April 1, 1952 J. L. BETTS, JR., ET AL 2,591,498

PROCESS FOR BROMINATING XYLENE

Filed April 13, 1949 3 Sheets-Sheet 1

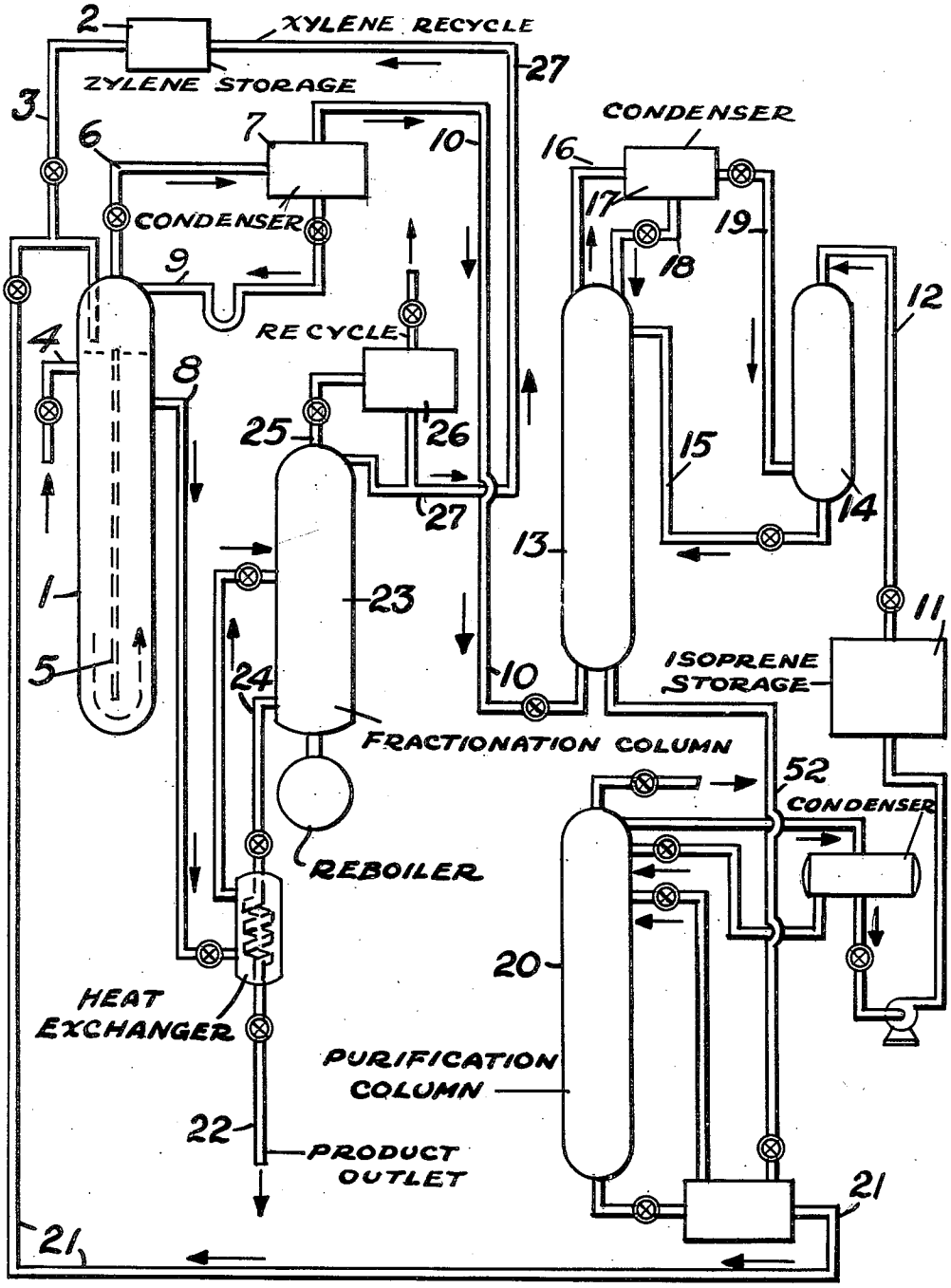


Fig.—1

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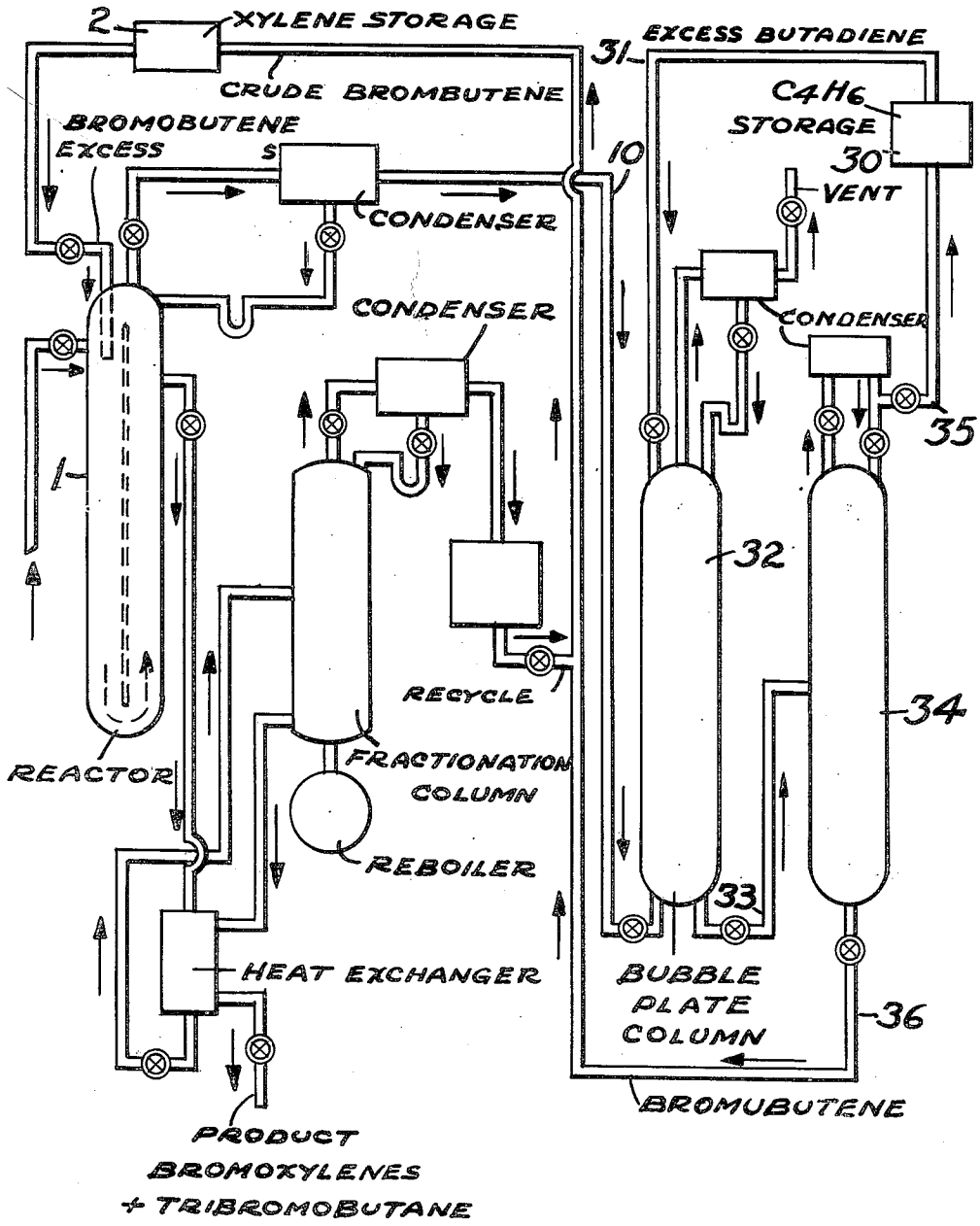


Fig. - II

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PROCESS FOR BROMINATING XYLENE

Filed April 13, 1949 3 Sheets-Sheet 3

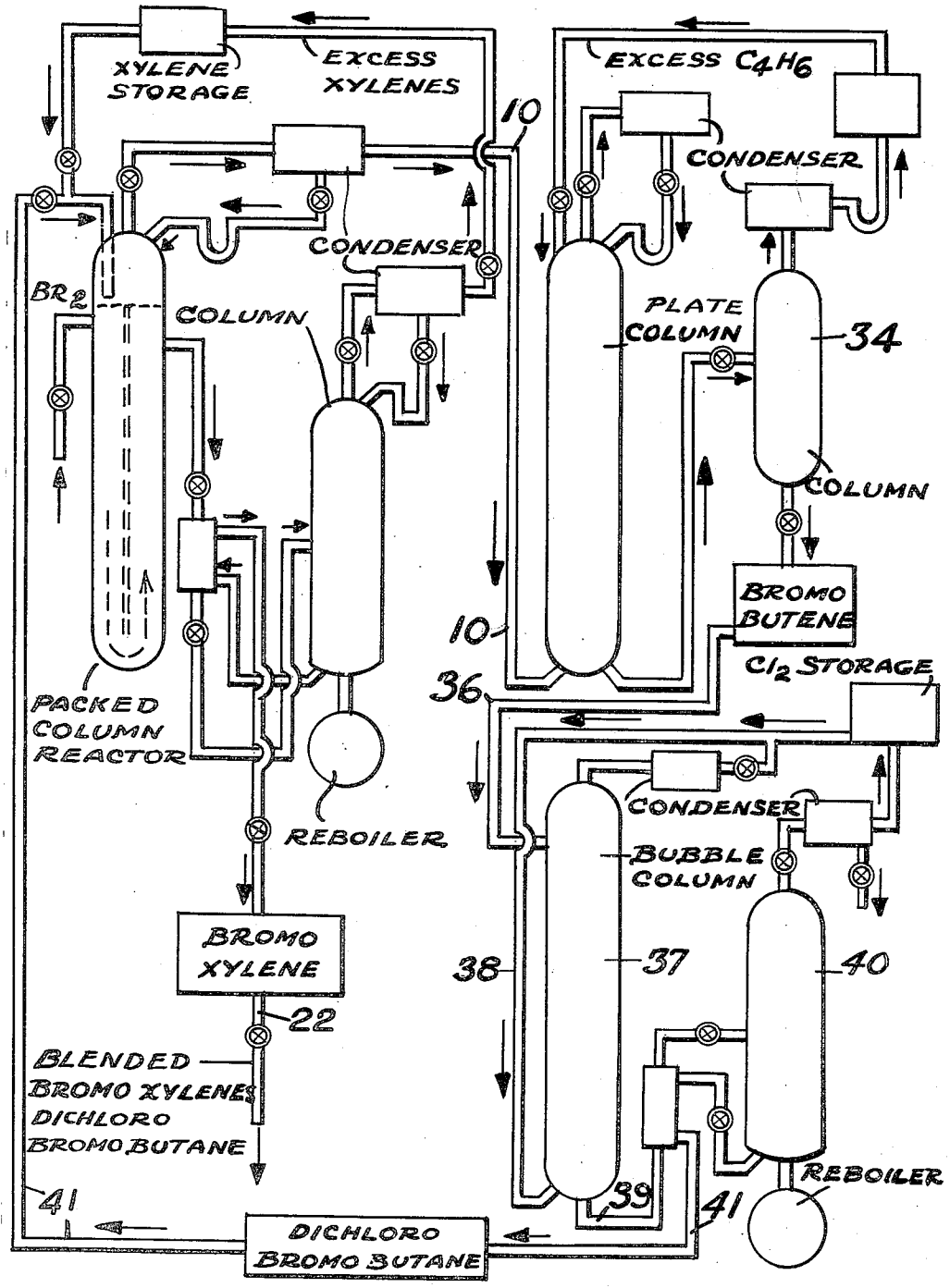


Fig.—III

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UNITED STATES PATENT OFFICE

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PROCESS FOR BROMINATING XYLENE

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Application April 13, 1949, Serial No. 87,204

7 Claims. (Cl. 252—386)

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This invention relates to an improved process for manufacturing what have been called "lead scavenging agents." In accordance with this invention xylene is brominated to form bromo xylene, and as an integral part of this operation, hydrogen bromide gas evolved during the xylene bromination is used to brominate di-olefinic hydrocarbons either with or without the utilization of other halogens. The products formed by this process are a mixed combination of bromo-xylenes and di- or tri-halogenated alkanes well adapted for use as lead scavenging agents in motor fuel.

At the present time it is the general practice to incorporate a "lead scavenging agent" in leaded motor fuels. These agents are employed to react with lead anti-knock agents during combustion of the gasoline to form volatile lead compounds which may be evacuated from the engine. By this means, it is possible to substantially reduce the amount of lead deposit left in the engine and to reduce the corrosion of exhaust valves and other parts of the engine. Conventionally ethylene di-bromide and ethylene di-chloride are used as the scavenging agents. These compounds react with the lead during combustion to form lead bromide and lead chloride which are sufficiently volatile to be largely expelled from the engine on the exhaust stroke. However, certain difficulties in the use of these conventional lead scavenging agents have become apparent. One of the prime difficulties in the use of these agents is that the conventional mixture of ethylene di-bromide and ethylene dichloride is markedly unstable. This condition particularly manifests itself after a period of storage and may result in sufficient decomposition of the scavenging agent to reduce the effective concentration of the agent by one-third or more. A further difficulty of the conventional scavenging agents arises due to their volatility characteristics. This difficulty causes poor distribution of the scavenger agent in a multi-cylinder engine, particularly resulting in too high a ratio of scavenging agent to lead anti-knock agent in certain cylinders and a deficiency of scavenging agent relative to lead anti-knock agent in other cylinders.

It has therefore been appreciated that improved lead scavenging agents should be developed; particularly having improved properties of stability and having a volatility more nearly matching that of the lead anti-knock agent used which is conventionally tetraethyl lead. It has been discovered that mono-brominated xylenes admirably fulfill the requirements of a lead scavenging agent. It is also known that di- and tri-halogenated alkanes are suitable lead scavenging agents although these compounds are not normally as stable as desired. In accordance with the present invention a process is disclosed for producing mixtures of the mono-brominated xylenes and halogenated alkanes having excellent

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stability characteristics and having the properties of an improved scavenging agent.

In accordance with this invention in a first step of the process xylenes are brominated with bromine to yield the desired mono-bromoxylenes. In subsequent steps of the process, hydrobromic acid formed during the bromination of xylenes is utilized to react with di-olefinic compounds. If desired additional halogens may be utilized to also react with the di-olefinic compound, in either case yielding di- or tri-halogenated alkanes.

It is a particular feature of the process of this invention that the bromination of the xylenes may be economically conducted in a manner avoiding the loss of bromine in the form of hydrobromic acid or alternately avoiding the necessity for decomposing the hydrobromic acid to recover the bromine. It is a further feature of this invention that all steps of the process can be conducted so as to avoid loss of bromine from any part of the process. A still further feature is that di-olefins which have been at least partially halogenated are maintained in the reaction zone in which the bromine and xylene are reacted in a manner adapted to better control the bromination of the xylene.

It is to be understood that if desired any one or more of the isomers of xylene may be employed in the process. Preferably however the xylene feed stock comprises a mixture of meta, para, and ortho xylene as these compounds are conventionally obtained in petroleum refining operations. The presence of other aromatic compounds having approximately the boiling point of the xylenes is not deleterious in small quantities. Thus, for example, ethyl benzene which may frequently appear together with the xylenes may also be left in the feed stock to the process of this invention.

The di-olefinic compounds to be utilized are those di-olefins having from 4–5 carbon atoms. Specifically the suitable di-olefins are 1,3-butadiene, 1,2-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,2-pentadiene and 2-methyl butadiene 1,3. Each of these dienes may be utilized in the process of this invention to undergo reactions forming either di- or tri-halogenated alkanes.

The process of this invention may be fully understood by reference to the accompanying drawings in which:

Figure 1 shows the flow plan of a process for utilizing 2 molecules of hydrobromic acid derived from the xylene bromination to react with a di-olefinic compound;

Figure 2 illustrates the flow plan of a process for reacting hydrobromic acid derived from the bromination of xylenes together with di-olefinic hydrocarbons and bromine to yield a tri-halogenated alkane in admixture with the brominated xylene and;

Figure 3 illustrates the flow plan of a process for utilizing the hydrobromic acid obtained from

the xylene bromination together with a halogen which is preferably chlorine to react with diolefinic hydrocarbons to form a tri-halogenated alkane and preferably a di-chloromonobromoalkane.

Referring now to the drawings, a description will first be made of the manner in which the xylenes are brominated. This stage of the process is essentially the same in each of the flow plans illustrated so that reference may be made to any of the three figures of the drawings. While it is to be understood that any desired type of reactor may be utilized, a preferred form of packed column reactor is illustrated in the drawing identified by the numeral 1. The reactor 1 consists of a vertically elongated closed reaction vessel preferably filled with an inert packing material having an iron catalyst dispersed through the packing or impregnated on the packing.

A suitable packing material and catalyst combination is for example a ceramic type of packing mixed with or impregnated with about 1–5% of iron. Alternatively, the catalyst may consist of iron saddles, rings, or foilings, preferably mixed with conventional packing materials. It is only necessary that a quantity of iron be present varying from a trace to 5% or more based on the xylene present. The xylene to be brominated is removed from a refinery stream or a storage drum 2 and is introduced at the top of reaction zone 1 through line 3. Bromine is also introduced at the top of the reaction zone adjacent the point of introduction of the xylene through line 4. Conditions are maintained in the reaction zone to hold the bromine in liquid phase so that the bromine and xylene pass in liquid phase downwardly through the reaction vessel 1. A vertical partition 5 may be positioned in the reaction zone necessitating passage of the bromine and xylene down one side of the partition and up the other side of the partition back to the top of the reactor. Suitable temperatures for bromination cover the broad range of 0° F. to 150° F. but preferably the temperature is maintained above about 70° F. and below about 100° F. Under these conditions of temperature it is suitable to utilize atmospheric pressure in the reaction zone although pressures up to 50 p. s. i. may be used. The bromination reaction proceeds readily so that the residence time of the bromine and xylene in the reactor may be of the order of 1–4 hours. It is preferred that the input rate of xylene and bromine be such that an excess of xylene is added so as to completely react with the bromine without permitting unreacted bromine to leave the reactor. However in the description which follows the handling of any unreacted bromine will be described. The reaction of the bromine with xylene causes volatile hydrobromic acid to be formed which may be withdrawn overhead from reaction zone 1 through line 6. Any condensable product withdrawn is condensed in condenser 7 for return to zone 1 through line 9 while uncondensed hydrobromic acid is passed through line 10. The brominated xylene together with any unreacted xylene may be withdrawn from the top of the tower on the opposite side of the partition from that at which the xylene was introduced, to be removed through line 8. As will be brought out it is a particular feature of this invention that at least partially halogenated alkenes are maintained in reaction zone 1 during the bromination of the xylene to beneficially act as a diluent in the xylene bromination and to insure that unsaturated olefinic compounds cannot result from the process.

The mono-bromoxylenes are preferably withdrawn from column 1 through line 8 for purification in distillation zone 23. As illustrated, the stream of line 8 may be passed in heat exchange relationship with the bottoms of zone 23 for introduction to zone 23 at an intermediate point of the zone. The brominated xylenes will then be withdrawn from the bottom of distillation zone 23 through line 24 for eventual removal from the process from line 22. Any unreacted bromine or xylene together with any entrained hydrobromic acid is removed overhead from distillation zone 23 through line 25. Condenser 26 is operated so that bromine and hydrobromic acid will remain uncondensed for recycle to zone 1 and so that unreacted xylene will be condensed for return to tower 23 as reflux and for recycle to tower 1 through line 27.

Referring now specifically to Figure 1, one specific manner of adapting the principals of this invention will be described. In the embodiment illustrated in Figure 1, a diene of the type above-identified is reacted with the hydrobromic acid of line 10 to form a di-brominated alkane. For the purposes of illustration it will be assumed that the diene utilized is isoprene. The hydrobromic acid of line 10 is conducted to reaction zone 13. Isoprene obtained from a refinery process stream or a storage drum 11 is introduced to the process through line 12. As illustrated, it is preferred that a 2-stage reaction be conducted, in each stage of which isoprene is passed countercurrently to hydrobromic acid. Thus the two reaction vessels 13 and 14 may be used consisting of packed or unpacked towers. The isoprene of line 12 is introduced to tower 14, flowing downwardly through the tower and being removed from the bottom thereof through line 15 for introduction to the top of tower 13. Similarly hydrobromic acid is introduced to the bottom of tower 13 through line 10 and any unreacted hydrobromic acid is removed from the top of tower 13 through line 16. The stream of line 16 is preferably passed through a condenser 17 in order to condense all constituents other than hydrobromic acid for return to tower 13 through line 18. Hydrobromic acid is then removed from the condenser through line 19 for introduction to the bottom of tower 14. By this means it is possible to secure complete utilization of the hydrobromic acid as the flow rates of isoprene relative to hydrobromic acid are maintained to insure that no hydrobromic acid remains unreacted in the second tower 14. The reaction conditions of tower 13 may be chosen from a wide range of temperatures and pressures suitable for holding the diene in liquid phase but preferably the temperature maintained is in the range of about 0° F. to 100° F. and the pressure maintained is in the range of about 0 p. s. i. g. to 50 p. s. i. g. Two molecules of hydrobromic acid will react with each molecule of the diolefinic hydrocarbon to yield a di-brominated alkyl compound. In the specific case of isoprene, the compound formed will be 2,4-dibromo, 2-methyl butane. This reaction product together with any unreacted isoprene and with any entrained hydrobromic acid may be conducted through line 52 to a distillation column 20 operated so as to permit removal of the di-bromo alkane from the bottom of the tower and to permit removal of isoprene and hydrobromic acid overhead for recycle to towers 13 and 14. The di-bromo alkane withdrawn from the bottom of dis-

tillation column 20 is passed through line 21 for introduction to the xylene bromination zone 1 to act as a diluent in the xylene bromination and to insure complete saturation of the original diolefinic hydrocarbon employed. The dibromo alkane then follows the flow of brominated xylenes through the process illustrated for eventual removal from the system through line 22 yielding a product of mixed mono-bromo-xylenes and dibromo alkanes.

Referring now to Figure 2, a second embodiment of this invention is illustrated in which hydrobromic acid derived from the xylene bromination is reacted with a diolefin to form a monobromo alkene. The mono-bromo alkene is then passed to reaction zone 1 for conversion to a tribromo alkane. In the embodiment illustrated, the hydrobromic acid of line 10 is again conducted to a reaction system for reaction with a diolefinic hydrocarbon such as butadiene. Butadiene may be withdrawn from a refinery stream or from storage vessel 30 through line 31 for introduction to the top of the reaction column 32. The butadiene flows downwardly through the column, which is preferably a bubble plate column, countercurrent to a flow of hydrobromic acid moving upwardly through the column. The reaction conditions maintained are suitable for holding the diolefin in liquid phase and comprise temperatures of about −40° F. to 100° F. and pressures of about 0 to 100 p. s. i. g. Sufficient butadiene is introduced to supply at least one mole of butadiene per mole of hydrobromic acid. The overhead of column 32 after passing through a condenser may be vented as sufficient butadiene is utilized as described so that no unreacted hydrobromic acid remains. Consequently the stream removed from the bottom of vessel 32 through line 33 consists of a mixture of excess butadiene together with bromo butene. This stream of line 33 may be conducted to a fractionation zone 34 wherein unreacted butadiene is removed overhead for recycle to the reactor 32 through line 35 and wherein bromo butene is withdrawn as a bottoms product for return to reaction vessel 1 wherein the xylene is brominated. A description already having been made of the manner in which reaction zone 1 is operated, no further description will be made except to point out that the bromobutene introduced to reaction zone 1 together with xylene will undergo a bromination to form tribromobutane. It is apparent that sufficient bromine must be added to column 1 to supply the stoichiometric requirements of the bromobutene reaction as well as the xylene reaction. It is a particular feature of this process that the bromination of the alkene compound will proceed more readily than the bromination of the xylene so that complete bromination of the butene compound may be secured. Again as described in connection with Figure 1, the final product of this process is withdrawn from the system through line 22, consisting in this case of a mixture of brominated xylenes and a tri-bromo alkane.

Referring now to Figure 3, an alternative embodiment of this invention is illustrated permitting the preparation of a mixed hologenated alkane in admixture with brominated xylene. For the purpose of description it will again be assumed that butadiene is the diolefinic compound utilized. It will be observed that the parts of the apparatus and process corresponding to those shown in Figure 2 are identified by similar numerals and so will not be redescribed. Thus the initial bromination of the xylene and the utilization of the hydrobromic acid for reaction with butadiene is the same in Figure 3 as in Figure 2 so that bromobutene is obtained as the bottoms product of distillation zone 34 and removed through line 36. However in the embodiment illustrated in Figure 3 this bromobutene is not conducted back to reaction zone 1 but is conducted to a further reaction zone 37 in which the bromobutene may be reacted with chlorine. Reaction zone 37 may consist of a bubble plate column and is operated so that the bromobutene in liquid phase passes downwardly through the column countercurrently to a flow of chlorine introduced to the column through line 38. The conditions of temperature and pressure maintained in zone 37 are about −40° F. to 100° F. and about 0 to 100 p. s. i. g. Excess chlorine may be removed overhead from tower 37 for recycle to zone 37 and the chlorinated bromobutene may be removed from the bottom of zone 37 through line 39. In the specific case in which butadiene is utilized in the process the product of line 39 will consist of dichlorobromobutane. It is preferred that the stream of line 39 be purified in fractionation zone 40 so that any unreacted chlorine and any unreacted bromobutene may be recycled into the process. The dichlorobromobutane is then removed as the bottoms of tower 40 and is conducted through line 41 for introduction to reaction zone 1 together with the xylene. Again as described in connection with Figures 1 and 2 therefore the final product of the process described will be removed from the system through line 22 consisting of a mixture of bromo xylene and di-chlorobromobutane, or more generally, dichloro-bromoalkanes.

To aid in a more thorough understanding of this invention and to indicate the operability thereof the following three examples are given relating respectively to the processes of Figures 1, 2 and 3.

Example I

322 c. c. of bromine were added dropwise to 875 c. c. of xylene over a period of 6 hours, in the presence of 20 grams of iron filings. At a temperature of 70° F. and at atmospheric pressure, a 93% conversion of bromine to bromoxylenes was secured. The resulting hydrogen bromide was passed through 315 c. c. of isoprene at 32–40° F. with a yield of 96.7%, based on the hydrogen bromide. The product, 2,4-dibromo-2 methyl butane was tested for stability under simulated storage conditions. The test conducted was called a "zinc stability test" designed to indicate storage stability of the particular product when stored in a galvanized drum in the presence of moisture. Essentially the test consisted of refluxing a hydrocarbon solution of the scavenging agent in the presence of water and a spiral zinc strip. At the end of the five hour period the zinc strip was weighed and halogen analyses were obtained on the water. The percent halogen which reacted was then reported to indicate the stability of the scavenging agent. In the test conducted using the 2,4-dibromo-2 methyl butane as obtained in the above example, it was found that 25 to 30 mol per cent of the halide reacted. As will be seen, this is a high degre of reactivity indicating a relatively unstable scavenger agent. As contrasted to this, when the bromoxylenes as obtained in this example were tested by this zinc stability test, it was found that their reactivity was nil. Zinc corrosion data on the mixture of 2,4-dibromo-2 methyl-butane and bromoxylenes in the proportional

amounts synthesized in the process indicated in Example I showed that only 9.5 mol per cent halide reacted. It is therefore to be seen that the mixture of bromoxylenes and dibromo alkane obtained by this process is unexpectedly stable.

Example II

76.1 grams of mixed xylenes were placed in a flask with 2% of iron filings and 84.5 grams of bromobutene. Bromine was added slowly over a period of 70 minutes until 200.6 grams were added. During this time the temperature was maintained at 70–100° F. The product obtained weighted 309 grams which corresponds to a 99% conversion of bromine. The density of the product was 1.756. The product consisting of bromoxylenes and tribromobutane was tested for stability by the zinc stability test and 2.3 mol per cent halide reacted. The volatility of the mixture was found to approximate that of lead tetraethyl. Again the tribromobutane in the product was less unstable than expected since 7.7 mol per cent of the tribromobutane when tested along was found to be reactive in the zinc stability test.

Example III

76.1 grams of mixed xylenes were placed in a flask with 2% iron filings. Bromine was added slowly until 100.2 grams had been added. The temperature was maintained at 70–100° F. The HBr evolved was bubbled through 33.75 grams of butadiene. The conversion of xylenes to bromoxylenes was 92.5% based on the bromine. The conversion of butadiene to bromobutene was 103% based on the bromine. This was due to the fact that a small amount of bromine was entrained by the HBr gas and reacted with the butadiene to give tetrabromobutane or dibromobutene. Chlorine gas was then bubbled through the 84.4 grams of bromobutene produced, until a total weight of 124.4 grams of dichlorobromobutane was obtained. During this reaction, the temperature was maintained at 30–50° F. The conversion obtained was 97.2% of theoretical. The dichloro-bromo-butane and the bromoxylenes were then combined and the zinc stability test run on the mixture. This test showed that 3.05 mol per cent halide reacted. As contrasted to this, 5.2 mol per cent halide reacted when dichloro-bromo-butane was tested alone.

As brought out by the preceding examples, the di- or tri-halo alkanes obtained by the process of this invention are relatively unstable when tested by themselves. However, when admixed with bromoxylenes the stability of the mixture is materially better than the stability of the alkane compound. For comparative purposes, it may be noted that the reactivity of ethylene dibromide according to the zinc stability test described showed that 21 mol per cent of the halide reacted. It is, therefore, contemplated that the products of the processes described will provide improved scavenging agents for use in leaded gasolines particularly as regards the stability of these agents.

What is claimed is:

1. The process for producing lead scavenging agents consisting of contacting at least one isomer of xylene with bromine in the presence of an iron catalyst at temperatures of about 0° F. to 150° F. and pressures of about atmospheric up to 50 p. s. i. whereby mono bromo xylene and hydrobromic acid are formed and thereafter contacting at least one mol of the hydrobromic acid with a diolefin selected from the class of four and five carbon atom diolefins at temperatures of about −40° to 100° F. and pressures of about 0 to 100 p. s. i. g. and thereafter returning the product to the step of the process in which the xylene is brominated.

2. The process of claim 1 in which a stoichiometric excess of xylene relative to bromine is supplied to the xylene bromination step and in which two mols of hydrobromic acid are contacted with one mol of the diolefin.

3. The process of claim 1 in which one mol of hydrobromic acid is contacted with one mol of the diolefin and in which one mol of bromine per mol of xylene and about one mol of bromine per mol of the brominated alkene compound is supplied to the xylene bromination step.

4. A process for producing "lead scavenging agents" comprising a first step in which bromine and xylene are contacted in liquid phase in the presence of an iron catalyst at a temperature of about 0 to 150° F. and at a pressure of about atmospheric up to 50 p. s. i., whereby monobromo-xylene and hydrobromic acid are formed, and a second step in which the said hydrobromic acid and a 4 to 5 carbon atom diolefinic hydrocarbon are contacted at a temperature of about −40° to 100° F. and a pressure of about atmospheric to 50 p. s. i., whereby at least one bromine atom is added to the said hydrocarbon and thereafter contacting the said brominated hydrocarbon with a halogen selected from the group of bromine and chlorine at a temperature of about 0° to 100° F., whereby a saturated halogen substituted hydrocarbon is obtained.

5. The process defined by claim 4 in which the said halogen is chlorine.

6. The process of claim 4 in which the diolefinic hydrocarbon is selected from the class consisting of 1,3-butadiene, 1,2-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,2-pentadiene and 2-methyl-butadiene 1,3.

7. A process for producing "lead scavenging agents" comprising a first step in which bromine and xylene are contacted in liquid phase in the presence of an iron catalyst at a temperature of about 0 to 150° F. and at a pressure of about atmospheric up to 50 p. s. i., whereby monobromo-xylene and hydrobromic acid are formed, and a second step in which the said hydrobromic acid and a 4 to 5 carbon atom diolefinic hydrocarbon are contacted at a temperature of about −40° to 100° F. and a pressure of about atmospheric to 50 p. s. i., whereby at least one bromine atom is added to the said hydrocarbon and thereafter contacting the said brominated hydrocarbon with bromine in the presence of xylene in the said first step of the process, whereby a mixture of mono-bromo-xylene and a saturated bromine substituted hydrocarbon is obtained.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,725,156	Meisenburg	Aug. 20, 1929
2,168,260	Heisel et al.	Aug. 1, 1939
2,479,900	Calingaert et al.	Aug. 23, 1949
2,479,901	Calingaert et al.	Aug. 23, 1949
2,479,902	Calingaert et al.	Aug. 23, 1949