating hydrocarbons such as isobutane and benzene. The alkylation processes utilizing said alkylating agents and alkylatable hydrocarbons are carried out in the presence of catalysts such as aluminum chloride or substantially anhydrous hydrofluoric acid under alkylating conditions. The choice of the particular catalyst and operating conditions employed usually depends upon the particular alkylating agent and alkylatable hydrocarbon being utilized.

The choice of a particular alkylating agent for a particular alkylatable hydrocarbon is frequently determined not only by the type of alkylate desired, but also by the availability of the alkylating agent. However, in some instances where the choice is between various alkylating agents of substantially the same availability and reactivity, other factors such as the reaction by-products produced enter into the consideration. For example, when utilizing olefins as the alkylating agent the alkylation reaction can be considered broadly as a condensation reaction without the formation of by-products. However, when utilizing alkyl halides as the alkylating agent, hydrogen halide is liberated as a by-product of the alkylation reaction. The liberation of this hydrogen halide creates a major problem because said hydrogen halide must be either recovered and sold or otherwise disposed of. In many instances, this results in a waste of halogen values which seriously affects the economics of the process. Thus, in some instances where theoretically either an olefin or an alkyl halide could be utilized as the alkylating agent, the use of the alkyl halide is ruled out because of the recovery or disposal problems and/or economic loss of halogen values. This frequently means that alkyl halides are not used

where otherwise said alkyl halides would be the alkylating agent of choice.

The present invention provides a combination halogenation-alkylation process for the production of alkylates wherein an alkyl halide is utilized as the alkylating agent and wherein the above-described difficulties are eliminated. Broadly speaking, the present invention provides a process and an apparatus for the production of alkylates wherein a hydrocarbon is halogenated electrochemically in an electrolytic cell to provide an alkyl halide, said alkyl halide is utilized as the alkylating agent to alkylate an alkylatable hydrocarbon, and the hydrogen halide liberated in said alkylation reaction is recycled to said electrolytic cell with no loss of halogen values.

An object of this invention is to provide an integrated combination of steps for the production of alkylates. Another object of this invention is to provide an integrated halogenation-alkylation process for the production of alkylates. Still another object of this invention is to provide an integrated halogenation-alkylation process wherein an alkyl halide is utilized as the alkylating agent and the hydrogen halide liberated in the alkylation step is economically and efficiently utilized in the halogenation step. Another object of this invention is to provide an integrated combination of steps comprising electrochemical halogenation of a hydrocarbon to produce an alkyl halide which is used to alkylate an alkylatable hydrocarbon, and which process operates on captive halogen. Another object of this invention is to provide an improved process for the electrochemical halogenation of hydrocarbons. Another object of this invention is to provide a combination of apparatus which can be employed in carrying out the integrated halogenation-alkylation process of the invention. Still another object of this invention is to provide an improved electrode which can be employed in electrochemical reactions. Other aspects, objects and advantages of the invention will be apparent to those skilled in the art in view of this disclosure.

According to the invention, there is provided a process for the halogenation of a hydrocarbon, which process comprises: reacting said hydrocarbon with a halogen evolved at the active surface of an anode in an electrolytic cell during electrolysis of a halide-containing electrolyte in the presence of a promoter for said reaction; and recovering halogenated hydrocarbon from an effluent from said cell.

Further according to the invention, there is provided a process for the production of an alkylate, which process comprises: reacting a hydrocarbon with a halogen evolved at the active surface of an anode in an electrolytic cell during electrolysis of a halide containing electrolyte to form a halogenated hydrocarbon; alkylating an alkylatable hydrocarbon with said halogenated hydrocarbon in an alkylation zone in the presence of an alkylation catalyst under alkylation conditions to form an alkylate stream containing liberated hydrogen halide and alkylated hydrocarbon; recovering said alkylated hydrocarbon from said alkylate stream as said alkylate; recovering said hydrogen halide from said alkylate stream; and recycling said recovered hydrogen halide to said electrolytic cell.

Further according to the invention, there is provided a combination of apparatus which can be employed to carry out the process of the invention.

Still further according to the invention, there is provided an electrode which can be employed for carrying out electrochemical reactions.

It is to be noted that the invention provides a combination halogenation-alkylation process for the production of alkylates wherein the hydrocarbon to be halogenated is halogenated to an alkyl halide in an electrolytic cell utilizing an electrolyte which furnishes a halogen

ion, said alkyl halide is utilized to alkylate an alkylatable hydrocarbon, and the hydrogen halide liberated in said alkylation step is recycled to said electrolytic cell to supply halogen for said electrolyte.

The process of the invention is thus distinguished in at least two respects from the conventional halogenation-alkylation processes of the prior art wherein a conventional halogenation step such as light activated halogenation or heat activated halogenation is employed. First, hydrogen halide is not a by-product, and secondly, hydrogen is a by-product, in the process of the invention. These distinguishing features provide at least two outstanding advantages for the process of the invention. First, since hydrogen halide is not a by-product, the recovery or disposal problem is eliminated. The recycle of the hydrogen halide from the alkylation step to the electrochemical halogenation step makes it possible for the integrated process of the invention to operate on captive halogen and the only make-up halogen required is that necessary to replace mechanical losses. Furthermore, the halogen utilized in the process can be furnished by such relatively inexpensive materials as ordinary rock salt or hydrogen chloride and the necessity for utilizing the relatively expensive elemental chlorine is eliminated. Secondly, the hydrogen by-product, which is a valuable raw material, is obtained in a substantially pure state or can be readily purified.

FIGURE 1 is a diagrammatic flow sheet of one embodiment of the process of the invention and schematically illustrates, partly in cross-section, one combination of apparatus which can be employed in the practice of the invention.

FIGURE 2 is a diagrammatic flow sheet of another embodiment of the process of the invention and schematically illustrates, partly in cross-section, another combination of apparatus which can be employed in the practice of the invention.

FIGURE 3 is a perspective view, partly in cross-section, illustrating one type of electrolytic cell which can be employed in the practice of the invention.

FIGURES 4 and 5 are schematic illustrations, partly in cross-section, of other electrolytic cells which can be employed in the practice of the invention.

FIGURE 6 is a schematic illustration in cross-section of one type of anode which can be employed in the electrolytic cells employed in the practice of the invention.

Referring now to the drawings, wherein like numerals are employed to designate like elements, the invention will be more fully explained. It will be understood that said drawings are diagrammatic in nature and that many valves, pumps, control apparatus, etc., not necessary to illustrate the invention to those skilled in the art, have been omitted for the sake of brevity. Although the invention is applicable to other halogens, as discussed further hereinafter, the following description of the drawings will be primarily in terms of chlorination. In FIGURE 1 there is shown an electrolytic cell **10** which is provided with an anode **11** and a cathode **12**. Said anode and said cathode can be formed from any material which is suitable therefor, such as carbon, iron, nickel, zinc, platinum, platinized titanium, carbonized titanium, etc. Usually, carbon is a preferred electrode material, particularly for the anode. Furthermore, any suitable type or form of anode and cathode known to the art can be employed in the practice of the invention. For example, said electrodes can be in the shape of solid bars, strips or plates, or cylinders. They can also be formed from porous materials in said shapes as discussed further hereinafter. Said cathode and said anode are connected to a suitable source of direct current in conventional manner by means of the lead wires **13** and **13'**, respectively. Said cell is provided with a suitable conduit means such as conduits **14** and **16** for the introduction and replenishing of the electrolyte therein. A suitable conduit means **17** is provided for introducing the hydrocarbon to be chlorinated into said cell in the region of and as a thin film on the surface of said anode **11**. Said cell is also provided with a suitable conduit **18** for withdrawing electrolyte and other effluent from the cell when desired and a suitable conduit **19** for withdrawing hydrogen which is liberated at the cathode. A suitable conduit means **21** is provided for withdrawing from the cell hydrocarbon which has been subjected to halogenation in the region of the anode **11**.

In the operation of said cell **10**, a suitable electrolyte solution, such as aqueous hydrogen chloride, is introduced via conduits **14** and **16**. Thereafter, current is applied to the electrodes of the cell in conventional manner and the hydrocarbon to be halogenated is introduced via conduit **17** in the region of and onto the active surface of the anode **11**. As discussed further hereinafter, the introduction of said hydrocarbon can be in any suitable manner so as to form a thin film on the electrolytically active surface of said anode. Such a thin film of hydrocarbon does not seriously reduce the efficiency of said anode or the conductivity of the cell. Due to the electrolysis of the electrolyte chlorine is evolved or liberated at the anode. The continuously changing film of hydrocarbon on the anode co-operates with a continuous chlorine liberation to provide optimum contact and reaction conditions between said hydrocarbon and said chlorine with resultant high halogenation efficiency. The hydrogen liberated at the cathode by said electrolysis is withdrawn from the cell via conduit **19**. In the embodiment of the invention illustrated in FIGURE 1 no electrolyte is usually withdrawn via conduit **18** when an aqueous hydrogen chloride electrolyte is being used. Recycle hydrogen chloride, from a source described further hereinafter, is introduced into said cell via conduit **16**. It will be noted that said recycle hydrogen chloride is introduced below the surface of electrolyte **15** and in the region of anode **11** so as to provide for continuous sweeping of said anode with fresh electrolyte. If desired, make-up hydrogen chloride can be introduced via conduit **14**. Said cell **10** is provided with a separator or diaphragm **22** which extends from the top of the cell toward the bottom thereof and divides same into an anode compartment and a cathode compartment as shown. This division of the cell into said compartments is advantageous in maintaining the described sweeping action on the anode with fresh electrolyte. This division is also advantageous when employing an alkali metal halide, such as sodium chloride, to prevent migration of sodium hydroxide from the cathode compartment to the anode compartment. In such instances, a flow of electrolyte into the anode compartment via conduit **16** and out of the cathode compartment via conduit **18** is utilized. Said separator **22** can be fabricated from a suitable plastic or other non-conducting material as shown. It will be understood that the walls of said cell are also fabricated of a suitable non-conducting material.

The hydrocarbon rises to the top of the electrolyte in the anode compartment and forms a layer **23** thereon as shown. Said hydrocarbon **23** which comprises both halogenated and non-halogenated hydrocarbons is withdrawn via conduit **21** and passed to alkylation zone **24**. A suitable alkylation catalyst is introduced into said zone **24** via conduit **26**. A suitable alkylation hydrocarbon is introduced into said zone **24** via conduit **27**. The process of the invention is particularly applicable to the alkylation of aromatic hydrocarbons such as benzene, toluene, xylene and the like and is particularly applicable to the alkylation of benzene (the preferred aromatic hydrocarbon). In some instances high aromatic content naphtha fractions boiling within the range of from about 175 to about 300° F., such as can be obtained from thermally cracked naphthas, can be employed as the source of the alkylatable aromatic hydrocarbon. The process of the invention is also applicable to the alkylation of hydrocarbons other than aromatic hydrocarbons, for example, isobutane and other alkylatable paraffinic hydrocarbons.

The catalyst employed in alkylation zone **24** can be

any suitable alkylation catalyst, e.g., sulfuric acid, substantially anhydrous hydrogen fluoride, and the so-called Friedel-Crafts metal halides. Included among said Friedel-Crafts metal halides are those such as aluminum chloride, aluminum bromide, boron trifluoride and the halides of such metals are zinc, tin, arsenic, antimony, zirconium, beryllium, titanium, iron, and the like. These metal halide catalysts are especially effective when present as complexes which are formed by interaction between the metal halides and hydrocarbons present in the reaction system. A particularly desirable catalyst is the complex of hydrocarbon with aluminum chloride. In addition to the catalyst it is desirable that the corresponding hydrogen halide be present in the reaction zone since this material maintains catalyst activity at a high level. The reaction rate and the conversion of the hydrocarbon feed is dependent on the amount of aluminum chloride in the aluminum chloride-hydrocarbon complex. However, the quantity of aluminum chloride in the complex can be varied over wide ranges to provide a corresponding range of feed reactant conversion. While the over-all activity of the catalyst is established by the aluminum chloride content, as stated, the presence of hydrogen chloride is required to provide a high activity. Usually the quantity of hydrogen chloride present is between about 0.5 and about 6 weight percent of the feed with about 2 to 4 weight percent being preferred. It is usually not necessary to add additional hydrogen chloride because hydrogen chloride is liberated in the alkylation reaction.

The aluminum chloride-hydrocarbon complex catalyst can be originally prepared by mixing aluminum chloride and kerosene in a weight ratio of about 8:5. During operation of the process, the original complex catalyst is replaced with complex catalyst formed in the process. The heat of hydrolysis of the catalyst is usually in the range 150–250, more usually in the order of about 200, calories per gram. Catalyst having higher heats of hydrolysis, e.g., 300–325 calories per gram, can also be used with good results. The viscosity of the catalyst is usually in the order of 8 to 16, more generally in the order of 10 to 12, centipoises at 100° F.

Conditions employed in alkylation zone **24** will depend somewhat upon the catalyst employed. When employing aluminum chloride-hydrocarbon complex catalyst the alkylation will generally be carried out at a temperature within the range of 50 to 110° F. with a pressure sufficient to maintain liquid phase conditions and to prevent vaporization of catalyst. Flow rates of reactants should be maintained such that a residence time within the range of about 5 to about 30 minutes, preferably about 10 to about 20 minutes, will be provided. The mol ratio of aromatic hydrocarbon to halogenated hydrocarbon entering the alkylation zone should be such as to furnish at least one mol of benzene per gram atom of halogen on the halogenated hydrocarbon. It is preferred to operate with an excess of aromatic hydrocarbon. Thus, the mol ratio of aromatic hydrocarbon to halogenated hydrocarbon is usually maintained within the range of 2:1 to 30:1, preferably 8:1 to 15:1. The volume ratio of catalyst to total hydrocarbon in zone **24** should be in the range of about 1:5 to 2:1, preferably about 1:1.

Alkylation zone **24** includes, in addition to a suitable contactor for carrying out the alkylation reaction, a separation zone wherein a hydrocarbon phase is separated from the catalyst phase. The hydrocarbon phase is withdrawn from zone **24** via conduit **28** and introduced into fractionation zone **29**. It will be understood that said fractionation zone can comprise any suitable number of fractionators for making the separations indicated or any other desired separation. For example, in the course of the alkylation reaction hydrogen chloride is liberated and this liberated hydrogen chloride is withdrawn from zone **29** via conduit **31**, introduced into conduit **16**, and then introduced into the anode compartment of cell **10** below the level of the electrolyte **15** therein. In this embodiment of the invention the thus recycled hydrogen chloride can be returned to said cell **10** in the gas phase. An overhead stream comprising unreacted alkylatable hydrocarbon is withdrawn from zone **29** via conduit **32**, passed into conduit **27**, and thus recycled to alkylation zone **24**. Another fraction comprising non-halogenated hydrocarbon, originally introduced into alkylation zone **24** along with the halogenated hydrocarbons in conduit **21**, is withdrawn from fractionation zone **29** via conduit **33**, and passed into conduit **17** for recycle to electrolytic cell **10**. The stream withdrawn via conduit **34** is comprised principally of monoalkyl aromatic compounds and is the alkylate product of the process. A heavy alkylate stream comprising principally polyalkylated aromatic compounds is withdrawn from zone **29** via conduit **36**.

The alkylate product stream withdrawn via conduit **34** is recovered substantially in the pure state and can be passed to a sulfonation zone (not shown) and therein contacted with a suitable sulfonation agent, for example, an excess of concentrated sulfuric acid, in conventional manner for the production of a biodegradable detergent.

In FIGURE 2 there is illustrated another embodiment of the invention employing an electrolytic cell **10'** which is substantially like that illustrated in FIGURE 1, the primary difference between said cells being that in the cell of FIGURE 2 the separator **22'** does not extend from the top of the cell as in FIGURE 1. The primary function of said separator **22'** is thus to serve as a baffle to promote the sweeping action of the fresh electrolyte introduced via conduit **16**.

The electrolytic cell of FIGURE 2 also differs from that of FIGURE 1 in that no separations are effected in the cell itself. Thus, a cell effluent comprising hydrogen chloride electrolyte, halogenated and non-halogenated hydrocarbons, and hydrogen is withdrawn from the cell via conduit **37** and introduced into a liquid-gas separator **38**. Said separator, as the name implies, effects a separation between the gas phase and the liquid phase of said cell effluent. Essentially pure hydrogen gas, liberated at the cathode of cell **10'**, is withdrawn from separator **38** via conduit **39** and passed to storage or further purification treatment if necessary or desired. The liquid phase in separator **38** is separated by gravity into an upper hydrocarbon phase **41** comprising halogenated and non-halogenated hydrocarbons, and a lower aqueous hydrogen chloride phase **42**. Said lean aqueous hydrogen chloride phase is withdrawn from separator **38** via conduit **43** having valve **44** therein and introduced into conduit **31** where it is combined with recycle hydrogen chloride gas produced in the subsequent alkylation reaction, and then recycled via conduit **16** to cell **10'**. The operation of valve **44** is controlled by means of liquid level controller **46** in known manner.

Said hydrocarbon phase **41** is withdrawn from separator **38** via conduit **47**, having valve **48** controlled by level controller **49** therein, and then introduced into alkylation zone **24** for subsequent treatment as described above in connection with FIGURE 1.

FIGURE 3 illustrates in more detail one form of electrolytic cell which can be employed in the practice of the invention. Said cell comprises a suitable container **51** fitted with a suitable top closure member **52**. Said container and said closure member can be of glass, plastic, rubber, or any other suitable non-conducting material. Said cell is provided with an anode **53** which comprises a porous carbon cylinder having one end closed as indicated and the open end tapped and threaded to receive a conduit **54** which can be conveniently fabricated from a suitable plastic, such as Teflon, and which serves as the hydrocarbon feed entry conduit. The upper end of said conduit **54** extends through closure member **52** to without said cell as indicated. Said hydrocarbon feed is introduced into the upper end portion of conduit **54** by means of conduit **55** at the T connection shown. If desired, the bottom and top surfaces of said porous anode **53** can be

coated with a porcelain cement or other suitable material so as to restrict the working surface of said anode to the vertical side only. Electrical connection to said anode **53** is provided by means of a length of copper wire **56** or other suitable conductor which extends downward through conduit **54** and presses against the bottom or other conducting surface of anode **53**. Said copper wire **56** extends through a suitable rubber septum **57** which provides a liquid seal in the upper end of conduit **54**.

As here illustrated, the cathode **58** comprises a sheet of nickel metal wrapped around a porous alundum separator **59**. Any other suitable cathode arrangement can be employed. For example, a platinum gauze cylinder can be employed as the cathode. The porous alundum separator provides physical separation between the anode compartment and the cathode compartment. A thermowell **61** extends downwardly through said closure member **52** and into the anode compartment for providing means to determine the working temperature of the cell. Conduit **62** is provided for the introduction of electrolyte into the anode compartment. It will be noted that said conduit **62** extends into the anode compartment below the top of cathode **58** and separator **59** so as to provide for the introduction of the electrolyte directly into the anode compartment.

The operation of the cell illustrated in FIGURE 3 is similar to the operation of the cell illustrated in FIGURE 2 and will be readily understood by those skilled in the art in view of the above description of said cell and the descriptions of the cells of FIGURES 1 and 2.

It will be understood it is within the scope of the invention to extend separator **59** upward to the top of the cell as in the cell of FIGURE 1 and withdraw the hydrocarbon as a separate phase if desired. In such instances separate electrolyte and hydrogen withdrawal conduits would also be provided as in the cell of FIGURE 1.

FIGURE 4 is a schematic illustration of another type of electrolytic cell which can be employed in the practice of the invention. This cell is similar to that illustrated in FIGURE 2, the principal differences being in the horizontal position of anode **11'**, and in the means for introducing or supplying the hydrocarbon as a thin film to the surface of said anode. In this embodiment of the invention the hydrocarbon to be halogenated can be passed from conduit **17'** via conduit **71** and diffuser **72** into the cell in the region of said anode **11'**. It will be noted that diffuser **72** is positioned in a plane below said horizontally disposed anode **11'**. Said diffuser **72** thus serves to introduce the hydrocarbon to be treated in the form of small globules or droplets which gravitate upwardly and contact the electrolytically active surface of anode **11'**. If desired, in another embodiment of the invention, the hydrocarbon to be treated can be passed from conduit **17'** via conduit **73** into emulsifier **74** wherein it is emulsified with the recycle and/or fresh electrolyte introduced thereinto via conduit **76**. Said emulsifier **74** can comprise any suitable means, such as a high speed mixer, for forming an emulsion between the hydrocarbon and aqueous electrolyte phases. The emulsion of electrolyte and hydrocarbon is withdrawn from emulsifier **74** via conduit **77** and passed into said cell via diffuser **72**. Said diffuser **72** liberates or releases the emulsion in the form of small droplets which gravitate upwardly and contact the active surface of anode **11'** as previously described. Effluent from said cell is withdrawn via conduit **37** and passed into liquid separator **38** wherein a separation is effected as described above in connection with FIGURE 2.

FIGURE 5 is a schematic illustration of another type of electrolytic cell which can be employed in the practice of the invention. This cell is similar to that illustrated in FIGURES 2 and 4, the principal difference being in the means provided for supplying the hydrocarbon to be treated to the surface of the anode in the form of a thin film. In the cell of FIGURE 5 the hydrocarbon to be treated is passed via conduits **17** and **17''** into a header **78** from which said hydrocarbon is sprayed in the form of fine droplets onto the surface of the anode **11**. Said header **78** can comprise any suitable type of spray header arrangement and is fabricated or adapted in accordance with the shape of anode **11** so as to blanket the active surface thereof with a thin film of the hydrocarbon.

FIGURE 6 illustrates one type of electrode which can be employed as the anode in the practice of the invention. This electrode is an additional feature of the invention. Said electrode comprises a hollow porous cylinder **79**, similar to that illustrated in FIGURE 3, which is tapped and threaded to receive an inlet conduit **81**. As in the anode of FIGURE 3, the top and bottom of the electrode **79** can be coated with a porcelain cement to restrict the active surface thereof to the vertical side wall, if desired. Said electrode is also provided with a suitable electrical connection means **56'**, similar to **56** in FIGURE 3, which is in contact with a conductive portion or portions of said electrode for connecting same to a source of electrical current. The interior of said electrode **79** is filled with a commercial grade of carbon black or other suitable particulate conducting material such as graphite, charcoal, powdered or finely divided porous carbon, activated carbon, etc. which has been impregnated with a suitable solution of a noble metal such as platinum or rhodium or mixtures thereof. Examples of metals which can be thus utilized in the practice of the invention are the Group VIII metals such as iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum, and mixtures thereof.

Any suitable method can be employed for impregnating or otherwise incorporating the particulate conducting material with said metals. For example, a suitable salt or other compound of said metals can be dissolved or dispersed in a suitable solvent and the resulting solution or dispersion employed as the impregnating medium in conventional manner to incorporate the desired amount of metal compound with the particulate conducting material. It will be understood by those skilled in the art that the choice of the metal compound and the solvent to be employed in such methods will depend upon the particular metal which it is desired to utilize. For example, some of said metals can be obtained in compounds which can be employed directly as the impregnating or incorporating medium, e.g., chloroplatinic acid. The amount of said metal compounds utilized to impregnate the particulate conducting material will usually be a small but effective amount within the range to deposit or otherwise incorporate an amount of the metal (calculated as the metal) within the range of from 0.1 to 10, preferably from 0.5 to 5, weight percent of the particulate conducting material.

The impregnated particulate conducting material can be activated in any suitable manner. If desired, said impregnated material can be treated with hydrogen in conventional manner to reduce the metal compounds. Said impregnated materials can also be treated with air or other oxidizing agent at elevated temperatures in conventional manner to convert said metal compounds to the oxide or other active form.

The above-described electrode of the invention comprising a hollow, porous carbon tube filled with said impregnated conducting material finds particularly advantageous use in acidic electrolytes such as the preferred hydrogen chloride electrolyte described herein. The fact that impregnated material is enclosed in the hollow, tubular electrode protects said impregnated material from the direct action of the acidic electrolyte. The protection afforded by the walls of the porous carbon tube is enhanced by the fact that the hydrocarbon to be halogenated is introduced into the interior of said electrode and said hydrocarbon thus affords further protection for the metals which are impregnated on the particulate conducting material. This is a significant advantage over merely impregnating the wall of the hollow, porous tube or other

type of porous electrode because in such instances the impregnating metal would be subject to the direct action of the acidic electrolyte and many of said metals are readily attacked by such acids.

The process of the invention is applicable to the halogenation of a wide variety of hydrocarbons. The invention is particularly applicable to the halogenation of cyclic and acyclic saturated hydrocarbons containing from 2 to 20 carbon atoms per molecule. Examples of such hydrocarbons include ethane, butane, 3-methylhexane, cyclohexane, 1,3-dimethylpentane, decane, dodecane, 8-ethyl hexadecane, and eicosane. Presently preferred hydrocarbons for treatment in accordance with the invention are the saturated acyclic hydrocarbons containing from 10 to 15 carbon atoms per molecule. The normal paraffinic hydrocarbons containing from 10 to 15 carbon atoms per molecule are particularly preferred when it is desired to produce an alkyl halide product which can be subsequently utilized to alkylate benzene to produce a valuable alkylate which can be subsequently sulfonated to produce valuable biodegradable detergents.

Any suitable electrolyte capable of furnishing a halide ion upon electrolysis can be utilized in the halogenation step of the invention. Thus, electrolytes capable of furnishing chloride, bromide or fluoride ions can all be utilized to produce alkyl halides which can be subsequently employed as alkylating agents to alkylate an alkylatable hydrocarbon in accordance with the invention. Electrolytes which furnish chloride or bromide ions are presently preferred because of their ready availability, cost, and ease of reaction. Chlorine-containing electrolytes are presently most preferred. Examples of suitable electrolytes include the alkali metal halides, either in aqueous solution or as the molten salt, and hydrogen halides in aqueous solution. Mixtures of aqueous hydrogen halide and alkali metal halides in aqueous solution can also be utilized in the practice of the invention. In general, aqueous electrolytes are preferred because they are less complex and provide good conductivity. Aqueous hydrogen chloride is the presently most preferred electrolyte.

It is also within the scope of the invention to employ non-aqueous solvents in preparing the electrolytes utilized in the practice of the invention. Any suitable non-aqueous solvent can be used so long as the primary species discharged at the anode is the halide radical of interest. Examples of non-aqueous solvents which can be so utilized are carbonyl chloride, selenium oxychloride, bromine trifluoride, mercuric bromide, and liquid hydrogen fluoride.

The process of the invention can be operated with a wide variation in conditions, and since many of the variables are interdependent, a change in one variable will necessitate a change in other variables. However, we have found that the halogenation step of the invention can be operated satisfactorily within the scope and the range of the variables given hereinbelow.

The electrolytes utilized in the electrolytic cells can be used in a wide range of concentrations. For example, when aqueous hydrogen chloride is the electrolyte, said electrolyte can range in concentration from about 0.4 to about 37 weight percent, preferably 15 to 25 weight percent. When aqueous solutions of alkali metal halides are utilized, the concentration of the alkali metal halide can range from about 0.4 weight percent to saturated, preferably from about 15 weight percent to saturated. When mixtures of aqueous hydrogen halide and aqueous alkali metal halide are utilized as the electrolyte, the concentration of the halide ion in said electrolyte can range from about 0.1 normal to saturated, preferably from about 4 normal to saturated.

The halogenation step of the invention can be carried out over a wide range of temperatures, ranging from a temperature just above the freezing point of the electrolyte up to about 900° F. Aqueous electrolytes comprising hydrogen halides and/or alkali metal halides can be utilized at the lower temperatures such as from about 32 to about 210° F., preferably from about 60 to about 190° F. If desired, the cell can be pressurized to permit utilization of said aqueous electrolytes at still higher temperatures. Although not illustrated in the drawings, it will be understood to be within the scope of the invention to provide said cells with suitable heating and/or cooling means such as a coil disposed in the electrolyte through which a heat exchange medium can be passed. It is also within the scope of the invention to provide heat exchange means on the hydrocarbon and electrolyte inlets for controlling the temperature thereof. Electrolytes comprising molten alkali metal halide salts can be utilized at temperatures of from about 400 to about 900° F., for example. In such instances the entire cell can be disposed in a suitable furnace.

The halogenation step of the invention can also be carried out over a wide range of pressures ranging from substantially atmospheric to superatmospheric. The pressure utilized is limited only by the materials employed in fabricating the electrolytic cells. Generally speaking, it is preferred to operate the cells at atmospheric or pressures slightly above atmospheric. Also, it is generally preferred to introduce the hydrocarbon to be treated into said cell as a liquid phase. With some hydrocarbons such as ethane and propane, and in some instances butane, this requires more pressure than is usually desirable. In such instances said hydrocarbon can be introduced as a gas with the cell being maintained under sufficient pressure to facilitate convenient operation and maintain the desired concentration of hydrocarbon in the active region surrounding the anode. Said hydrocarbons can very conveniently be introduced as gases through one of the porous anodes described herein.

Generally speaking, as will be understood by those skilled in the art, the hydrocarbon feed introduction rate will vary in accordance with the amount of active electrolytic surface available at the anode. As a guide, it is usually preferred to maintain said hydrocarbon introduction rate within the range of from 0.025 to 0.5 gallon, preferably from 0.1 to 0.3 gallon, per square foot of active anode area per hour.

The current supplied to the anode and cathode of the electrolytic cell will, of course, depend upon the size of the cell and the hydrocarbon feed rate, as well as the conversion efficiency desired. Generally speaking, the current supplied will be within the range of 0.02 to 1.0, preferably 0.01 to 0.8, Faraday per gram mol of hydrocarbon feed. Said current usually will be supplied at a current density within the range of from 5 to 500, preferably from 15 to 200, amperes per square foot of anode area. The current density is one of the more important variables in the process of the invention and, generally speaking, one should employ the highest current density possible, taking into consideration the other variables and the materials of construction employed in fabricating the cell, because at a given conversion level the monochloride to dichloride ratio in the halogenated product increases with increasing current density.

Generally speaking, when it is desired to increase or obtain the maximum production of monohalogenated hydrocarbons, it is desirable to carry out the halogenation under conditions to maintain the percent conversion at less than 20 percent, usually in the range of 10 to 20 percent.

An added feature of the invention is that the halogenation step can be carried out in the presence of a promoter if desired. Any suitable promoter which is compatible in the system in which it is employed and which is effective in promoting the electrochemical halogenation can be utilized in the practice of the invention. Examples of suitable promoters are iodine, ferric chloride, antimony chloride, sulfur chloride, iodoform and others. Said promoters, as well as the promoters discussed in the succeeding paragraph, are employed in small but effective amounts and

can be introduced into the system by incorporation in the hydrocarbon feed or the electrolyte. It is usually preferred to incorporate said promoters in the hydrocarbon feed. When incorporated in the hydrocarbon feed said promoters are usually employed in an amount within the range of from 0.001 weight percent to saturation, preferably within the range of 0.05 to 0.3 weight percent of said hydrocarbon feed. It is, however, within the scope of the invention to employ amounts of said promoters which are outside said ranges.

We have discovered that free radical initiators are particularly effective promoters for the electrochemical halogenation of hydrocarbons. Thus, while the invention is not to be limited by any theory as to reaction mechanism, the halogenation reaction mechanism is presently believed to be halogen evolution at the anode followed by a halogenation reaction which is at least in part a free radical mechanism. This is supported by our discovery. Because of their greater effectiveness, the free radical initiators are the presently preferred promoters. Any suitable free radical initiator which decomposes at usable rates under the reaction conditions to furnish free radicals can be used in the practice of the invention. Suitable initiators for furnishing free radicals include the organic peroxide and azo compounds which have half lives in the range of 0.05 to 50, preferably 0.05 to 20, hours under reaction conditions. Representative examples of suitable free radical initiators include, among others, the following: di-tert-butyl peroxide; tert-butyl hydroperoxide; benzoyl peroxide; azobisisobutyronitrile; tert butylbenzene hydroperoxide; dicumyl peroxide; hydroxyheptyl peroxide; cyclohexanone peroxide; t-butyl peracetate; di-t-butyl diperphthalate; t-butyl perbenzoate; methyl ethyl ketone peroxide; p-methane hydroperoxide; pinane hydroperoxide; 2,5-dimethylhexane-2,5-dihydroperoxide; cumene hydroperoxide; and the like.

While the invention has been described above and elsewhere herein in terms of employing a single electrolytic cell having a single pair of electrodes such as illustrated in the drawings, the invention is not limited thereto. Any suitable type of electrolytic cell can be employed in the practice of the invention. Included among the suitable cells are well known DeNora cell, the Nelson cell, the Allen-Moore cell, and various diaphragm and bell-type cells. Thus, it is within the scope of the invention to employ a multiplicity of single cells such as illustrated in the drawings and combined or integrated in any suitable manner, such as in the commercially available DeNora cell.

The following examples will serve to further illustrate the invention.

Example I

A chlorination cell similar to FIGURE 3 was assembled. The anode was a hollow, porous carbon cylinder with one end closed and the open end tapped to take a ¼-inch Teflon hydrocarbon feed entry tube. The cylinder was approximately 2.5 cm. O.D. by 3.7 cm. long, with a 0.7 cm. wall thickness. The bottom and the top surfaces were coated with a porcelain cement in order to restrict the working surface to the vertical side only. This provided an outer surface area of 29 cm.^{2}. The anode was fashioned from a porous carbon block (National Carbon Grade 60) which had a pore volume of 0.3 cm.^{2}/g. with the pores ranging from 10 to 60 microns in diameter.

Electrical connection to the anode was by means of a length of copper wire extending downward through the hydrocarbon feed tube and pressed against the bottom of the anode. The wire was connected to the positive side of a D.C. power supply. The hydrocarbon feed entry tube was connected to a supply of n-dodecane. The cathode was a conventional platinum gauze cylinder. The cell was filled with an aqueous solution of HCl containing approximately 20 weight percent CHl.

Current was applied to the cell and at a temperature of 190–200° F., a current density of 17.2 milliamperes per cm.^{2} of anode area (500 ma. total), and at a terminal voltage of 1.5 to 1.6 volts a stream of n-dodecane was introduced to the cell through the porous anode at a feed rate of 0.82 millimole/cm.^{2}/hr. which amounted to 0.78 Faraday per gram mol of n-dodecane feed. The gaseous and liquid products in the cell effluent were collected and analyzed. Analysis of the hydrocarbon phase showed a 12.6 mol percent conversion to chlorinated products and said chlorinated products had a distribution of 10.5, 54.6, and 34.9 mol percent for primary monochlorides, secondary monochlorides, and dichlorides, respectively. The current or electrical efficiency to chlorinated products was 44 percent.

Example II

Employing an apparatus and electrolyte essentially the same as that of Example I, another run was carried out with a similarly-shaped anode fashioned from a porous carbon block (Stackpole Grade 139) which had a pore volume of 0.2 cm.^{3}/g. with the pore diameters ranging from 0.1 to 10 microns. The anode had an outer surface area of 30 cm.^{2}.

At a temperature of 212° F., a current density of 83 ma./cm.^{2}, and at a terminal voltage of 1.5 volts, a stream of n-dodecane was admitted through the anode at a feed rate of 5.3 millimoles of hydrocarbon/cm.^{2}/hr. which amounted to 0.59 Faraday per gram mole of n-dodecane feed. The hydrocarbon effluent from the cell was analyzed by conventional methods including gas-liquid chromatography. Conversion to halogenated hydrocarbon was 19.2 mol percent with a 7:1 ratio of monochloride products to dichloride products. The current efficiency was 73 percent.

The above Examples I and II illustrate the electrochemical halogenation step of the invention.

Example III

A hollow, porous carbon anode of 2.4 cm. outside diameter and 2.5 cm. long (prepared from the Stackpole Grade 139 Carbon of Example II) was modified by filling its hollow interior with an impregnated commercial carbon black (Shawinigan) upon which there was deposited a mixture of platinum and rhodium in an amount of about three weight percent. The carbon black had been impregnated with an aqueous solution of chloroplatinic acid and rhodium chloride having a concentration such that there was about a 10:1 ratio of platinum metal to rhodium metal. The impregnated carbon black and anode were heat treated at 1800° F. in air before use. The anode had an outer surface area of 19 cm.^{2}.

Said anode was employed in an apparatus essentially the same as that described above in Example I to carry out another run using an HCl electrolyte containing about 20 weight percent CHl. Current was applied to the cell and at a temperature of 190 to 200° F., a current density of 15.8 milliamperes per square centimeter of anode area (300 ma. total), and at a terminal voltage of 1.5 to 1.6 volts, a stream of n-dodecane was introduced to the cell through said anode at a feed rate of 0.69 millimole per cm.^{2} per hour which amounted to 0.85 Faraday per gram mol of n-dodecane feed. The gaseous and liquid products in the cell effluent were collected and analyzed. Analysis of the hydrocarbon phase showed an 18.1 mol percent conversion to chlorinated C_{12} hydrocarbons and said chlorinated hydrocarbon products had a distribution of 13.5, 53.4, and 33.1 mol percent for primary monochlorides, secondary monochlorides, and dichlorides, respectively. The current or electrical efficiency to chlorinated products was 57 percent.

The above Example III illustrates the operation of the new electrode of the invention when employed as an anode.

Example IV

Employing an apparatus and electrolyte essentially the same as that of Example I, another run was carried out

with a similarly shaped anode fashioned from a porous carbon block using the Stackpole Grade 139 Carbon of Example II. Said anode had an outer surface area of 29 cm.^{2}.

Current was applied to the cell and at a temperature of 190 to 200° F., a current density of 17.2 milliamperes per cm.^{2} of anode area (500 ma. total), and at a terminal voltage of 1.5 to 1.6 volts, a stream of n-dodecane saturated with benzoyl peroxide (approximately 0.1 weight percent) was introduced to the cell through said porous anode at a feed rate of 0.91 millimole per cm.^{2} per hour which amounted to 0.70 Faraday per gram mol of n-dodecane feed. The gaseous and liquid products in the cell effluent were collected and analyzed. Analysis of the hydrocarbon phase showed an 11.6 mol percent conversion to chlorinated C_{12} hydrocarbons and said chlorinated hydrocarbons had a distribution of 9.8, 74.8, and 15.4 mol percent for primary monochlorides, secondary monochlorides and dichlorides, respectively. The current or electrical efficiency to chlorinated products was 38 percent.

Example V

Another run was carried out employing the apparatus and electrolyte of Example IV with the same hydrocarbon feed rates and the same current conditons, the only difference being that the n-dodecane hydrocarbon feed was saturated with iodine instead of benzoyl peroxide.

Analysis of the hydrocarbon phase from the cell effluent showed an 8.8 mol percent conversion to C_{12} chlorinated hydrocarbons and said chlorinated hydrocarbons had a distribution of 8.7, 76.5, and 14.8 mol percent for primary monochlorides, secondary monochlorides, and dichlorides, respectively. The current or electrical efficiency to chlorinated products was 29 percent.

Example VI

Another run was carried out employing the apparatus and electrolyte of Example IV with the same hydrocarbon feed rates and the same current conditions, the only difference being that no promoter was present in the n-dodecane hydrocarbon feed.

Analysis of the hydrocarbon phase from the cell effluent showed a 7.2 mol percent conversion to chlorinated C_{12} hydrocarbons and said chlorinated hydrocarbons had a distribution of 6.0, 74.6, and 19.4 mol percent for primary monochlorides, secondary monochlorides and dichlorides, respectively. The current or electrical efficiency to chlorinated products was 25 percent.

Comparison of the above Examples IV, V, and VI illustrates the advantages of carrying out the electrochemical halogenation step of the invention in the presence of a promoter therefor, and the particular effectiveness of the free radical initiators as promoters.

Example VII

The hydrocarbon effluent stream from Example II above, containing the chlorinated dodecanes and unconverted dodecanes, is passed to an agitated alkylation reactor vessel where it is contacted with 20 moles of benzene for each mole of dodecyl chloride in the presence of one volume of catalyst (a complex of $AlCl_3$ and hydrocarbon material containing about 40–60 weight percent $AlCl_3$) for each volume of the hydrocarbon feed. Said catalyst contains about 4 weight percent of HCl as promoter. After a 15-minute residence time at 70° F. and 50 p.s.i.g. the mixture is passed to a settler vessel and allowed to settle, the catalyst complex is withdrawn from the bottom of the settler and the hydrocarbon phase is subjected to stripping whereby the by-product HCl liberated by the alkylation of said benzene with said dodecyl chloride is removed. Said by-product HCl is combined with the lean acid stream separated from the chlorination cell effluent and the now fortified acid is then recycled to said cell. The now acid-free hydrocarbon phase is fractionated. The unreacted benzene is recovered and recycled to the alkylation vessel, the unconverted dodecane is recycled to said electrolytic cell, and the light alkylate is separated from the heavy alkylate by-product and recovered. The yield of light akylate product (dodecylbenzene) is 92.0 weight percent based on the weight of the alkyl chloride. The yield of heavy alkylate is 10.3 weight percent.

The above Example VII illustrates the real and effective co-operation which is obtained by the recycle of the by-product HCl from the alkylation step of the invention to the chlorination step of the invention. Since for each mol of chlorine which is added to the hydrocarbon in the chlorination step to produce alkyl chloride, there is liberated one mol of hydrogen chloride in the alkylation step when said alkyl chloride reacts with the benzene, and since said liberated hydrogen chloride is recycled to and utilized in said chlorination step to supply chlorine, the integrated process of the invention operates essentially completely on captive chlorine. It is only necessary to add sufficient chlorine values to make up the mechanical and entrainment losses.

While certain embodiments of the invention have been described for illustrative purposes, the invention obviously is not limited thereto. Various other modifications will be apparent to those skilled in the art in view of this disclosure. Such modifications are within the spirit and scope of the invention.

We claim:

1. A process for the production of an alkylate, which process comprises: reacting a hydrocarbon with a halogen evolved at the active surface of an anode in an electrolytic cell during electrolysis of a halide containing electrolyte to form a halogenated hydrocarbon; alkylating an alkylatable hydrocarbon with said halogenated hydrocarbon in an alkylation zone in the presence of an alkylation catalyst under alkylation conditions to form an alkylate stream containing liberated hydrogen halide and alkylated hydrocarbon; recovering said alkylated hydrocarbon from said alkylate stream as said alkylate; recovering said hydrogen halide from said alkylate stream; and recycling said recovered hydrogen halide to said electrolytic cell.

2. A process for the production of an alkylate, which process comprises: reacting a saturated hydrocarbon containing from 2 to 20 carbon atoms per molecule with an evolved halogen selected from the group consisting of chlorine, bromine, and fluorine at the active surface of the anode in an electrolytic cell during electrolysis of a halide containing electrolyte capable of liberating said halogen to form a halogenated hydrocarbon; alkylating an alkylatable hydrocarbon with said halogenated hydrocarbon in an alkylation zone in the presence of an alkylation catalyst under alkylation conditions to form an alkylate stream containing liberated hydrogen halide and alkylated hydrocarbon; recovering said alkylated hydrocarbon from said alkylate stream as said alkylate; recovering said hydrogen halide from said alkylate stream; and recycling said recovered hydrogen halide to said electrolytic cell.

3. A process for the production of an alkylate, which process comprises: contacting a saturated hydrocarbon containing from 2 to 20 carbon atoms per molecule with an evolved halogen selected from the group consisting of chlorine, bromine, and fluorine in the region of its evolution at the anode of an electroyltic cell during electrolysis of a halide containing electrolyte capable of liberating said halogen to form a halogenated hydrocarbon; alkylating an alkylatable hydrocarbon with said halogenated hydrocarbon in an alkylation zone in the presence of an alkylation catalyst under alkylation conditions to form an alkylate stream containing liberated hydrogen halide and alkylated hydrocarbon; recovering said alkylated hydrocarbon from said alkylate stream as said alkylate; recovering said hydrogen halide from said alkyl-

ate stream; and recycling said recovered hydrogen halide to said electrolytic cell.

4. The process of claim 3 wherein said halogen is chlorine and said liberated hydrogen halide is hydrogen chloride.

5. A process for the production of an alkylate, which process comprises: subjecting a halide containing electrolyte to electrolysis in an electrolytic cell whereby a halogen selected from the group consisting of chlorine, bromine, and fluorine is liberated at the anode of said cell; introducing a saturated hydrocarbon containing from 2 to 20 carbon atoms per molecule into said cell as a thin film on the active surface of said anode whereby said halogen and said hydrocarbon react during said electrolysis to form halogenated hydrocarbon, said hydrocarbon having dispersed therein a small but effective amount of a promoter for the formation of said halogenated hydrocarbons; separating a hydrocarbon phase containing said halogenated hydrocarbon from said electrolyte and passing same to an alkylation zone; introducing an alkylatable hydrocarbon into said alkylation zone; alkylating said alkylatable hydrocarbon with said halogenated hydrocarbon in said alkylation zone in the presence of an alkylation catalyst under alkylation conditions to form an alkylate stream containing liberated hydrogen halide and alkylated hydrocarbon; recovering said alkylated hydrocarbon from said alkylate stream as said alkylate; recovering said hydrogen halide from said alkylate stream; and recycling said recovered hydrogen halide to said electrolytic cell.

6. The process of claim 5 wherein said halogen is chlorine, said electrolyte is an aqueous solution of hydrogen chloride, and said liberated hydrogen halide is hydrogen chloride.

7. The process of claim 5 wherein said promoter is a free radical initiator.

8. A process for the production of an alkylate, which process comprises, in combination, the steps: subjecting an aqueous hydrogen chloride electrolyte to electrolysis in an electrolytic cell to liberate chlorine at the anode of said cell; introducing a paraffin hydrocarbon having from 2 to 20 carbon atoms per molecule and having dispersed therein a small but effective amount of an organic peroxide into said cell as a thin film on the electrolytically active portion of said anode during said electrolysis whereby said hydrocarbon reacts with said liberated chlorine to form chlorinated hydrocarbons, said peroxide being effective as a promoter for the formation of said chlorinated hydrocarbons; separating a hydrocarbon phase containing said halogenated hydrocarbon from said electrolyte; passing said separated hydrocarbon phase to an alkylation zone; introducing an alkylatable hydrocarbon into said alkylation zone; alkylating said alkylatable hydrocarbon with said chlorinated hydrocarbon in said alkylation zone in the presence of an alkylation catalyst under alkylation conditions to form an alkylate stream containing alkylated hydrocarbon and liberated hydrogen chloride; separating said hydrogen chloride from said alkylate stream; returning said separated hydrogen chloride to said electroyltic cell; and separating said alkylated hydrocarbon from said alkylate stream as said alkylate.

9. The process of claim 8 wherein said organic peroxide is benzoyl peroxide.

10. A process for the production of a detergent grade alkylate, which process comprises, in combination, the steps of: subjecting a halide containing electrolyte to electrolysis in an electrolytic cell whereby a halogen selected from the group consisting of chlorine, bromine, and fluorine is evolved at the anode of said cell; introducing a paraffin hydrocarbon having from 10 to 15 carbon atoms per molecule into said cell as a thin film on the electrolytically active surface of said anode during said electrolysis whereby said hydrocarbon reacts with said halogen to form a halogenated hydrocarbon; alkylating an aromatic hydrocarbon with said halogenated hydrocarbon in an alkylation zone in the presence of an alkylation catalyst under alkylation conditions to produce an alkylaromatic containing alkylate and hydrogen halide; fractionating said alkylate to recover said alkylaromatic as said detergent grade alkylate; and recycling said hydrogen halide to electrolytic cell.

11. A process for the production of a detergent grade alkylate, which process comprises, in combination, the steps of: subjecting an aqueous hydrogen chloride electrolyte to electrolysis in an electrolytic cell to liberate chlorine at the anode of said cell; introducing a mixture of paraffin hydrocarbons having from 10 to 15 carbon atoms per molecule into said cell as a thin film on the electrolytically active portion of said anode during said electrolysis whereby said hydrocarbons react with said liberated chlorine to form chlorinated hydrocarbons; removing a hydrocarbon phase containing said chlorinated hydrocarbons from said cell; introducing said hydrocarbon phase into an alkylation zone; introducing alkylatable aromatic hydrocarbon into said alkylation zone; alkylating said aromatic hydrocarbon with said chlorinated hydrocarbons in said alkylation zone in the presence of an alkylation catalyst under alkylation conditions to form an alkylate stream containing liberated hydrogen chloride; fractionating said alkylate stream into non-alkylated aromatic hydrocarbon, non-chlorinated paraffin hydrocarbons, light alkylate, heavy alkylate, and hydrogen chloride streams; recycling said hydrogen chloride stream to said electrolytic cell; recycling said non-alkylated aromatic hydrocarbon to said alkylation zone; and recovering said light alkylate stream as said detergent grade alkylate.

12. The process of claim 11 wherein said aromatic hydrocarbon is benzene.

13. A process for the halogenation of a hydrocarbon, which process comprises: reacting said hydrocarbon with a halogen evolved at the active surface of an anode in an electrolytic cell during electrolysis of a halide containing electrolyte in the presence of a promoter for said reaction; and recovering halogenated hydrocarbon from an effluent from said cell.

14. A process for the halogenation of a hydrocarbon, which process comprises: subjecting an aqueous hydrogen chloride electrolyte to electrolysis in an electrolytic cell to liberate chlorine at the anode of said cell; introducing a saturated hydrocarbon having from 2 to 20 carbon atoms per molecule and having dispersed therein a small but effective amount of an organic peroxide into said cell as a thin film on the electrolytically active portion of said anode during said electrolysis whereby said hydrocarbon reacts with said liberated chlorine to form a chlorinated hydrocarbon, said peroxide being effective as a promoter for the formation of said chlorinated hydrocarbon; separating a hydrocarbon phase containing said chlorinated hydrocarbon and also non-chlorinated hydrocarbon from said electrolyte; and recovering said chlorinated hydrocarbon from said hydrocarbon phase.

15. A process according to claim 14 wherein said organic peroxide is benzoyl peroxide.

16. Apparatus for the production of an alkylate, comprising, in combination: an electrolytic cell provided with an anode and a cathode; means for connecting said anode and said cathode to a source of electrical current; conduit means for introducing an electrolyte into said cell; conduit means for introducing a hydrocarbon to be halogenated into said cell as a thin film onto the active surface of said anode; alkylation means for alkylating an alkylatable hydrocarbon with an alkylating agent; conduit means for passing a hydrocarbon phase comprising halogenated hydrocarbon and non-halogenated hydrocarbon from said cell to said alkylation means; a fractionation means; conduit means for passing an alkylate stream from said alkylation means to said fractionation means; conduit

means for passing hydrogen halide from said fractionation means to said electrolytic cell; and conduit means for passing non-halogenated hydrocarbon from said fractionation means to said electrolytic cell.

17. A process according to claim **13** wherein said promoter is a free radical initiator.

18. A process according to claim **17** wherein said promoter is benzoyl peroxide.

19. A process according to claim **13** wherein said promoter is iodine.

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DELBERT E. GANTZ, *Primary Examiner.*

C. R. DAVIS, *Assistant Examiner.*