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PARADICHLOROBENZENE

2,527,606

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2 Sheets-Sheet 1

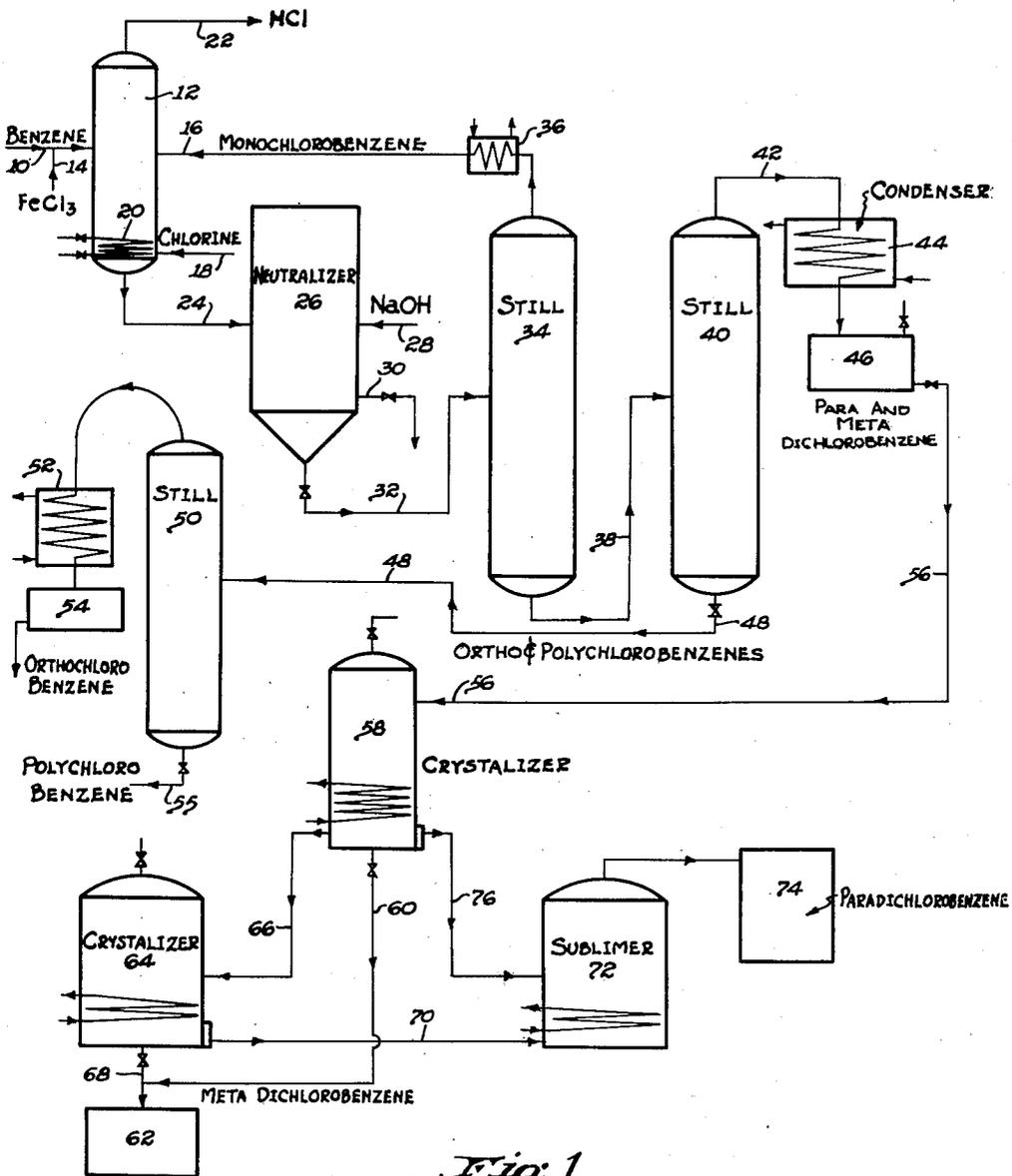


Fig. 1.

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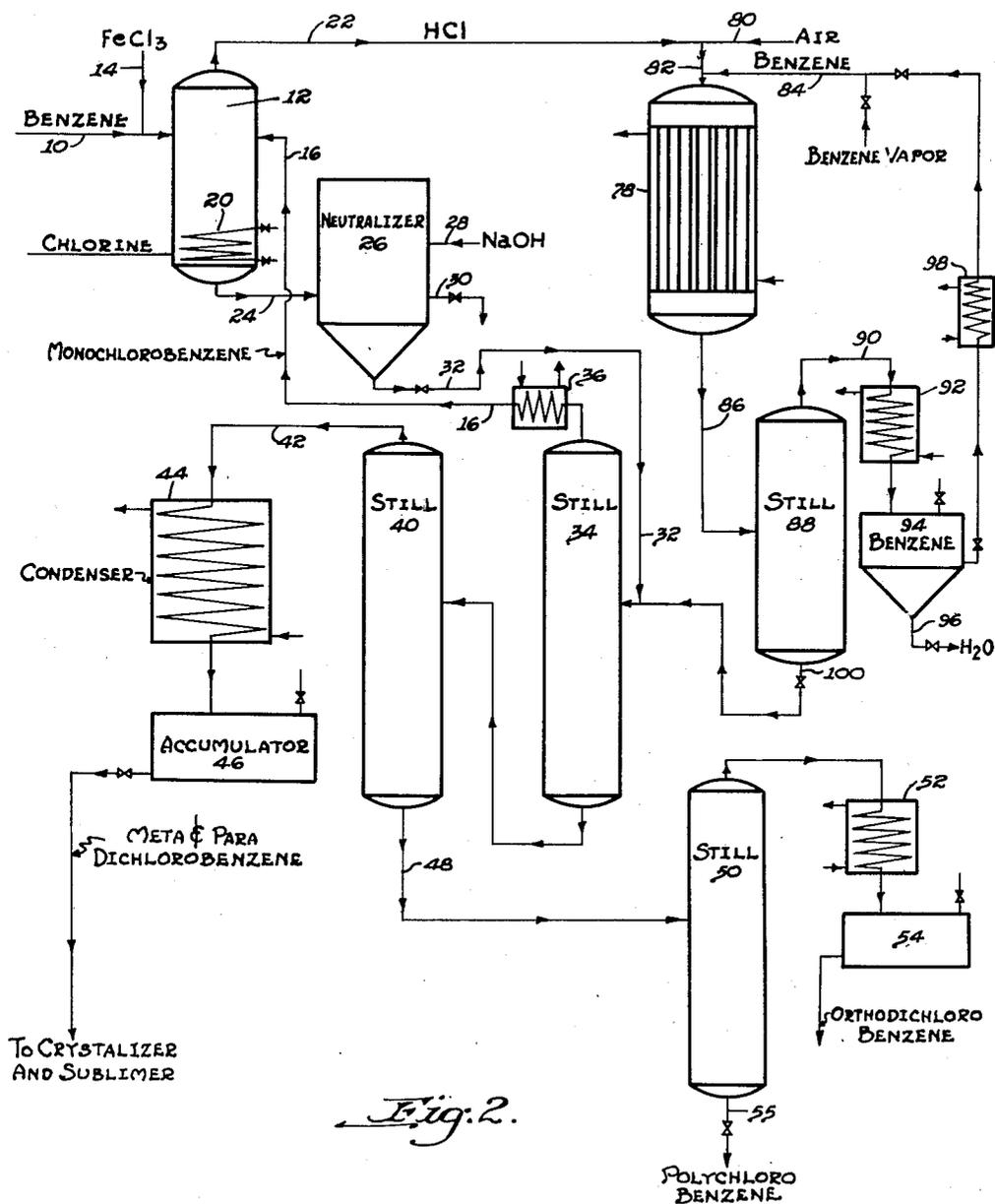


Fig. 2.

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## UNITED STATES PATENT OFFICE

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## PARADICHLOROBENZENE

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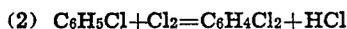
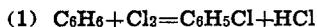
Application July 24, 1946, Serial No. 685,959

3 Claims. (Cl. 260—650)

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This invention relates to paradichlorobenzene. More particularly the invention relates to the chlorination of benzene to produce dichlorobenzenes, especially paradichlorobenzene.

In the past paradichlorobenzene has been made as a by-product in the chlorination of benzene to produce monochlorobenzene. In this process benzene is usually chlorinated to produce approximately 90% monochlorobenzene with a mixture of 10% of dichlorobenzenes in which the para isomer predominates. I have discovered a process by which benzene may be chlorinated to produce from 94 to 98% of dichlorobenzenes, with a production of not more than two to six percent of polychlorobenzenes. In the chlorination of benzene in accordance with my invention, two reactions are involved, namely—



In chlorinating benzene to produce the dichlorobenzenes it is important to avoid excessive chlorination which will produce polychlorobenzenes in which three or more of the hydrogen atoms in the benzene ring are replaced by chlorine. The polychlorobenzenes are difficult to refine, have restricted uses, and involve a substantial loss.

If the chlorination of the monochlorobenzene is controlled so that not more than 50% of the monochlorobenzene is converted to the dichlorobenzenes, the reaction may be carried out to form the dichlorobenzenes with a comparatively small production of polychlorobenzenes. If the chlorination is controlled so that less than half of the monochlorobenzene is converted to dichlorobenzenes, then the formation of polychlorobenzenes may be further reduced. Thus it becomes a question of economics of controlling the chlorination reaction in the conversion of the monochlorobenzene for the production of dichlorobenzenes, or whether to increase the production of polychlorobenzenes or to increase the amount of monochlorobenzene that must be separated from the chlorination reaction products and recycled for further chlorination.

I have found that under carefully controlled conditions equal molecular mixtures of benzene and monochlorobenzene can be chlorinated to produce dichlorobenzenes with a relatively small amount of polychloro products. This discovery provides a means of preparing the dichlorobenzenes directly from benzene in good yields by the simple expedient of recycling monochlorobenzene. Furthermore, it provides for the production

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of the monochlorobenzene for recycle in the same equipment and at the same time as the production of dichlorobenzenes.

To obtain the maximum production of dichlorobenzenes a mixture of forty to fifty mol percent of benzene with sixty to fifty mol percent of monochlorobenzene is introduced into a chlorinating step and the reaction controlled by the addition of the theoretical amount of chlorine, so that, of the material supplied to the chlorination step, the benzene will all be converted to monochlorobenzene and the monochlorobenzene will all be substantially converted to dichlorobenzenes. Accordingly the products issuing from the chlorination stage will comprise monochlorobenzene and dichlorobenzene, and there will be substantially as much monochlorobenzene in the product leaving the chlorinator as the amount of monochlorobenzene introduced with the feed to the chlorination step.

The primary object of the present invention is to provide a process of chlorinating benzene to produce dichlorobenzenes, the major portion of which is paradichlorobenzene.

A further object of the invention is to provide a process for producing dichlorobenzenes from monochlorobenzene with a minimum production of polychlorobenzene.

A still further object is to provide a process by which benzene and monochlorobenzene may be simultaneously chlorinated while avoiding the production of polychlorobenzene.

From the above-mentioned chlorination reactions it will be seen that one mol of hydrochloric acid is produced for each mol of monochlorobenzene and dichlorobenzenes produced. This hydrochloric acid is set free as a gaseous hydrogen chloride and may be used to produce monochlorobenzene in the following manner. The hydrochloric acid is treated with benzene in the presence of air wherein the air presumably oxidizes the hydrochloric acid to produce chlorine and the chlorine, in turn, reacts with the benzene to form the monochlorobenzene, the over-all reaction being the production of monochlorobenzene and water. This monochlorobenzene may be added to the benzene entering a chlorinating step to be converted to dichlorobenzene. By such a process the chlorine consumed in the production of byproduct hydrochloric acid may be utilized in the manufacture of dichlorobenzene.

Accordingly another object of the invention is to provide a process of making dichlorobenzene by which hydrochloric acid produced in the

chlorination reaction may be utilized in producing more dichlorobenzenes.

With these and other objects in view, the invention consists in the process of producing dichlorobenzenes which is hereinafter described and particularly defined in the claims.

The various features of the invention are illustrated in the accompanying drawings in which

Figure 1 is a diagrammatic flow sheet showing apparatus that may be used in the chlorination of benzene to produce substantially only dichlorobenzenes; and

Figure 2 is a diagrammatic flow sheet showing apparatus in which the process illustrated in Figure 1 may be carried out while utilizing hydrochloric acid produced in the process for making monochlorobenzene that forms part of the charge stock to the chlorination reaction.

The chlorination of the mixture of benzene and monochlorobenzene to produce dichlorobenzenes may be carried out as follows, referring to Figure 1:

Benzene is introduced through a line 10 into a chlorination chamber 12. Preferably a catalyst, which may be ferric chloride or any one of the various catalysts which are used in the Friedel-Crafts reaction, is introduced into the benzene through a line 14. Monochlorobenzene is introduced into the chlorinator through a line 16. This mixture passes downwardly through the chlorinator 12 and flows countercurrent to chlorine which is introduced into the chlorinator through a line 18. In the chlorinator presumably the benzene is converted to monochlorobenzene and the monochlorobenzene is converted to dichlorobenzenes. In the chlorinating reactions hydrochloric acid in the form of hydrogen chloride vapors is released and this vapor passes out of the top of the chlorinator through a line 22. The chlorination is an exothermic reaction and therefore must be carefully controlled. To accomplish this a cooling coil 20 is located within the chlorinator 12. The preferred temperature of 35° C. is maintained in the chlorinator, this temperature ranging from 30° to 40° C.

The mixture of chlorobenzenes passes from the chlorinator 12 through a line 24 into a neutralizer 26 where traces of acid dissolved in the chlorobenzenes are neutralized with sodium hydroxide solution introduced through a line 28. The sodium chloride solution produced is decanted and removed through an outlet 30 and the neutralized chlorobenzenes flow from the neutralizer through a line 32 into a still 34. In the still 34 the monochlorobenzene is removed overhead and passes through a condenser 36 to the line 16. The dichlorobenzenes, together with any polychlorobenzenes, will leave the bottom of the still 34 through a line 38 and enter the mid portion of a still 40. In the still 40 para- and metadichlorobenzene pass overhead through a line 42, then through a condenser 44 into an accumulator 46. The orthodichlorobenzene, together with any polybenzenes, passes from the bottom of the still 40 through a line 48 and enters the mid portion of a still 50. Orthodichlorobenzene passes overhead from the still 50 to a condenser 52 and is collected in an accumulator 54. Polychlorobenzene is removed from the bottom of the still 50 through a line 55.

The mixture of para- and metadichlorobenzenes flows from the receiver 46 through a line 56 to a crystallizer 58. By cooling the mixture the paradichlorobenzene is crystallized and may be separated from the metadichlorobenzene. The

metadichlorobenzene is removed from the bottom of the crystallizer 58 through a line 60 and passes to a receiver 62. After the metadichlorobenzene is removed the paradichlorobenzene preferably is liquefied and passes to a crystallizer 64 through a line 66 where it is again cooled and crystallized. The metadichlorobenzene is withdrawn from the bottom of the crystallizer 64 through a line 68 and passes into the receiver 62. The crystallized paradichlorobenzene is then liquefied and flows from the crystallizer 64 through a line 70 to a sublimator 72 where the paradichlorobenzene is vaporized and passes to an accumulator 74. In some cases paradichlorobenzene of sufficiently high purity may be recovered with one stage of crystallization and in such case the paradichlorobenzene may be passed from the crystallizer 58 through a line 76 to the sublimator 72.

The chlorination reactions involved in making dichlorobenzenes produce one mol of hydrochloric acid for each mol of mono- or dichlorobenzene product made. It is important, therefore, that the hydrochloric acid should be utilized advantageously. Otherwise the loss of chlorine in the manufacture of hydrochloric acid would add a high cost to the manufacture of the dichlorobenzenes. To accomplish this the hydrochloric acid is used in the chlorination of benzene to produce monochlorobenzene. This monochlorobenzene then is further chlorinated to produce dichlorobenzene.

The utilization of hydrochloric acid produced in the reaction is illustrated more particularly in the apparatus of Figure 2. In Figure 2 the chlorinator 12, the neutralizer 26 have the same construction and are used for carrying out the same process as that described with reference to Figure 1. The hydrochloric acid used in the chlorination step passes through the line 22 to the top of an oxidizing converter 78. The hydrochloric acid is mixed with preheated air introduced into the line 22 through a line 80 and to this mixture of air and hydrochloric acid is added benzene vapor which passes into a line 82 through a line 84. In the converter 78 preferably is placed a catalyst which is made up of chlorides of iron and copper that are deposited on Florida earth or another inert carrier. The catalyst is maintained at a temperature of approximately 175° to 225° C. wherein the benzene is chlorinated to monochlorobenzene. In the reaction chamber the hydrochloric acid is oxidized to set chlorine free with water vapor. The chlorine thereupon reacts with the benzene to form the monochlorobenzene, the overall reaction being the production of monochlorobenzene and water. An excess of benzene is used to insure an absorption of all the chlorine from the hydrochloric acid and the reaction mixture passes from the converter 78 through a line 86 to the mid portion of a still 88. In the still 88 the excess benzene with water is passed overhead through a line 90 and then flows through a condenser 92 into a decanter 94. The water is removed through an outlet 96 and the benzene is passed through a vaporizer 98 in the line 84.

Since the hydrochloric acid formed in the chlorination step contains the same amount of chlorine that is utilized in producing the monochlorobenzene and the dichlorobenzene in the chlorination step, therefore this hydrochloric acid should produce enough monochlorobenzene for the entire output of the dichlorobenzenes. However, a small amount of benzene is lost in the converter 78 and still 88 so that a small amount of benzene is added through the line 10

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of Figure 2 to provide the necessary benzene to balance the reaction. Accordingly the larger portion of the product being chlorinated in the chlorination chamber 12 is monochlorobenzene. However in the reaction chamber 12 approximately equal parts of monochlorobenzene and dichlorobenzenes leave through the line 24 to pass to the neutralizer.

Monochlorobenzene, passes out of the bottom of the still 38 through a line 100 into the mid portion of the still 34. This monochlorobenzene is mixed with the mixture of chlorinated benzenes passing through the line 32 from the neutralizer 26. The mixture of chlorinated benzenes is distilled in still 34 and monochlorobenzene passes from the top of the still 34 through a cooler 36 to the line 16 by which it enters the chlorinating chamber 12. The mixture of dichlorobenzenes and polychlorobenzenes flows from the bottom of the still 34 into the mid portion of still 40 wherein it is distilled, a mixture of meta- and paradichlorobenzene passing overhead from the still 40 through a line 42 to the condenser 44 and accumulator 46. From the accumulator 46 the mixture of meta- and paradichlorobenzenes may be further refined in crystallizers and sublimators similar to the described in connection with Figure 1. The orthodichlorobenzene with the polydichlorobenzenes flow from the bottom of still 40 through a line 48 to the mid portion of still 50. By the distillation in still 50 orthodichlorobenzene is passed overhead into a condenser 52 and is collected in an accumulator 54. The polychlorobenzenes are removed from the bottom of the still through a line 55.

The chlorination reaction which is carried out in the chamber 12 may be carried out with or without a catalyst. The most effective catalysts are of the type of Friedel-Crafts reaction catalysts such as aluminum chloride, zinc chloride, iron chloride, or metallic fluorides. A comparatively small amount of catalyst is required in order to promote the reaction. For example, with a mixture of 434 gallons of benzene and 496 gallons of recycle monochlorobenzene 32½ lbs. of aluminum chloride is used as a catalyst. Approximately the same amount of any of the metal halides used for the Friedel-Crafts reaction might be used in place of aluminum chloride. The use of a catalyst acts to produce more paradichlorobenzene than when no catalyst is used. For example, when using a catalyst the following products may be produced in the chlorination reaction:

	Percent
Paradichlorobenzene -----	61.4
Orthodichlorobenzene -----	33.7
Metadichlorobenzene -----	2.8
Polychlorobenzenes -----	2.1
	100.0

When operating without a catalyst and utilizing substantially the same temperature 35° C. in the chlorination chamber the following products are produced:

	Percent
Paradichlorobenzene -----	52.5
Orthodichlorobenzene -----	37.0
Metadichlorobenzene -----	5.7
Polychlorobenzenes -----	4.8
	100.0

An excess of monochlorobenzene may be used in

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the charge in order to maintain substantially the same amount of monochlorobenzene in the materials issuing from the chlorination chamber as is introduced into the chlorination chamber. For example, the charge may vary from forty to fifty percent benzene to sixty to fifty percent monochlorobenzene. If more monochlorobenzene is maintained in the reaction mixture in the chlorination chamber this excess of monochlorobenzene will pass over to the still and will have to be separated by distillation in the still 34. This means a larger amount of monochlorobenzene being recycled and cuts down the production of dichlorobenzene. Slightly less than fifty percent of monochlorobenzene being present in the chlorination products issuing from the chlorination chamber has been found to be the most economical mixture for carrying out the reaction.

The preferred form of the invention having been thus described, what is claimed as new is:

I claim:

1. A process of producing dichlorobenzenes from benzene and monochlorobenzene while avoiding the appreciable production of polychlorobenzenes, said process comprising: reacting at a temperature between 30° and 40° C. a mixture of substantially equal molecular portions of benzene and monochlorobenzene with chlorine while in contact with a Friedel-Crafts type catalyst to convert the benzene to dichlorobenzenes, the volume of chlorine supplied to the reaction being controlled so that the reaction products leaving the chlorination reaction zone contain from 40% to 50% of monochlorobenzene and from 60% to 50% of dichlorobenzenes by weight, the major portion of the dichlorobenzenes being paradichlorobenzene.

2. A process of producing dichlorobenzenes from benzene and monochlorobenzene while avoiding the appreciable production of polychlorobenzenes, said process comprising: reacting at a temperature of 30° to 40° C. a mixture of substantially equal molecular portions of benzene and monochlorobenzene with chlorine while in contact with a Friedel-Crafts type of catalyst to convert the benzene to dichlorobenzenes, the volume of chlorine being supplied to the reaction mass being equal to that required to produce substantially equal portions of monochlorobenzene and dichlorobenzenes in the reaction mass, the major portion of the dichlorobenzenes being paradichlorobenzene.

3. The process defined in claim 1 in which the reaction mixture is distilled to take overhead the monochlorobenzene in the mixture with return of the monochlorobenzene to the chlorination zone.

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