April 5, 1955

J. D. HEAD

2,705,730

PRODUCTION OF AROMATIC FLUORIDES

Filed Nov. 25, 1949

2 Sheets-Sheet 1

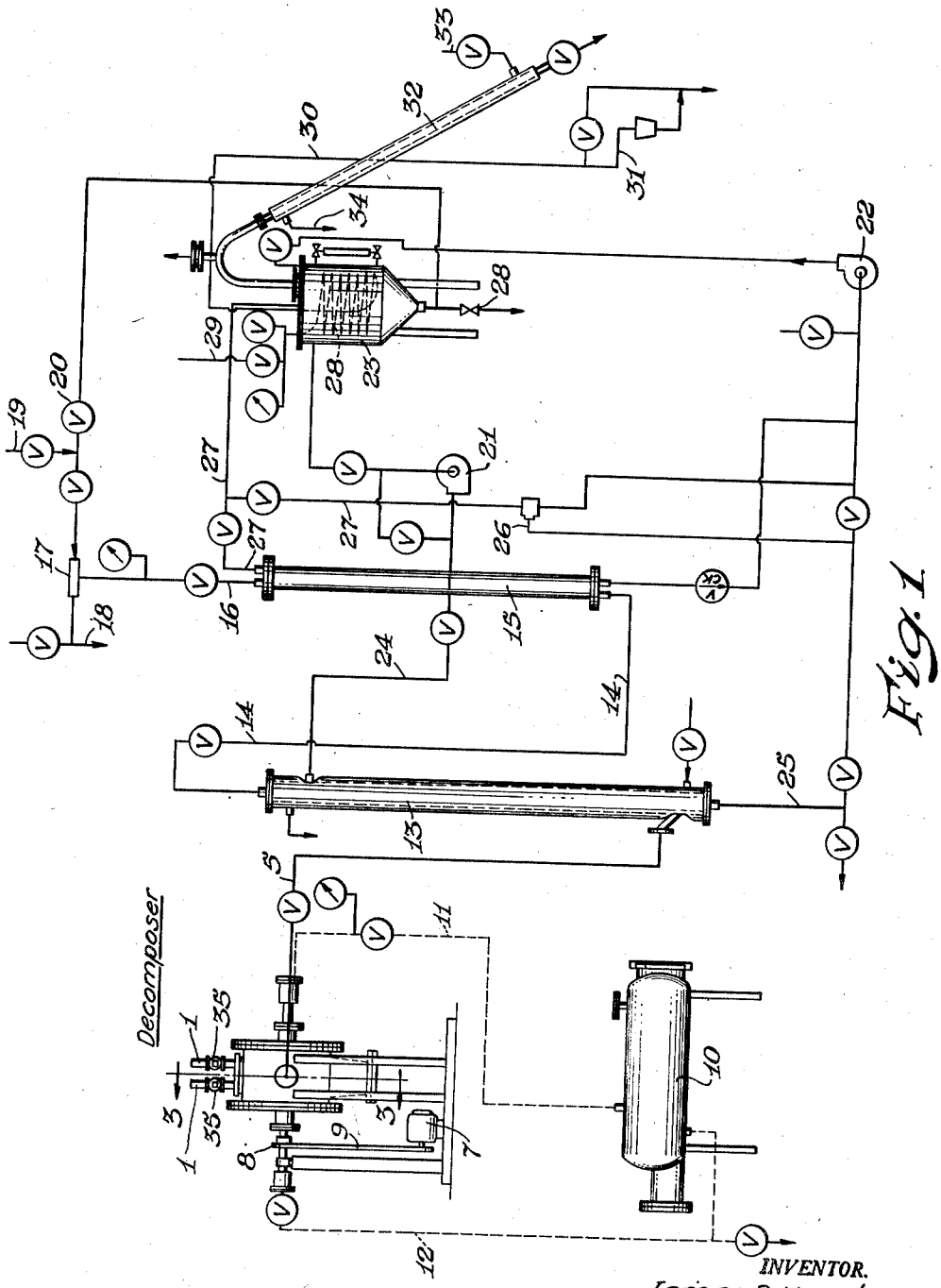


Fig. 1

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2 Sheets-Sheet 2

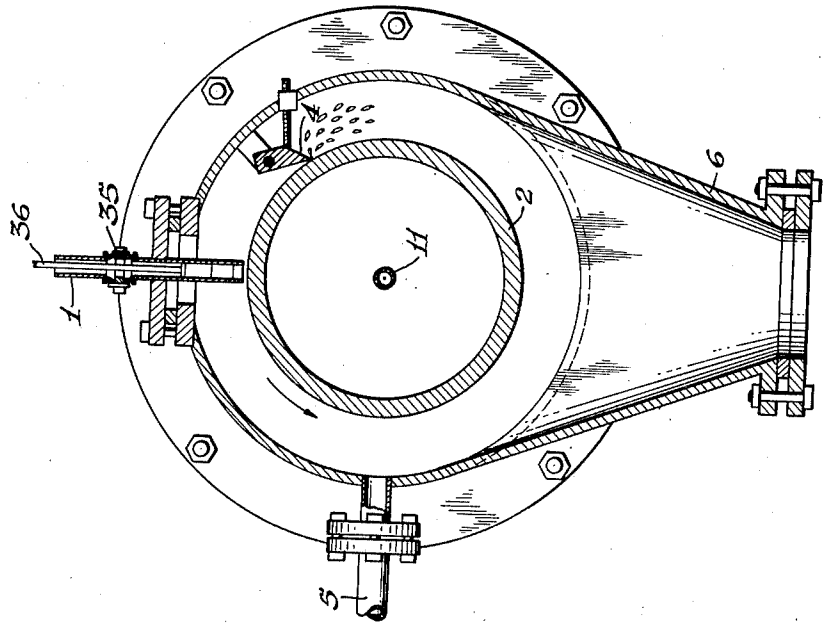


Fig. 3

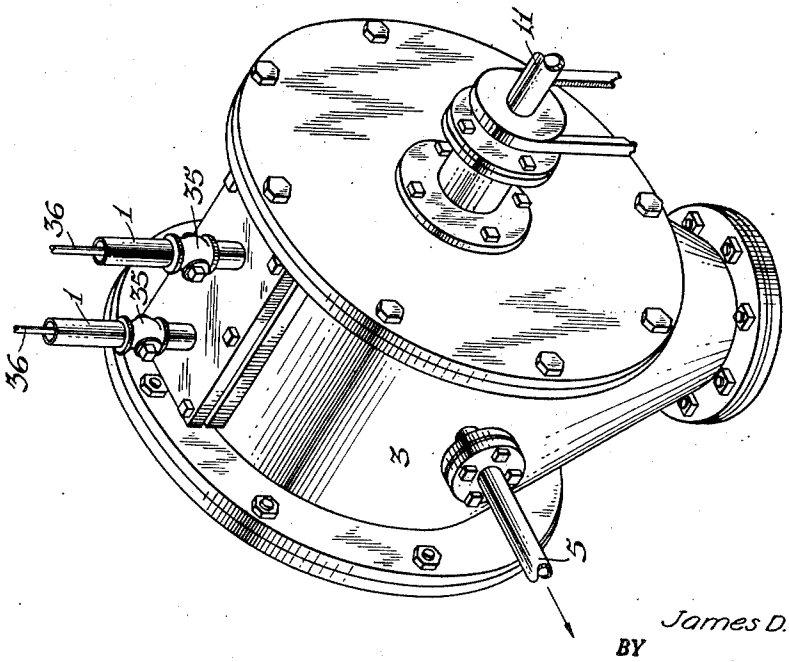


Fig. 2

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PRODUCTION OF AROMATIC FLUORIDES

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Application November 25, 1949, Serial No. 129,263

9 Claims. (Cl. 260—612)

This invention relates to an improved method for the production of aromatic fluorides by the thermal decomposition of aromatic diazonium fluoborates.

In 1927 Balz and Schiemann (Berichte, vol. 60, page 1186) disclosed that the thermal decomposition of an aromatic diazonium fluoborate yields the corresponding aromatic fluoride, with the liberation of boron trifluoride and nitrogen. Considerable literature concerning this reaction has developed in the intervening years, and the preparation of a great many aromatic fluorides by this method has now been reported. However, so far as is known, this method has never been adapted to the commercial scale production of aromatic fluorides, and it has not been known that the method could be adapted to such commercial scale production. It has now been found that aromatic diazonium fluoborates can be decomposed by a substantially improved method which provides a practicable way for producing aromatic fluorides.

In the drawings,

Fig. 1 is a schematic flow diagram illustrating the process of the invention.

Fig. 2 is an isometric sketch of the exterior of the decomposer shown in Fig. 1.

Fig. 3 is a section of the decomposer taken through the line 3—3 in Fig. 1.

The principal object of the present invention is to provide an improved method for preparing aromatic fluorides from aromatic diazonium fluoborates. Another object of the invention is to provide an improved method for accomplishing the thermal decomposition of the aromatic diazonium fluoborates to the corresponding aromatic fluorides. More specific objects and advantages are apparent from the description and the drawings which illustrate and disclose but do not limit the invention.

According to the invention, an aromatic diazonium fluoborate is applied in a solid state to a surface that is heated to a temperature at which the fluoborate decomposes to produce the corresponding fluoride in the vaporous state. The aromatic fluoride is then condensed, collected and purified. The method of decomposing a diazonium fluoborate that comprises applying it in a solid state to a heated surface is another aspect of the invention.

The reaction which is believed to occur when an aromatic diazonium fluoborate decomposes is illustrated by Equation 1, below, which shows the production of an aromatic fluoride, nitrogen, and boron trifluoride,

(1) $$RN{=}NBF_4 \rightarrow RF + N_2 + BF_3$$

in which R is an aromatic radical. In addition to the simple decomposition reaction indicated above, charring of the organic material almost always accompanies the reaction.

Fig. 1 of the drawings illustrates the overall process of the invention. The diazonium fluoborate (in the form of pellets) to be decomposed is placed in feeding tubes **1**, from the bottom of which it is applied to a slowly turning roll **2** (see Fig. 3). Material volatilized on the roll passes through a line **5**, and carbonaceous matter is scraped from the roll by a doctor blade **4** (see Fig. 3) and drops into a hopper **6** (see Fig. 3) beneath the roll. The roll is driven by a motor **7**, power being transmitted to a wheel **8** through a chain **9**. The roll is heated by Dowtherm (the eutectic mixture of biphenyl oxide and biphenyl) which passes from a Dowtherm boiler **10** through a line **11** to the interior of the roll; Dowtherm is returned to the

boiler through a line **12** and is there reheated before being recycled. The gaseous decomposition products pass through the line **5** to a tower **13** where they are bubbled through an alkaline solution that fills the tower to about 40 per cent of its height. Substantially all of the desired fluoride is converted to the liquid phase and remains in the tower. Gaseous material passes on to the top of the tower and through a vent at the top thereof into a line **14**. Through the line **14**, the gaseous material passes into the bottom of a column **15**, which is an open column in which entrained liquid is separated from the gases. Non-absorbed gases leave the column **15** through a line **16**, and enter the vacuum side of a steam ejector **17** from which they are discharged from the collection system through a vent **18**. The steam ejector maintains the system under vacuum during the decomposition and collection steps of the process. Steam to operate the ejector enters through a line **19**, a valve **20** being closed during normal operation of the equipment.

An aqueous alkaline absorbing solution is circulated by two pumps **21** and **22**; the pump **21** draws the absorbing solution from a receiver **23** and pumps it through a line **24** into the column **13**. Absorbing solution flows from the bottom of the column **13** through a line **25**, and is returned to the receiver **23** by the pump **22**. A determined level of absorbing solution is maintained in the column **13** by means of a section of piping **26** which is raised so that its highest point is the height desired in the column **13**. The pressure in the column **15**, in the raised section of the pipe **26**, and in the receiver **23** is maintained in balance by means of an equalizing tie-in **27** which provides open interconnections among these pieces of equipment.

In the embodiment of the invention illustrated in Fig. 1, decomposition is interrupted periodically and the desired aromatic fluoride is separated from the absorbing solution by distillation. The distillation is conducted from the receiver **23** which is equipped with a steam coil **28** which receives steam through a line **29**, and which is drained through a line **30** to a steam trap **31**. During the progress of this distillation, if desired, auxiliary heat can be supplied to the collector **23** by admitting steam from the line **19** to the bottom of the collector by opening the valve **20**. The aromatic fluorides separated by the distillation are collected in a condenser **32** which is cooled by means of cooling water that is admitted to the condenser through a line **33** and is exhausted through a line **34**.

Figure 2 is an isometric view of one form of decomposer within the scope of the invention. Fig. 2 shows the general exterior appearance of the decomposer, and illustrates, in particular, the relationship of the line **5** (through which products leave the decomposer) and of the line **11** (through which Dowtherm is admitted to the interior of the roll). A pair of plug cocks **35** is also shown in Fig. 2. The plug cocks are used in conjunction with the pellet feeders, and are equipped with holes that match the holes of the feeders. When the plug cocks are in their normal operating position the holes thereof match the holes of the feeders, and plungers **36** rest on top of the pellets in the feeders and simultaneously drive the pellets against the roll and provide a seal so that air is not admitted through the feeders to break the vacuum inside the decomposer. When it is desired to supply new pellets to the feeders the plungers are removed from the feeders, and the plug cocks are turned to their closed position to prevent loss of vacuum. Additional pellets are then placed in the feeders on top of the cocks; the plungers are replaced; and the plug cocks are turned to their open position so that the new charge is available for feeding onto the roll.

The interior construction of the decomposer is illustrated in Fig. 3. The roll turns (counter-clockwise in the embodiment illustrated in Fig. 3) and acquires a thin coating of the diazonium fluoborate to be decomposed as the feeder area is passed. The diazonium fluoborate decomposes in the course of the revolution of the roll; the aromatic fluoride is removed from the decomposer through the line **5**; and carbonaceous residue is removed from the roll by the doctor blade. Alternatively, the diazonium fluoborate, in a comminuted form, is ap-

plied to the roll (in a thickness not greater than about 0.06 inch and preferably not greater than about 0.03 inch) by a conveying system (e. g., a screw conveyer or a vibrating feeder).

In general, the improved method of the invention is applicable to the decomposition of all aromatic diazonium fluoborates. However, aromatic diazonium fluoborates are produced by a reaction that is illustrated by Equation 2, below,

(2) $RNH_3Cl+HNO_2+HBF_4 \rightarrow RN_2BF_4+HCl+2H_2O$

Certain substituents in the radical R interfere with the diazotization and formation of the diazonium fluoborate. Examples of such interfering substituents include —OH, —SO_3H, —NO_2, —COOH. Accordingly, the improved method of the invention is usually practiced using diazonium fluoborates free of the aforementioned radicals. Halo, alkyl and alkoxy substituents in no way interfere with the diazotization and formation of the diazonium fluoborate. Furthermore, the use of aromatic diazonium fluoborates having halo, alkyl or alkoxy substituents, and particularly the use of a halo alkoxy benzene diazonium fluoborate, e. g., 3-chloro-6-methoxy benzene diazonium fluoborate, results in the production of aromatic fluorides having particular utility for the production of oxygen carrying chelates (see J. Am. Chem. Soc., vol. 68, p. 2254 et seq.). Accordingly, a preferred embodiment of the invention involves the decomposition of aromatic diazonium fluoborates wherein the aromatic radical is halo-, alkyl-, or alkoxy-substituted, most desirably one wherein the aromatic radical is both halo- and alkoxy-substituted, e. g., 3-chloro-6-methoxy benzene diazonium fluoborate. The halo substituents can be fluoro, chloro, bromo or iodo. The alkyl substituent, or the alkyl part of the alkoxy substituent, can be primary, secondary or tertiary; the number of carbon atoms is limited only by practical considerations. For practical reasons the alkyl or alkoxy substituent usually has not more than about 16 carbon atoms.

Decomposition is effected in the practice of the invention by contacting the diazonium fluoborate with a heated surface. Neither the nature of the surface nor its shape is critical, as the decomposition can be effected on a curvey or straight surface, composed of a metal, glass, or any material that can be adequately heated (e. g., by a heat transfer medium, by gaseous combustion products, or by radiation) to accomplish decomposition. A rotating cylindrical surface is particularly convenient because carbonaceous matter which forms in the course of the decomposition is removed from the heated surface before new diazonium fluoborate is applied thereto, and this carbonaceous matter can be easily removed from a cylindrical roll, e. g., by a doctor blade as is illustrated in the drawings. It is usually preferred that the heated surface be a metal surface, most desirably nickel, because a metal surface is most conveniently heated. For example, in the embodiment of the invention illustrated in Fig. 1 a Dowtherm boiler is used to provide heat which is made available by passing Dowtherm through the interior of a metal cylinder.

The temperature at which the diazonium fluoborate decomposes to produce the corresponding vaporous fluoride is a well known constant for the various known aromatic diazonium fluoborates. For example, Organic Reactions, vol. 5, Roger Adams, Editor in Chief, John Wiley and Sons, Inc., New York, N. Y. (1949), lists the decomposition temperatures of many aromatic diazonium fluoborates on pages 217 to 226. The boiling points of the aromatic fluorides produced by the decomposition are, of course, also known. Although the decomposition can be carried out at the temperature of decomposition, it is usually preferred that a somewhat higher temperature be used in the process of the invention. This is true because the rate at which decomposition occurs is a direct function of the temperature at which decomposition is carried out. Therefore, using a temperature somewhat higher than the decomposition temperature is usually advantageous because this practice makes possible greater utilization of the equipment. It is usually most desirable to carry out decomposition at a temperature from about 100° C. to about 150° C. higher than the decomposition temperature. When the diazonium fluoborate is 3-chloro-6-methoxy benzene diazonium fluoborate, the optimum temperature is between 290° C. and 310° C.

The temperature at which the decomposition is carried out and the minimum length of time that must be allowed for decomposition are interrelated. Thus, when the decomposition is carried out in accordance with the most desired procedure (i. e., by applying the diazonium fluoborate to a heated surface at a temperature from 100° C. to 150° C. higher than the decomposition temperature of that particular diazonium fluoborate) decomposition is effectively accomplished, and the carbonaceous residue is conveniently removed from the heated surface, if from about 10 to about 25 seconds are allowed for decomposition to occur. If a temperature lower than the most desired temperature is used to effect the decomposition, a materially longer time must be allowed for the decomposition to be effected (e. g., as much as about 30 minutes if the decomposition temperature approaches the minimum at which decomposition occurs).

When decomposition is accomplished, the products thereof are condensed, and are treated with an aqueous alkaline solution. The condensation can be effected in any convenient type of condenser, but it is usually advantageous to carry out the condensation in a unit where the aqueous alkaline solution is contacted directly with the decomposition products. When the condensation is effected in this way the condensation is carried out, and the acidic decomposition products are dissolved in the aqueous alkaline solution simultaneously. An aqueous sodium hydroxide solution is a desirable aqueous alkaline solution, as it is relatively inexpensive and readily available. A solution containing from 1 to 20 per cent of sodium hydroxide is satisfactory for the purpose. (The terms "per cent" and "parts" are used herein to refer to per cent and parts by weight, unless otherwise indicated.) It is usually desirable to cool any units (e. g., the tower **13** and the receiver **23**) where the decomposition products contact the aqueous solution; the heat of solution of, e. g., BF_3 is thus dissipated. Any convenient method is used to separate the aromatic fluoride from the other materials with which it is associated, but a steam distillation is quite effective for this purpose as other materials present are not sufficiently volatile that they interfere with such a separation.

The process illustrated in Fig. 1 shows the decomposer and the absorbing systems operated under vacuum. This is not essential to the method of the invention; in fact, it is believed that there would be some advantage to admitting an inert gas to the decomposer to carry the products through the collection system under a slight positive pressure. The inert gas would then be vented from the end of the collection system just as gas that is not absorbed in the absorption system is vented in the process illustrated in Fig. 1. The sole purpose of either vacuum or an inert gas is to carry the products from the decomposer through the absorption system.

The following examples illustrate the new process but are not to be construed as limiting the scope of the invention.

Example 1

An aromatic diazonium fluoborate was decomposed to the corresponding aromatic fluoride according to the following procedure:

3-chloro-6-methoxy benzene diazonium fluoborate was pressed into pellets approximately two inches in diameter by four inches in length under a total pressure of about 15 tons. These pellets (a total of 27 pounds) were then melted onto a nickel roll having a length of 10 inches and a diameter of 12 inches, which roll was enclosed in a housing, was rotated at about 3 revolutions per minute, and was maintained at a temperature between about 290° C. and about 300° C. Carbonaceous matter which adhered to the roll was scraped therefrom by a doctor blade so situated that the material traveled on the roll about 80 per cent of the circumference thereof before being removed. The diazonium fluoborate was applied to the roll over a period of about 210 minutes. The pressure inside the decomposer and a collection system used to isolate the desired product was maintained between about 5 pounds per square inch absolute and about 6 pounds per square inch absolute. The products of the decomposition of the diazonium fluoborate were removed from the housing surrounding the roll and passed into a tower having an internal diameter of about 4 inches and a height of about 8 feet, which tower was filled with 5 per cent sodium hydroxide to a height of about three feet and was cooled externally to maintain the temperature of the caustic solution between about 20° C. and about

25° C. The caustic solution in the tower was removed therefrom at a rate of about one-half gallon per minute, and was pumped into a collector where the organic material settled; the caustic which rose to the top of the collector was returned to the top of the tower at a rate of about one-half gallon per minute. The collector (which contained about 10 gallons of caustic when operation was started) was also cooled externally to maintain the temperature of the caustic solution between about 20° C. and about 25° C. The gases which were not condensed or absorbed in the tower were then passed through a second tower having an internal diameter of about 4 inches and a height of about 5 feet. This second tower was free of absorbing solution, and merely provided a place where entrained liquid could be separated from the gases. The gases from the top of this second column were passed to the vacuum side of a steam ejector to provide vacuum for the entire system. When the organic layer in the collector filled a substantial portion of the volume thereof, decomposition was interrupted, and the 4-chloro-2-fluoroanisole produced by the decomposition was removed from the collector by a steam distillation. The 4-chloro-2-fluoroanisole so recovered was dried over anhydrous sodium sulfate and purified by fractionation in a Podbielniak column; the total recovery of pure compound amounted to 6.2 pounds, which corresponds to a 38 per cent yield of the product.

Example 2

A procedure similar to that described in Example 1 was carried out except that: (1) the diazonium fluoborate was not pelleted, but was granular in form, and was fed to the roll by means of a screw conveyor; (2) the roll was operated at a temperature between about 300° C. and about 310° C.; (3) the total pressure inside the system was between about 11 pounds per square inch absolute and about 12 pounds per square inch absolute; and (4) 10 pounds of the diazonium fluoborate were charged in the course of about 90 minutes. The recovery of 165 grams of 4-chloro-2-fluoroanisole corresponded to a conversion of about 6 per cent.

I claim:

1. An improved method of thermally decomposing an aromatic diazonium fluoborate that comprises (1) continuously conveying the fluoborate in its solid state into contact with a surface heated to a temperature at which the fluoborate decomposes to produce the corresponding vaporous fluoride and simultaneously effecting motion of the surface relative to the conveying system to spread the fluoborate on the surface as a thin coating, (2) collecting the decomposition products, (3) subjecting the collected decomposition products to the action of an aqueous alkaline solution, and (4) separating the aromatic fluoride from the alkaline solution.

2. A method as claimed in claim 1 in which the aromatic diazonium fluoborate has not more than four substituents each of which is of the class consisting of halo, alkyl, and alkoxy.

3. A method of converting 3-chloro-6-methoxy benzene diazonium fluoborate to 4-chloro-2-fluoro anisole that comprises (1) continuously conveying the fluoborate in its solid state into contact with a nickel roll heated to a temperature between about 290° C. and about 310° C. and simultaneously rotating the roll to spread the fluoborate thereon as a thin coating, (2) collecting the decomposition products, (3) subjecting the collected decomposition products to the action of a 5 per cent aqueous

sodium hydroxide solution, and (4) separating the 4-chloro-2-fluoroanisole from the aqueous solution.

4. An improved method of thermally decomposing an aromatic diazonium fluoborate to the corresponding aromatic fluoride that comprises continuously conveying the fluoborate in its solid state into contact with a surface heated to a temperature at which the fluoborate decomposes to the fluoride and simultaneously effecting motion of the surface relative to the conveying system to spread the fluoborate on the surface as a thin coating.

5. A method according to claim 4 in which the diazonium fluoborate is applied to the heated surface as a pellet.

6. A method according to claim 4 in which the diazonium fluoborate is applied to the heated surface in comminuted form.

7. A method according to claim 4 in which the heated surface is a cylindrical metallic surface heated to a temperature from about 100° to about 150° C. higher than the decomposition temperature of the aromatic diazonium fluoborate.

8. An improved method of thermally decomposing an aromatic diazonium fluoborate to the corresponding aromatic fluoride that comprises continuously conveying the fluoborate in its solid form into contact with a cylindrical roll heated to temperature at which the fluoborate decomposes to the fluoride, rotating the roll at a rate such as to spread the fluoborate on the surface as a thin coating and to allow the fluoborate thus spread to decompose leaving a carbonaceous residue, and scraping the residue from the surface of the roll before the rotation thereof brings it into the next successive contact with the fluoborate.

9. An improved method of thermally decomposing an aromatic diazonium fluoborate to the corresponding aromatic fluoride that comprises continuously conveying the fluoborate in its solid form into contact with a cylindrical metal roll heated to a temperature from 100° to 150° C. higher than the decomposition temperature of the fluoborate, spreading the fluoborate on the surface of the roll in a thickness not greater than about 0.06 inch while rotating the roll at a rate such that the fluoborate thus spread remains on the heated surface for at least about 10 seconds to decompose leaving a carbonaceous residue, and scraping the residue from the surface of the roll before the rotation thereof brings it into the next successive contact with the fluoborate.

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