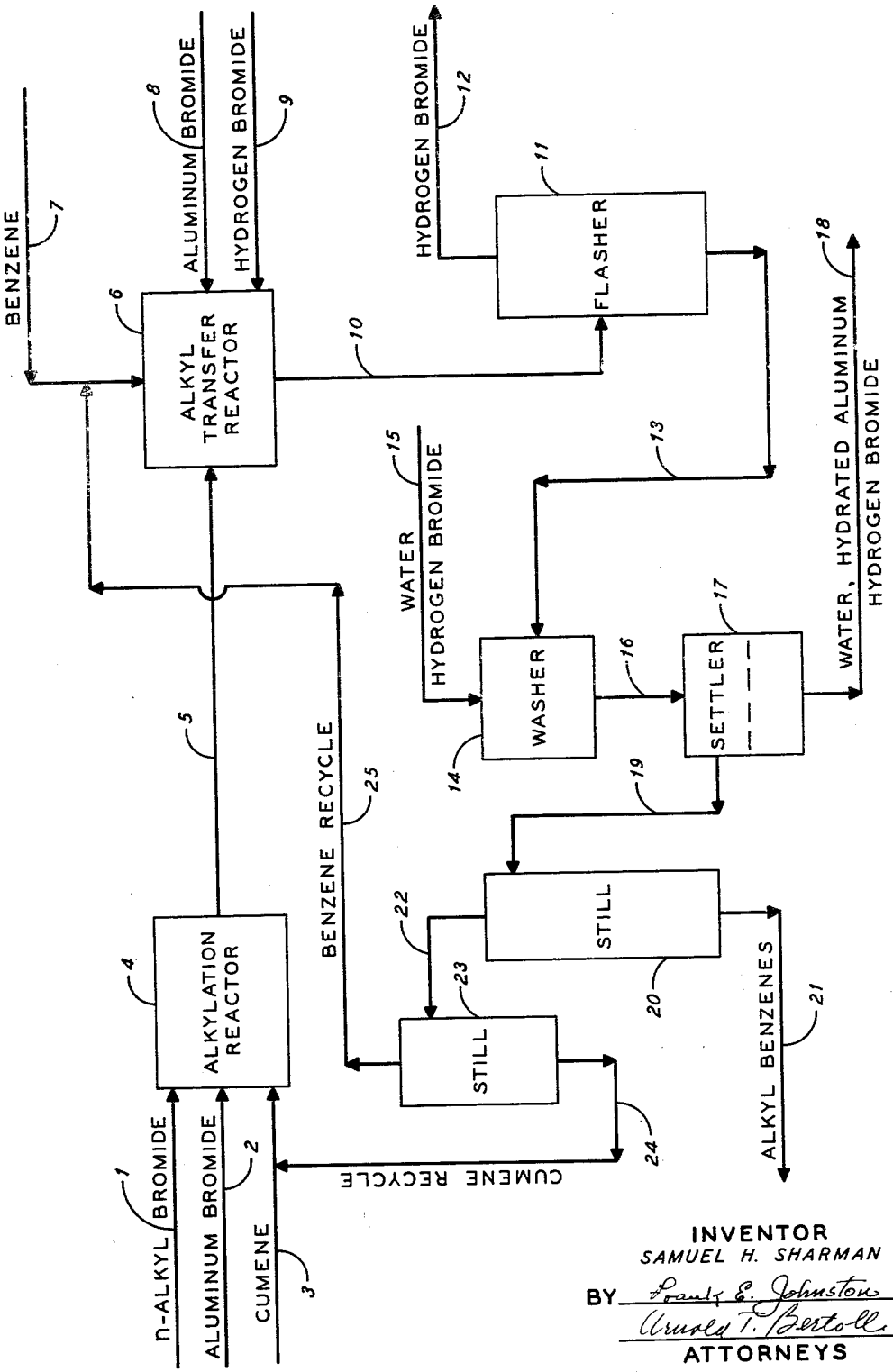
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PREPARATION OF PRIMARY NORMAL ALKYL BENZENES

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PREPARATION OF PRIMARY NORMAL ALKYL BENZENES

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The present invention relates to a process for producing monoalkyl benzenes having 8 to 20 carbon atoms in the alkyl groups, and more particularly to a mixture of alkyl benzenes having 8 to 20 carbon atoms in the alkyl groups, the alkyl groups being of normal or straight-chain structure and joined to benzene nucleus predominantly in primary position.

Alkyl benzenes having 8 to 20 carbon atoms in the alkyl groups have long been known. Their use as intermediates in the manufacture of surface-active agents by sulfonation for the preparation of synthetic detergents has been widespread. Of these alkyl benzenes the most outstanding and successful type has been the polypropylene benzenes, the sulfonates of which form the bulk of the synthetic detergents now commercially available. These are prepared by the alklation of benzene, usually with hydrogen fluoride catalyst, as shown for example in U.S. Patent No. 2,477,382, followed by sulfonation, for example as shown in U.S. Patent No. 2,477,383. The polypropylene alkyl groups in the alkyl benzenes as thus prepared are of branched chain structure and are attached, for the most part, to the benzene nucleus through a secondary or tertiary carbon atom, i.e., one whose valence is satisfied by 4 or 3 other carbon atoms and with none or but one hydrogen atom.

While the polypropylene benzene sulfonates have enjoyed wide commercial success, and still form the bulk of synthetic detergents on the market, they are alleged to possess a serious disadvantage.

Polypropylene sulfonates after use are asserted to resist breakdown or degradation, as by bacterial attack, into innocuous products. Remaining unchanged, they interfere with sewage treating processes, for example, by causing undesired foaming, and pollute water supplies. In other words, detergents produced from polypropylene benzenes are biologically hard materials, e.g., they resist the action of bacteria normally operative in similar environments in ingesting and breaking down organic material into less complex, harmless products. It is therefore desirable to be able to prepare synthetic detergents which are more amenable to decomposition, i.e., materials which are biologically soft, as a result of which they are readily broken down into harmless products.

It is also known that, as opposed to the polypropylene benzenes, certain other alkyl benzenes give rise to detergent materials which are biologically soft, i.e., are readily decomposed after use. Alkyl benzenes which are biologically soft, have the alkyl group containing 8 to 20 carbon atoms in normal or straight-chain structure. And of these, particularly useful are the straight-chain primary alkyl benzenes, in which the alkyl group is attached to the benzene nucleus through a primary carbon atom, i.e., one whose valence is satisfied by two carbon atoms and two hydrogen atoms. Primary normal alkyl benzenes of 8 to 20 carbon atoms in the alkyl groups are not only biologically soft, but also possess good foam properties, as shown for example in U.S. Patent No. 2,956,-025. Normal secondary alkyl benzene sulfonates, on the other hand, do not have the ability to improve the foam characteristics of detergent mixtures.

It is therefore an object of the present invention to

provide a process for the increased production of C_8–C_{20} normal primary alkyl benzenes.

Broadly, the invention has to do with the alkylation of cumene with a normal primary alkyl bromide of 8 to 20 carbon atoms, in the presence of an alkylating catalyst, such as aluminum bromide or aluminum chloride. The alkylated cumene is then, in the presence of benzene and additional catalyst, such as aluminum bromide, subjected to an alkyl transfer reaction, whereby unsubstituted cumene is recovered and a mixture of monoalkylated benzenes predominating in normal primary C_8–C_{20} alkyl benzene is obtained. This mixture is then isolated for use in the preparation of detergents.

More particularly, in the alkylation step the primary normal C_8–C_{20} alkyl bromide is contacted with an excess of cumene at alkylation temperatures in the range —35° C. to +10° C., preferably —15° C. to —5° C. Time of reaction can vary from minutes, for example 5 minutes, to 5 hours, depending on temperature and availability of fresh catalyst.

As stated, the cumene is employed in excess, the purpose being to minimize dialkylation. Accordingly, at least 8 moles of cumene, preferably at least 10 moles, for each mole of the alkyl bromide will be found satisfactory. There is no critical upper limit with respect to the amount of excess cumene, this limit being governed by the size of equipment and handling considerations involved in transferring large quantities of materials. As an example of an upper limit, 12 moles up to 20 moles of cumene for each mole of alkyl bromide can be cited.

The alkylation catalyst, on the other hand, can be employed in proportions of 0.1 to 1.0 mole for each mole of the alkyl bromide. The preferred catalyst is aluminum bromide (Al_2Br_6). While aluminum chloride can be employed, it is not so desirable as aluminum bromide because its use results in a mixture of halides with consequent separation problems.

It has been observed that in the alkylation step the rate of reaction slows down appreciably after a certain amount of alkyl bromide has been converted, this amount usually being of the order of around 50 mole percent. Accordingly, in order to expedite reaction, larger quantities of catalyst or longer reaction times are required, or a fresh portion of catalyst can be introduced into the reaction mixture. In some instances, this may be accomplished efficiently by transferring the first alkylation product into a secondary alkylation zone, into which the fresh catalyst and cumene can be introduced and the alkylation reaction carried forward. When thus proceeding, time of reaction can be decreased towards the lower limit of the time range, and the equipment fully utilized.

The alkylation mixture comprising n-primary alkyl cumene, secondary alkyl cumene, excess cumene and catalyst is then subjected to the alkyl transfer reaction. In conducting this reaction the alkylation mixture is contacted with excess benzene in the presence of additional aluminum bromide or aluminum chloride at a temperature in the range of 0° C. to 10° C., preferably 4° C. to 6° C.

The proportions of benzene and alkyl transfer catalyst for each mole of alkyl bromide used can range respectively from 150 to 400 moles, preferably around 200 moles, and from 0.1 to 1.0 mole, preferably about 0.2 to 0.5 mole. Here also, the amount of excess benzene is such as to minimize dialkylation of the benzene, as in the alkylation step, and to force the transfer equilibrium in the desired direction.

Although, as noted, the alkylation reaction gives rise to hydrogen bromide, it has been found that addition of hydrogen bromide during the alkyl transfer reaction, although not necessary, may be advantageous. A trace

amount up to, for example, 1 mole of hydrogen bromide per mole of alkyl bromide will be found satisfactory.

Following the alkyl transfer reaction, which may take from about ½ to 3 hours, usually around 2 hours, the mixture including n-primary alkyl benzene, secondary alkyl benzene, cumene, in some cases trace amounts of alkyl cumene, excess benzene and catalyst is ready for isolation of the desired alkyl benzene mixture. This isolation of product can be effected by employing conventional means and procedures. To illustrate, the alkyl transfer reaction mixture is treated to liberate hydrogen bromide formed during the course of the process. This can be accomplished by mere flashing, for example, in a rotary wiped film evaporator at a temperature of about 70° C. and a vacuum of 100 mm. Hg. Total contact time under these conditions is short, of the order of 1 to 2 minutes. The essentially hydrogen bromide-free mixture is then admixed with water to separate the organic matter. This can be accomplished by mixing with, for example, an equal volume of water at room temperature. The water mixture is maintained on the acid side, i.e., at a pH below 7, down to pH 1, by the addition of a suitable acid. Again, hydrogen bromide is the preferred acid to facilitate recovery of that hydrogen bromide produced by the alkylation and that introduced in the alkyl transfer step.

After the water treatment the mixture is allowed to settle, whereupon an upper organic phase and a lower aqueous inorganic phase are formed, the upper phase comprising benzene, cumene, and the desired alkyl benzenes; and the lower phase, water, hydrogen bromide, and hydrated aluminum.

The upper organic phase containing cumene, benzene, and the alkyl benzenes may also contain trace quantities of hydrogen bromide. The presence of this acid is undesirable in the distillation zone and may be easily removed by a wash with aqueous base, e.g., dilute solutions of sodium hydroxide, sodium carbonate or bicarbonate, potassium carbonate, etc. After washing and phase separation, the organic mixture is then subjected to the treating step to isolate the alkyl benzenes. This may be conveniently accomplished in a still, wherein an overhead fraction of benzene and cumene is separated from the alkyl benzenes recovered as a bottom fraction. Further, the cumene and benzene can be separated as by distillation and re-used in the process.

The following examples illustrate the preparation of the invention:

EXAMPLE 1

Fifty ml. of purified cumene was placed in a 100 ml. reaction flask fitted with a paddle stirrer and protected from atmospheric moisture with a Drierite filled drying tube. After cooling to −15° C. with a Dry Ice-acetone bath, 2.263 g. of recently distilled Al_2Br_6 (0.00425 mole) was introduced by rapid mechanical transfer. Within 1 minute a solution of 6.006 (0.0241 mole) silica-treated n-dodecylbromide in 10 ml. cumene was added, with stirring, over a period of 15 seconds. Temperature was maintained between −11° and −16° C. In 8 minutes a 5 ml. sample was removed and hydrolyzed by standard techniques for analysis by gas liquid partition chromatography. The results showed that reaction was 84% complete and that the alkyl aromatic portion of the mixture contained more than 66.5% of the various possible n-dodecyl cumene isomers (ortho-, meta-, and para-).

The remaining reaction mixture was then transferred into a stirred, freshly prepared solution of 4.626 g. Al_2Br_6 (0.00867 mole) in 65 ml. purified cumene at −15° C. Twenty-four minutes later a 20 ml. sample was withdrawn and analyzed as above. The reaction was 98% complete and yields of n-dodecyl cumenes greater than 65.9% were obtained.

Thirty-five milliliters of the remaining mixture was quickly transferred into a stirred solution of 5.796 Al_2Br_6 (0.0109 mole) in 250 ml. benzene at 6° C. Approximately 2 g. (0.025 mole) anhydrous hydrogen bromide was bubbled through the system within 1 minute. With maintenance of temperature and stirring, 20 ml. samples were withdrawn at 5, 18, 57, and 99 minutes for analysis. The progress of the transfer reaction could thus be followed. The dodecyl aromatic content of the last sample was 96.7% dodecyl benzenes and 3.3% dodecyl cumenes with the isomer distribution among alkyl benzenes being the following:

	Percent
1-phenyl dodecane	72.3
2-phenyl dodecane	9.1
3-phenyl dodecane	5.5
4,5,6-phenyl dodecanes	13.1

The unexpected high ratio of primary to secondary alkyl benzenes obtained in accordance with the invention is illustrated by the following example, in which benzene is alkylated with the same alkyl bromide under substantially the same conditions of temperature, catalyst, and catalyst concentration. In order to prevent freezing at the low temperatures called for, an equal volume of an inert low boiling saturated hydrocarbon solvent, such as petroleum ether, was added to the benzene.

EXAMPLE 2

Direct Alkylation of Benzene

Benzene, 140 ml., and petroleum ether (boiling point 30–60° C.), 140 ml., were placed in a 500 ml., three-neck flask, fitted with a mechanical stirrer, a thermometer, and an adding funnel. The reaction mixture was protected from atmospheric moisture by a drying tube filled with anhydrous calcium sulfate (Drierite). After cooling to −15° C. in a Dry Ice-acetone bath, 2.86 g. of purified Al_2Br_6 was added by rapid mechanical transfer from a weighing vial to the reaction flask. The mixture was stirred an additional 3 minutes during which time the Al_2Br_6 dissolved. A solution of 12.5 g. of freshly silica-treated n-dodecyl bromide in 35 ml. of benzene was then added drop-wise over a period of about two minutes to the stirred solution of catalyst. The alkyl bromide-benzene solution was pre-cooled to 5° C. in order to minimize local heating. The reaction temperature was maintained at about −15° C. by control of the rate of addition. The reaction was allowed to continue for 70 minutes, after which time the reaction was 98% completed. The reaction mixture was transferred to a separatory funnel. The mixture was hydrolyzed by shaking vigorously with 50 ml. of 3 N HCl. Then 25 ml. of pentane was added and the mixture again shaken. After separation of the phases the upper organic phase was washed once with 5% sodium bicarbonate, twice with water, and then dried with anhydrous calcium sulfate. The bulk of the solvent was removed by boiling, and a portion of the remaining liquid analyzed by gas-liquid partition chromatography. The product contained the following alkyl benzenes:

1-phenyl dodecane	46.5
2-phenyl dodecane	19.0
3-phenyl dodecane	11.3
4,5 and 6-phenyl dodecanes	23.2

As a further illustration of the preparation of the invention, reference is now made to the accompanying drawing wherein in block diagram flow there are shown the alkylation zone, the alkyl transfer zone, separation of the reaction mixture, and recycle of benzene and cumene, condition of reaction and proportion of reactant being of the order already given.

Referring to the drawing wherein the reaction conditions and proportions of reactants recited are merely illustrative, primary normal C_8–C_{20} alkyl bromide, one mole; aluminum bromide catalyst, 0.5 mole; and cumene, 10 moles, are introduced through lines **1**, **2**, **3**, respectively, into alkylation zone **4**. The temperature in zone **4** is maintained at approximately −5° C.

After about 2 hours, the alkylation mixture is passed through line 5 into alkyl transfer zone 6. Benzene, 160 moles, is introduced through line 7, Al_2Br_6, 0.4 mole, through line 8, and hydrobromic acid, 1 mole, through line 9. Temperature in the alkyl transfer zone is maintained at around 5° C.

Following reaction, i.e., after about one hour, the alkyl transfer reaction mixture through line 10 is introduced into flasher 11 for the removal of hydrogen bromide through line 12. Temperature in the flasher is 70° C. at a pressure of 100 mm. Hg.

The essentially hydrogen bromide-free mixture is then passed through line 13 into mixing zone 14, which may be a stirred tank reactor. Water acidified with hydrogen bromide is introduced into mixing zone 14 through line 15, in a volume amount equal to that of the alkyl transfer reaction mixture. The whole is stirred to wash the organic material, for example, for 2 minutes at room temperature.

The washed product is then passed through line 16 into settler 17, wherein the mixture is allowed to settle and form an upper organic phase and a lower aqueous inorganic phase. The aqueous phase is withdrawn from the settler 17, through line 18. The upper organic phase, comprising benzene, cumene, and the alkyl benzenes is withdrawn from the settler through line 19. As hereinabove indicated, any residual hydrogen bromide may be removed by rewashing the organic layer with a dilute aqueous base, e.g., sodium hydroxide, or sodium bicarbonate, after which it is charged to still 20. In still 20 a fraction of cumene and benzene is separated from the bottoms fraction of the desired alkyl benzenes, which latter are taken off through line 21. The fraction comprising cumene and benzene is taken through line 22 into still 23, wherein separation of benzene and cumene is effected. The benzene can be returned to the alkyl transfer zone through line 25 joining with line 7. Cumene, on the other hand, can be returned to the alkylation zone 4 by means of line 24, joining line 3.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. Process for the production of a C_8–C_{20} monoalkyl benzene mixture predominating in an alkyl benzene content in which the alkyl groups having 8 to 20 carbon atoms are of primary straight-chain structure, which comprises alkylating an excess of cumene at a temperature in the range −35° C. to 10° C. with primary straight-chain alkyl bromide of 8 to 20 carbon atoms in the presence of aluminum bromide catalyst to produce mono-

alkyl-substituted cumene, subjecting the resulting alkylate in the presence of an excess of benzene and additional aluminum bromide to a temperature in the range 0° C. to 10° C. to produce unsubstituted cumene and a mixture of monoalkylated benzene predominating in primary straight-chain C_8–C_{20} alkyl benzene, and recovering said mixture.

2. Process according to claim 1, wherein in alkylating the cumene with the alkyl bromide, the cumene is present in proportions of 8 to 20 moles for each mole of the alkyl bromide.

3. Process according to claim 1, wherein the benzene is employed in proportions of 160 to 400 moles for each mole of the alkyl bromide.

4. Process for the production of a C_8–C_{20} monoalkyl benzene mixture predominating in an alkyl benzene content in which the alkyl groups, having 8 to 20 carbon atoms are of primary straight-chain structure, which comprises alkylating cumene with a primary straight-chain structure C_8–C_{20} alkyl bromide at a temperature in the range −35° C. to +10° C. in the presence of aluminum bromide alkylation catalyst, the proportions of cumene and aluminum bromide alkylating catalyst, for each mole of alkyl bromide, ranging, respectively, from 8 to 20 moles, and 0.1 to 1.0 mole, contacting the resulting alkylated cumene to a temperature in the range of 0° C. to 10° C. in the presence of benzene and additional aluminum bromide catalyst, to produce mono-alkylated benzene and unsubstituted cumene, the proportions of benzene and additional aluminum bromide catalyst, for each mole of original alkyl bromide employed, ranging, respectively, from about 150 to 400 moles and 0.1 to 1 mole, and recovering a mixture of C_8–C_{20} alkyl benzenes predominating in primary straight-chain C_8–C_{20} mono-substituted benzene.

5. Process according to claim 4, wherein the cumene is alkylated with the alkyl bromide at a temperature in the range −15° C. to −6° C., and the benzene is contacted with the alkylated cumene at a temperature of about 4° to 6° C.

6. Process according to claim 5, wherein the proportion of cumene alkylated with the alkyl bromide ranges from 10 to 12 moles for each mole of the alkyl bromide.

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