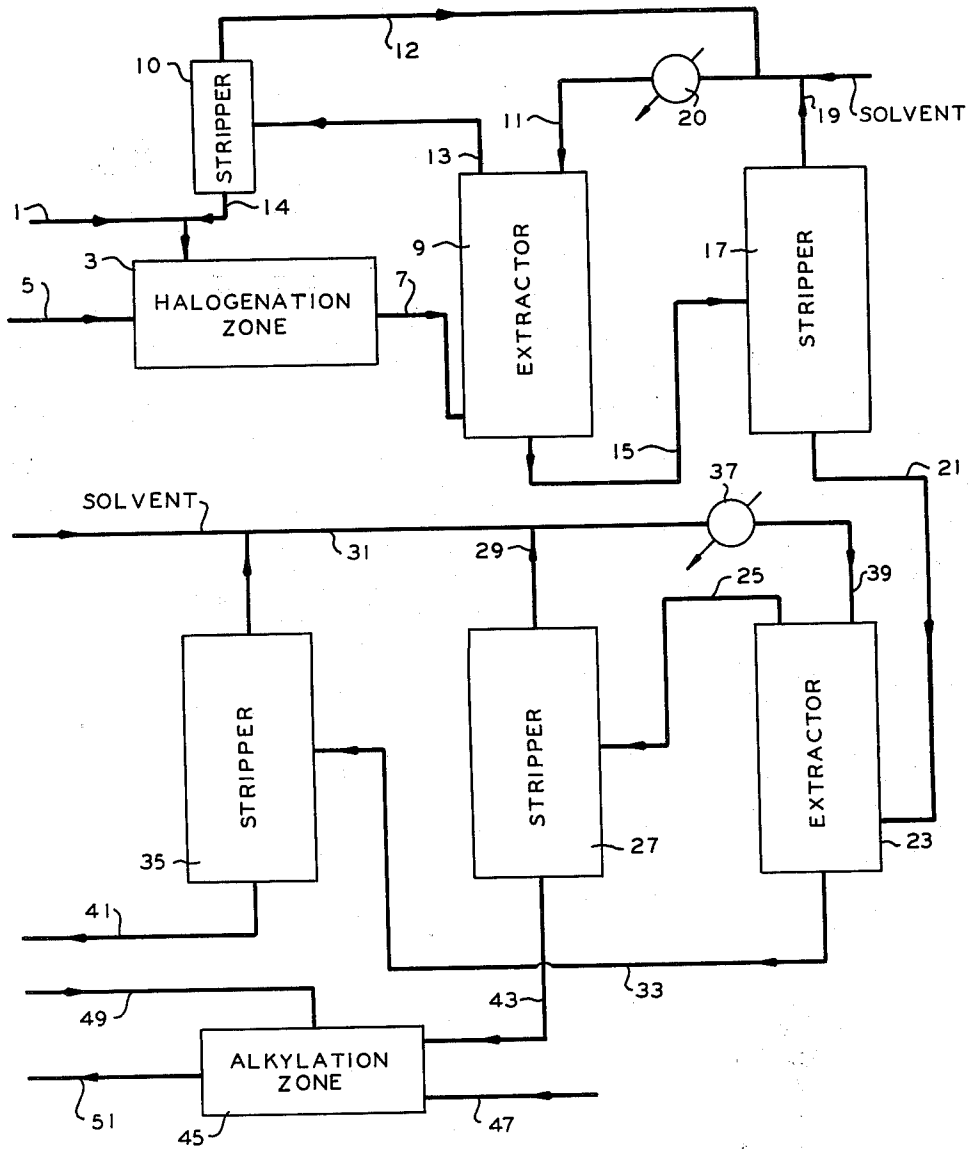
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SOLVENT EXTRACTION OF HALO-PARAFFINS FROM PARAFFINS

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SOLVENT EXTRACTION OF HALO-PARAFFINS FROM PARAFFINS

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This invention relates to solvent extraction separations. In another aspect this invention relates to an integrated process for the production of detergent alkylates.

Various chemical processes are being practiced in which halogenated paraffins are used as solvents and employed as intermediates in processes such as alkylation and hydrolysis. The paraffins are halogenated by various known methods. Several of the processes using halogenated paraffins operate more efficiently if the halogenated paraffins are separated from the paraffinic hydrocarbons prior to their use. Likewise, separation of mono- and polyhalogenated hydrocarbons improves the efficiencies of processes which require the use of one or the other. One such process is the production of detergent alkylate wherein an aromatic such as benzene is alkylated with monochloroalkanes. In this particular process it has been found that polychlorides cause formation of heavy by-products which rapidly reduce the life of the $AlCl_3$ alkylation catalyst. Cyclic hydrocarbons are also produced from the polychlorides, and these undesired products codistill with the desired alkylate. Because of the adverse effects of the polychloroalkanes in this process, the n-paraffins are chlorinated at low conversion levels to reduce the formation of polychloroalkanes. Because of the chlorination of paraffins at low conversion levels, if the chlorides are not separated from the paraffins prior to the alkylation step, the problem of recycling large amounts of unchlorinated paraffins is present. It is extremely difficult and expensive to separate mixtures of halogenated paraffins from paraffins when their boiling points do not differ greatly. Mixtures of this type are frequently obtained when a paraffin feed stock containing molecules of consecutive carbon numbers and differing by a spread of more than 2 carbon atoms, for example, a mixture of C_{12}, C_{13}, C_{14} and C_{15} paraffins, is subjected to halogenation.

Accordingly, an object of this invention is to provide a method for the separation of halogenated paraffins from mixtures with paraffinic hydrocarbons.

Another object of this invention is to provide a method for the separation of monohalogenated paraffins from polyhalogenated paraffins. Still another object of this invention is to provide an improved integrated halogenation-separation-alkylation process for the production of detergent grade alkylate.

According to this invention an improved process is provided for the concentration of halogenated paraffins which comprises extracting halogenated paraffins from mixtures with paraffinic hydrocarbons with liquid SO_2 and removing the liquid SO_2 from the resulting extract.

In a specific embodiment of this invention an improved integrated process is provided which comprises halogenating paraffinic hydrocarbons, solvent-extracting the resultant halogenated paraffins, and alkylating an aromatic, such as benzene, with the recovered halogenated paraffins.

The solvent extraction process of this invention is applicable for the separation of halogenated paraffins from paraffinic hydrocarbons. It is also applicable to the separation of halogenated paraffins, e.g., the separation of monohalogenated paraffins from polyhalogenated paraffins. This invention is most applicable to the separation of halogenated paraffins containing 8 to 20 carbon atoms per molecule from paraffins of the same range of carbon

atoms and more preferably of a range of 10 to 16 carbon atoms per molecule. The preferred paraffins to be halogenated are obtained by separating them from a paraffin-containing stream such as kerosene. This separation is made at a temperature of about 600° F. by adsorption of the desired paraffins on 5A molecular sieves, which are well known in the art, using vapor phase adsorption and vapor phase desorption. Elution or desorption can be effected by a variety of methods, as, for example, by decreasing the pressure above the sieve bed containing the adsorbed paraffins. The paraffins are halogenated by contacting them with a halogen, preferably chlorine or bromine, for about 5 to 30 minutes, preferably in the presence of ultraviolet light at a temperature of from about −20 to +40° C., a mol ratio of paraffin/halogen of from 3:1 to 10:1, a pressure up to about 500 p.s.i.a. The extraction process for separating the halogenated paraffins is generally carried out at a temperature of from about −25 to about 50° C., preferably from about −15 to about 25° C. The volume ratio of liquid SO_2 to paraffin-halogenated paraffin mixture is generally in the range of about 0.5:1 to 5:1. The extraction of the halogenated paraffin with the liquid SO_2 may be carried out batchwise or continuously and also in a single stage or a multistage operation. The contacting of the feed mixture with the liquid SO_2 is carried out by various means such as in vessels equipped with stirrers, perforated trays, or other well-known means for effecting contacting of the feed with the solvent. Following the contacting of the mixture with liquid SO_2, the paraffins and some SO_2 are separated as the raffinate phase, and the halogenated paraffins are removed with the remainder of the liquid SO_2 as the extract phase. The raffinate can be recycled to the halogenation zone after removal of the SO_2. The extract phase, which contains most of the liquid SO_2, the halogenated paraffins and some paraffinic hydrocarbons, is processed for removal of SO_2, after which the extracted material from this first extraction can be further treated with additional liquid SO_2 to effect separation of the polyhalogenated paraffins and the monohalogenated paraffins. The SO_2 is separated from the halogenated hydrocarbons by distillation or by treating the extract with water to dissolve the SO_2, thereafter separating a halogenated hydrocarbon phase from an aqueous phase. The SO_2 can be recovered from the water and recycled to the extraction step. Preferably, anhydrous liquid SO_2 is used as the extractant in this invention. However, liquid SO_2 containing not more than about 2 percent water may be used.

A particular utility for the concentrated, halogenated paraffins produced by this invention is in the alkylation of suitable aromatics, such as benzene, toluene, xylene, naphthalene, biphenyl, phenanthrene, anthracene, pyrene, chrysene, ethylbenzene, and the like. In the alkylation of benzene for use as a detergent alkylate, the chloro- and bromo-alkanes are preferred.

The catalyst employed in the alkylation process can be any suitable alkylation catalyst, that is, 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 a halide of such metals as zinc, tin, arsenic, antimony, zirconium, beryllium, titanium, iron, and the like. These metal halide catalysts are especially effective when used in the form of complexes which are formed by interaction between the metal halide and hydrocarbons. A particularly desirable catalyst is a complex of hydrocarbon with aluminum chloride. An aluminum chloride-hydrocarbon complex catalyst can be prepared, for example, by reacting $AlCl_3$ with isobutane or other branched chain paraffins in the presence of an olefin such as ethylene. Such complexes normally contain about 55–65 percent by weight

$AlCl_3$, the remainder being hydrocarbon. 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 in the conversion of the hydrocarbon feed is dependent on the amount of aluminum chloride in the aluminum chloride hydrocarbon complex. While the over-all activity of the catalyst is established by the aluminum chloride content, the presence of hydrogen chloride is required to maintain a high activity. While hydrogen chloride can be added, if desired, the hydrogen chloride produced by the alkylation process itself will generally be sufficient to maintain high catalyst activity.

Conditions employed in an alkylation process will depend somewhat upon the catalyst employed. When employing aluminum chloride hydrocarbon complex catalysts the alkylation will generally be carried out at a temperature within the range of 50 to 135° F. with a pressure sufficient to maintain liquid phase conditions. Flow rates of reactants should be maintained such that the residence time is 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 hydrocarbons to halogenated hydrocarbons entering the alkylation process should be such as to furnish at least one mol of aromatic hydrocarbon per gram atom of halogen on the halogenated hydrocarbon. It is preferred to operate with an excess of aromatic hydrocarbons. 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 25:1. The volume ratio of catalyst used to total halogenated paraffin in the process should be in the range of about 0.5:1 to 10:1, preferably about 2:1.

This invention will now be described more fully with reference to the accompanying drawing which shows a schematic flow diagram and apparatus representative of one embodiment of the invention.

A paraffin stream from a molecular sieve separation (not shown) is introduced into halogenation zone **3** through conduit **1**. A halogen is introduced into zone **3** through conduit **5**. The reactants are thoroughly contacted in zone **3** and the resulting mixture is withdrawn through conduit **7** and introduced into extractor **9**. Solvent is introduced into extractor **9** through conduit **11**. The solvent flows downwardly countercurrent to the paraffin-halogenated paraffin mixture to remove the halogenated paraffins. Raffinate phase is removed and passed to stripper **10** through conduit **13**. In stripper **10** heat is added by means not shown to vaporize the SO_2 from the raffinate, and the vaporized solvent is recycled to the extraction zone through conduit **12**, cooler **20**, and conduit **11**. The bottoms from stripper **10** are recycled to zone **3** through conduit **14** and conduit **1**. Extract phase is removed through conduit **15** and introduced into stripper **17**. Heat is added to stripper **17** by means not shown to vaporize the solvent which is removed through conduit **19**, passed through cooler **20** and recycled to extractor **9**. Make-up solvent is introduced to conduit **19** ahead of cooler **20**. The kettle product from stripper **17** is passed through conduit **21** into extractor **23**. Solvent is introduced to extractor **23** through conduit **39**. The solvent flows downwardly countercurrent to the kettle product from stripper **17**, to remove the polyhalogenated paraffins. Raffinate phase is removed through conduit **25** and introduced into monohalogenated paraffins stripper **27**. Heat is added to stripper **27** by means not shown to vaporize solvent which is removed through conduit **29** and introduced into conduit **31**. The kettle product from stripper **27** is passed through conduit **43** into alkylation zone **45**. The extract phase from exterior **23** is passed through conduit **33** and introduced into polyhalogenated paraffin stripper **35**. Polyhalogenated paraffins are removed through conduit **41** as kettle product. Solvent vaporized by heat added to stripper **35** by means not shown is removed through conduit **31**. Make-up solvent is added to conduit **31**. The combined solvent in conduit **31** is passed through cooler **37**, conduit **39** and introduced into extractor **23**. Alkylation catalyst is introduced to zone **45** through conduit **47**. An aromatic hydrocarbon is introduced to zone **45** through conduit **49**. Reaction mixture is removed from zone **45** through conduit **51**. This mixture is passed to a recovery system (not shown) for separation of the alkylate, catalyst, unreacted aromatic and halogenated paraffins.

The following specific examples will give a better understanding of the invention but are not intended to limit the invention.

EXAMPLE I

A 50 ml. mixture of chlorinated dodecane and dodecane was charged to a vessel along with 100 ml. of liquid SO_2. The vessel was equipped with a stirrer. After the components were charged to the vessel, the stirrer was turned on, the two phases were mixed together for 45 minutes, at a temperature of −12° C. The dodecane-chlorinated dodecane mixture contained 83.1 mol percent dodecane, 15.1 mol percent chlorododecane and 1.8 mol percent dichlorododecane.

The two phases were then allowed to separate and the phases were drawn off. The SO_2 was flashed from the extract and raffinate phases, and then both phases were analyzed by gas-liquid chromatography. The chromatography column used was a 10-foot column containing 70 mesh glass beads coated with 0.25 weight percent, based on the beads, n-decylphthalate. The column was operated at 130° C. This column separated the primary and secondary monochlorides, as well as the paraffin and dichloroparaffin.

Results

	Grams
Weight of extract phase	[1] 2.5
Weight of raffinate phase	[2] 34.9
Weight of SO_2 in extract phase	143

[1] (SO free).
[2] (SO_2 free).

Analyses of phases

Raffinate phase:

	Moles
28.5 grams dodecane	0.1672
5.5 grams sec-chlorododecane	0.0269
0.56 gram primary chlorododecane	0.0027
0.35 gram dichlorododecane	0.0014
6.41 grams total chlorides	0.0310

Extract layer:

1.02 grams dodecane	0.0060
1.0 gram sec-chlorododecane	0.0051
0.11 gram primary chlorododecane	0.0005
0.31 gram dichlorododecane	0.0013
1.42 grams total chlorides	0.0068

The above analyses were then used to calculate the relative distribution coefficients and the weight percent solvent load.

The weight percent solvent load is defined as:

$$\text{Weight percent solvent load} = \frac{(\text{Weight of material extracted})\ (100)}{(\text{Weight of solvent phase including material extracted})}$$

The relative distribution coefficients are defined as:

$$\text{Relative distribution coefficient} = \frac{(Aex)(Braf)}{(Araf)(Bex)}$$

where

Aex=moles cholride in extract
Araf=moles chloride in raffinate
Bex=moles reference material in extract
Braf=moles reference material in raffinate

Sample calculation:

Relative distribution coefficient for chlorides relative to dodecane

$$=\frac{(0.0069)(0.1672)}{(0.0310)(0.0060)}=6.2$$

$$\text{Weight percent solvent load}=\frac{(2.5)(100)}{143+2.5}=1.7$$

Calculated Distribution coefficients

Relative to dodecane:

Total chlorides	6.2
Chlorododecane	5.3
Dichlorododecane	25.9
Dichlorododecane relative to chlorododecane	4.9

From these data it is readily apparent that the chlorides have been concentrated in the extract phase of the extraction step.

EXAMPLE II

To prepare a detergent alkylate according to the method of this invention, 140 mols of a paraffin stream containing paraffins of from 10 to 16 carbon atoms per molecule is contacted with 28 mols of chlorine at a temperature of 10° C. and a pressure of 250 p.s.i.a. in the presence of ultraviolet light for about 10 minutes. Approximately 20 mol percent of the resultant mixture comprises monochlorinated paraffins and polychlorinated paraffins while the remainder of the paraffins are not chlorinated. This mixture of chlorinated paraffins and paraffinic hydrocarbons is then contacted with liquid SO_2 in a multitray extraction column at a temperature of −10° C. in a volume ratio of liquid SO_2 to the mixture of 2:1. The phases are separated and the extract phase is heated to vaporize the liquid SO_2. The stripped extract is then contacted with additional liquid SO_2 at −10° C. and a volume ratio of liquid SO_2 to extract of 1:1 in a multitray extraction column. The raffinate from this extraction is heated to vaporize residual liquid SO_2 and recovery of monochlorinated paraffins. These monochlorinated paraffins are then contacted with benzene and aluminum chloride complex catalyst at a temperature of 70° F. and a pressure of 70 p.s.i.a. for 15 minutes, using 20 mols of benzene per mol of monochlorinated paraffin and two volumes of total feed per volume of aluminum chloride complex catalyst. The alkylation product is separated from the catalyst and the unreacted reactants are removed by distillation to recover a high purity monoalkylated benzene.

In a similar run wherein the chlorination zone effluent is charged directly to the alkylation step, much shorter catalyst life of the alkylation catalyst is encountered and larger amounts of heavy alkylate are produced.

Along with the advantages shown from the above data and specific embodiment, the extraction process of this invention provides a ready means for separating halogenated paraffins from paraffinic hydrocarbons, thus allowing one to recycle the paraffins to a halogenation zone which, when operating at low conversion for ultimate production of monohalides, a large amount of paraffins travels through the process. Furthermore, if monohalogenated paraffins are to be employed in an alkylation reaction, this process can be utilized for the separation of the monohalides from the polyhalides to obtain longer catalyst life and avoid heavy alkylate by-products. Also, in the alkylation process, the removal of paraffins prior to the alkylation avoids the problem of recycling large amounts of inert material through the alkylation zone.

To one skilled in the art it will be evident that many variations and modifications of this invention can be practiced in view of the foregoing disclosure that will come within the spirit and scope of the invention.

That which is claimed is:

1. A process for separating a mixture of compounds having 8 to 20 carbon atoms per molecule comprising paraffins, mono-halo-paraffins, and poly-halo-paraffins, said halo- being selected from chloro- and bromo-, which comprises:

contacting said mixture with liquid SO_2 at a temperature between −25 and 50° C. with a volume ratio of liquid SO_2 to mixture of from 0.5:1 to 5:1 to form an extract phase rich in SO_2 and said halo-paraffins and a raffinate phase rich in said paraffins;

separating said phases;

contacting said halo-paraffins in said extract phase with liquid SO_2 at a temperature between −25 and 50° C. with a volume ratio of SO_2 to halo-paraffins of from 0.5:1 to 5:1 to form a raffinate phase rich in mono-halo paraffins and an extract phase rich in poly-halo paraffins;

separating said phase rich in mono-halo-paraffins from said phase rich in poly-halo-paraffins; and

recovering said paraffin, said mono-halo paraffin, and said poly-halo-paraffins from their respective phases.

2. The process of claim **1** wherein said compounds have 10 carbon atoms per molecule and said halo- is chloro-.

3. A process for separating a mixture of compounds having 8 to 20 carbon atoms per molecule comprising paraffins and halo-paraffins, said halo- being selected from the group consisting of chloro- and bromo-, which comprises: contacting said mixture with liquid SO_2 at a temperature between −25 and 50° C. with a volume ratio of liquid SO_2 to mixture of from 0.5:1 to 5:1 to form an extract phase rich in said halo-paraffins and liquid SO_2 and a raffinate phase rich in said paraffins; and separating the SO_2 from said extract phase.

4. The process for separating a mixture of compounds having 8 to 20 carbon atoms per molecule comprising monohalo-paraffins and polyhalo-paraffins, said halo- being selected from the group consisting of chloro- and bromo-, which comprises: contacting said mixture with liquid SO_2 at a temperature between −25 and 50° C. with a volume ratio of liquid SO_2 to mixture of from 0.5:1 to 5:1 to form an extract phase rich in said polyhalo-paraffins and liquid SO_2 and a raffinate phase rich in said monohalo-paraffins; and separating the SO_2 from said extract phase.

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