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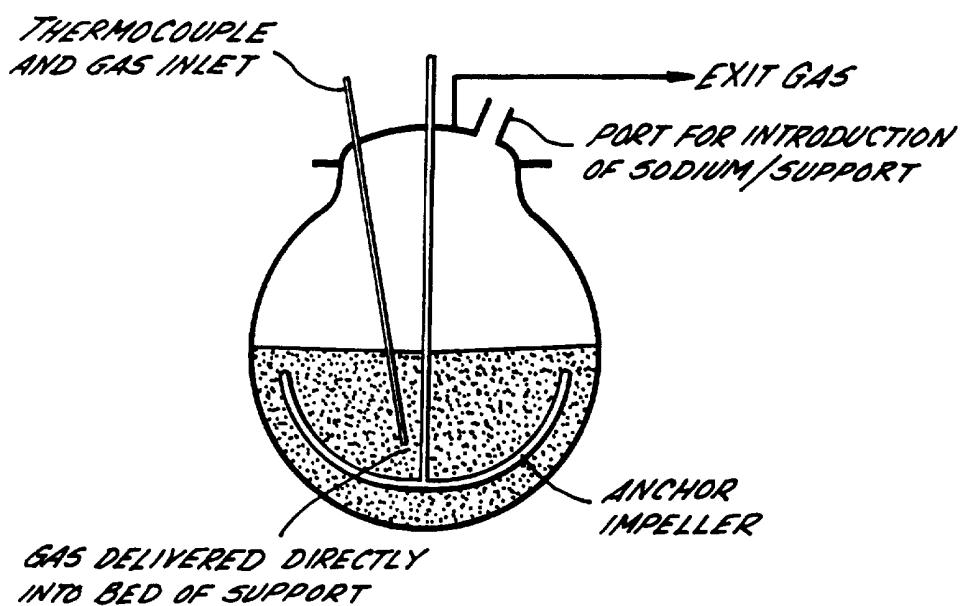
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EP 0467053 A1 WO 94/03237 A1 US 4639309 A

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(54) Process for the destruction of halocarbons

(57) A process for the destruction of halocarbons comprises supporting metallic sodium at a temperature above its melting point on a solid particulate carrier material and contacting the halocarbon or halocarbons in a gaseous state with the supported sodium to react the halocarbon or halocarbons with the sodium to form elemental carbon and sodium halide or halides.

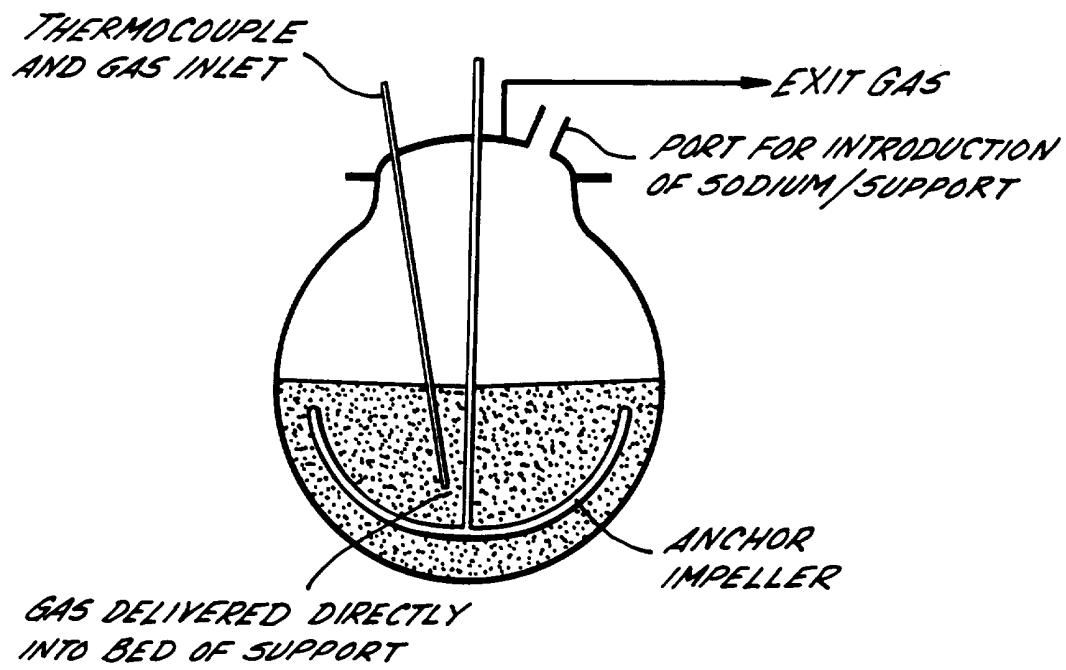
FIG. 1.



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FIG. 1.



PROCESS FOR THE DESTRUCTION OF HALOCARBONS

This invention relates to a process for the destruction of halocarbons.

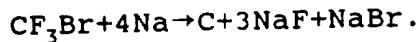
5 In recent years the effect of halogenated hydrocarbons (hereinafter referred to as halocarbons) on the environment has been the cause of considerable concern throughout the world with much attention being given both to the reduction of production of
10 halogenated hydrocarbons and also the disposal of the considerable stocks of these compounds which exist worldwide, for example for use in refrigeration equipment, fire extinguishers, etc. Due to the international agreement reached in the Montreal
15 Protocol and subsequent national legislation there has been considerable interest in particular in finding effective ways of destroying these compounds in an environmentally acceptable manner.

It has been realised for some time that
20 destruction of halocarbons by reaction with sodium is theoretically environmentally desirable because potentially it enables halocarbons to be converted entirely to benign solid products that have no deleterious properties and thus volatile compounds
25 which are capable of depleting ozone in the earth's ozone layer and contributing to the greenhouse effect are effectively completely disposed of without any risk to the environment.

Thus, for example, bromo-trifluoro methane, which
30 is commonly known as Halon 1301, is used as a fire extinguisher agent. However, it has a very high ozone depletion potential and is a powerful greenhouse gas. There is therefore considerable interest in finding an effective means for disposing of stocks of this halon.

It is known that Halon 1301 can be reacted with molten sodium to convert it into carbon, sodium fluoride and sodium bromide by the following reaction:-

5



Thus all of the products of the reaction are solid and, moreover, have potential value. Also they 10 have no adverse environmental effects.

However, there are several practical problems in carrying out the above-mentioned chemical reaction.

The reaction with molten sodium is very 15 exothermic and complex in that the gaseous halocarbon reacts with the liquid sodium to produce solids. The exothermic nature of the reaction means that unless the mixture is kept well stirred, hot spots with 20 sparking and glowing can develop. Furthermore, the reaction mixture becomes sticky and very viscous as more and more solid products build up and the mixture tends to bind into a solid mass.

The resulting mixture can become very difficult 25 to stir and sodium can become trapped and inaccessible to halocarbon in the body of the sticky, solid mass. Unreacted sodium remaining at the end of a reaction is both an economic loss and potentially hazardous and it must therefore be neutralised, typically by reaction with methanol.

It has now been discovered that if the molten 30 sodium is dispersed on a solid particulate support material the reaction is much more controllable. Hot spots sparking and glowing do not develop and the temperature in the reactor can easily be controlled by limiting the flow of halocarbon gas entering the 35 reactor. Alternatively or additionally the reactor

can be jacketed and a cooling medium circulated through the jacket to control the reaction temperature.

Moreover, the reaction mixture remains free
5 flowing and easily stirrable throughout the reaction. This means that low-power motors can be used or a fluidised bed system can be employed. Moreover, very high utilisations of sodium can be achieved particularly, as the Applicants have discovered, if
10 the process is carried out under pressure. As the reaction is mass transfer limited, the increased pressure generates greater driving force and therefore maintains a high overall reaction rate. The supported sodium is in thin layers and therefore there is no
15 opportunity for thick product layers to form that could inhibit the reaction.

It has also been found that it is possible to operate the process so that at the end of a reaction it is unnecessary to destroy any unreacted sodium. It
20 is also possible to admit more molten sodium and disperse it on the solid support together with the solid products and repeat the halocarbon destruction reaction again and again. It has been shown experimentally that the same support can be re-used at
25 least twenty times.

Thus, according to the present invention there is provided a process for the destruction of halocarbons which process comprises supporting metallic sodium at a temperature above its melting point on a solid
30 particulate carrier material and contacting the halocarbon or halocarbons in a gaseous state with the supported sodium to react the halocarbon or halocarbons with the sodium to form elemental carbon and sodium halide or halides.

35 As will be realised, the process of the present

invention can be applied to any halocarbon which exists in, or can be brought into, the vapour state for contact with the supported sodium in accordance with the method of this invention. However, the 5 invention has particular applicability to halons, CFCs (chlorofluorocarbons), HCFCs (hydrochlorofluorocarbons), HFCs (hydrofluorocarbons) and halogenated solvents. These particular halocarbons are those which have given particular concern from an 10 environmental point of view.

As mentioned above, the sodium metal used in the method of the invention is at a temperature above its melting point. It is preferred that the sodium is held at a temperature in the range from 98°C to 500°C, 15 and more preferably at a temperature in the range of 98°C to 300°C.

The solid particulate carrier material may, for example, be silica, alumina, sand, glass beads, carbon, salts or any other similar solid materials in 20 a finely divided form. Preferably the particle size is below 500 µm. Sand has been found to be a particularly useful carrier material being relatively inexpensive and freely available. However, it is envisaged that other support materials may have 25 particular usefulness for certain applications, for example carbon, this of course being one of the products of the chemical reaction which forms the basis of the process.

The halocarbon will usually be passed in gaseous 30 form into a reactor vessel containing the supported molten sodium. If the halocarbon is in liquid form it will be vaporised before being passed into the reactor vessel.

Although both of the main steps of the method of 35 the invention, as defined above, can be carried out in

the same reactor vessel the molten sodium may be dispersed on a heated solid support material in a preparation vessel preferably under a blanket of inert gas such as nitrogen, the supported molten sodium 5 being then passed into the main reactor vessel where it is contacted with the gaseous halocarbon.

Alternatively, the sodium may be dispersed on the heated solid particulate support material under a blanket of inert gas in the same reactor as that in 10 which the halocarbon destruction is subsequently to be carried out. Then, the halocarbon in gaseous or vaporised form may be admitted to a reactor which is filled with inert gas and which contains the supported molten sodium.

15 Although the reactor, or main reactor, may have a fixed bed of supported sodium it is usually preferred that the particulate support material with sodium supported thereon is kept in motion, e.g. by stirring or by use of a fluidised bed technique, this having 20 the advantage that reaction products are not permitted to combine into a continuous phase and therefore cause the bed to solidify.

25 Preferably the amount of sodium dispersed on the particulate support material prior to the halocarbon destruction reaction is from 1 to 50 weight percent, and more preferably from 5 to 15 weight percent.

30 The temperature of the supported sodium may be controlled by controlling the rate at which halocarbon is admitted to the reaction chamber and/or by use of a cooling jacket placed around the reactor. It is necessary, from time to time, to remove the solid products of the reaction, namely carbon and sodium halides, from the reactor. This can be done in a semi-batch mode by removing a proportion of the solid 35 material at the end of a halocarbon reaction phase and

quenching it in water or alcohol to remove any residual sodium. The sodium halides can be dissolved away and the carbon removed. The particulate base support material can then be removed, dried and then 5 re-used. An equivalent amount of support material may be added each time solid product and support material is removed from the reactor. The products can then be worked up for value. For example, bromine can be recovered from aqueous sodium bromide by passing in 10 chlorine gas.

An operation in semi-batch manner can also involve dispersing further sodium on the support material in the reactor vessel when the majority of the sodium has been consumed in a first batch.

15 Alternatively, when the majority of the sodium has been consumed in a first batch further supported sodium can be added from a sodium preparation vessel to the reactor vessel and the halocarbon destruction reaction repeated. As mentioned above, some of the 20 solid material (i.e. particulate support material and products) may be withdrawn from the reactor vessel and this may be done before an addition of sodium or supported sodium so as to maintain the percentage of sodium dispersed on the support materials within a 25 preferred range, as indicated above.

As an alternative to a batch or semi-batch mode of operating the method, the process can be operated in a continuous manner in which supported sodium is continuously fed from a sodium preparation vessel into 30 the main reactor vessel at such a rate that the sodium is largely consumed by the time the solid materials (i.e. the particulate support material together with solid products) flow out of the reactor vessel.

As also indicated above, solid materials may be 35 withdrawn from the reactor and thereafter quenched in

water or an alcohol to remove any residual sodium and to dissolve sodium halides, the particulate support material being then treated as desired and returned for re-use in the process.

5 A factor which has been found to be important in the operation of the method of the present invention has been the pressure at which the process is performed. Bearing in mind that the reaction between molten sodium and gaseous halocarbons tends to be very
10 vigorous and exothermic it is perhaps surprising that any suggestion should be made that the reaction be carried out at a pressure greater than atmospheric pressure. However, the Applicants have found that by carrying out the method of the invention above
15 atmospheric pressure, or by causing or allowing the pressure to increase above atmospheric pressure as the reaction proceeds, has an effect that the reaction proceeds more completely and that little or no sodium remains in the solid mixture after reaction which has
20 to be disposed of as described above by reaction with water or alcohol. This clearly has considerable advantages in that the process is not only simplified but more efficient use is made of the sodium. It is not entirely understood how the increase in pressure
25 should have this desirable effect but, as mentioned hereinbefore, it is conjectured as the reaction is mass transfer limited, the increased pressure generates greater driving force and therefore maintains a high overall reaction rate. Preferably
30 the increase in pressure over atmospheric pressure is at least $\frac{1}{2}$ Bar absolute. The effect of operating under pressure as compared with a similar process in which the destruction of the halocarbon is not under pressure is shown in the following specific examples.

Example 1

Non-Pressurised Destruction of Halon 1301

(Bromo-trifluoro methane)

The reactor as shown diagrammatically in Figure 1
5 consists of a 500 ml reaction flask complete with
flange head with several inlets into the reactor. One
inlet is for the stirrer, another inlet is a combined
thermocouple and gas delivery point for the direct
introduction of nitrogen and halon into the support.
10 Another inlet is used for charging sand and sodium to
the reactor, and one is used for the gas exit stream
from the reactor to the wash bottle.

A charge of 202.58 g of pre-dried sand (average
particle size 145 μm) was added to the reactor vessel
15 and heated under a nitrogen purge and gentle agitation
to 200°C. When the sand had attained this
temperature, a charge of 10.45 g of sodium was added
to the sand through the inlet. The support was
maintained at 200°C while the sodium charge was
20 allowed to disperse evenly over the support, at 125
rpm. After 10 mins. when an even dispersion had been
achieved the nitrogen flow and heating mantle were
shut off in preparation for the halon introduction.
The halon flow was set at approx. 250 cc/min and the
25 halon was allowed to flow into the reactor, where it
reacted with the sodium and was destroyed. The
agitation was set and maintained at 125 rpm through
the course of the experiment. At 60 secs. into the
reaction an exotherm had been observed and the support
30 temperature had risen from 203°C to 214°C. This
exotherm continued and the support temperature rose
steadily until it peaked after 14 mins. at a
temperature of 287°C. The temperature of the support
then fell steadily. After 30 mins. and at a
35 temperature of 224°C the halon flow to the bed was

stopped. The reaction was deemed complete and the vessel was allowed to cool to room temperature under nitrogen.

5 226.58 g of support, products and any unreacted sodium were recovered from the vessel.

A 55.98 g sample was taken for analysis. The sample contained 0.54 g of unreacted 10 sodium.

Therefore the total unreacted sodium remaining on the support was 2.19 g. The sodium added at the start of reaction was 10.45 g.

15 Therefore 8.26 g of sodium reacted with 13.53 g of halon 1301.

Consumption of sodium was 79%.

20 Example 2

Pressurised destruction of the halon 1301.

The reactor consists of a 500 ml reaction flask complete with flange head with several inlets into the reactor. One inlet is for the stirrer, another inlet 25 is a combined thermocouple and gas delivery point for the direct introduction of nitrogen and halon into the support. Another inlet is used for charging sand and sodium to the reactor, and one is used for the gas exit stream from the reactor to the recirculating 30 pump, which recirculates the gas to the gas inlet port.

Essentially the equipment is the same as for Example 1. However this experiment was operated in a sealed system, with the pressure of the system being 35 controlled by the regulator on the halon cylinder.

Also a recirculating pump was used to continually recirculate the gas in the reactor through the support.

The particulate support for this experiment 5 consisted of 170.6 g from the support used in Example 1, which remained after the 55.98 g sample was removed for analysis. In addition 57.45 g of fresh pre-dried sand was added, giving a total support weight of 228.05 g. There was 1.65 g of unreacted sodium 10 remaining on the support from the 170.6 g portion used from Example 1.

This support of 228.05 g was added to the vessel and heated under a nitrogen purge and gentle agitation to 200°C. When the support had attained this 15 temperature, a charge of 11.99 g of sodium was added to the support through the inlet. The support was maintained at 200°C while the sodium charge was allowed to disperse evenly over the support, at 100 rpm. After 10 mins. when an even dispersion had been 20 achieved the nitrogen flow and heating mantle were shut off in preparation for the halon introduction.

The pressure in the reactor at this stage is 1 atm. (absolute) of nitrogen and any pressures referred to hereinafter are gauge pressures.

25 The regulator on the halon 1301 cylinder was set at 0.5 Bar and the recirculating pump connected to seal the reactor system. The stirrer was set at 100 rpm and the halon flowrate set at approx. 250 cc/min.

At the start of the halon introduction when the 30 pump was switched on and the halon flowrate set, a drop in temperature reading was observed. This was due to the pressure created from the pump displacing the support from around the thermocouple. Therefore it was a few minutes before equilibrium was 35 established and the temperature rise due to the

exotherm truly recorded. At 2 mins. the temperature of the support was 190°C and the pressure in the reactor had risen to 0.2 Bar. At 4 mins. the temperature of the support was 197°C and the pressure in the reactor had risen to 0.3 Bar. The support continued to rise steadily in temperature and pressure until at 27 mins. the exotherm peaked at a temperature of 287°C and a pressure of 0.45 Bar. Then the support temperature steadily fell, but the pressure in the reactor gradually increased to match the set cylinder pressure of 0.5 Bar. After 40 mins. at a temperature of 138°C and a pressure of 0.5 Bar the reaction was stopped and the reactor allowed to cool to room temperature under nitrogen.

15

258.35 g of support, products and any unreacted sodium were recovered from the reaction vessel.

20

A 58.24 g sample was taken for analysis. The sample contained 0.23 g of unreacted sodium.

Therefore the total unreacted sodium remaining on the support was 1.02 g.

25

The sodium present on the support from Example 1 was 1.65 g, the sodium added was 11.99 g, giving a total of 13.64 g of sodium available.

Therefore the total sodium used in this reaction was $13.64 - 1.02 = 12.62$ g.

30

Therefore 100% utilisation of the 11.99 g sodium added this experiment was achieved, plus an additional 0.63 g of sodium bound on the support from the previous experiment Example 1 was consumed, destroying in total 20.43 g of the halon 1301.

35

This indicates that the pressurised system, of
Example 2, is a significant improvement over the non-
pressurised system. Not only was the fresh charge of
sodium completely consumed in the reaction, but also
the sodium remaining on the support from the previous
5 experiment, Example 1, had been more efficiently
reacted.

CLAIMS:

1. A process for the destruction of halocarbons which process comprises supporting metallic sodium at 5 a temperature above its melting point on a solid particulate carrier material and contacting the halocarbon or halocarbons in a gaseous state with the supported sodium to react the halocarbon or halocarbons with the sodium to form elemental carbon 10 and sodium halide or halides.

2. A process as claimed in claim 1 wherein the contacting of the halocarbon with the sodium is performed at an elevated pressure.

15

3. A process as claimed in claim 1 wherein the pressure is caused or permitted to rise during the contacting step.

20

4. A process as claimed in any one of the preceding claims wherein the particle size of the solid particulate material is below 500 μm .

25

5. A process as claimed in any one of the preceding claims wherein the step of supporting the metallic sodium on a solid particulate material is performed in a reaction vessel separate from that in which the contacting of halocarbon with the sodium is performed.

30

6. A process as claimed in any one of the preceding claims when performed as a semi-batch process in which a part of the solid reaction mixture is removed after a first reaction phase and/or fresh 35 sodium alone or supported sodium is added before a

second reaction phase.

7. A process as claimed in any one of claims 1 to 5 when performed as a continuous process in which supported sodium is continuously supplied to the reaction vessel and solid reaction product material is continuously removed from the reaction vessel.

8. A process as claimed in any one of the preceding claims wherein the solid particulate carrier material is maintained in motion during the contacting of the halocarbon with the sodium, for example by stirring or by a fluidised bed procedure.

9. A process as claimed in any one of the preceding claims wherein the amount of sodium dispersed on the particulate support material prior to contacting with the halocarbon is from 1 and 50 weight percent, preferably from 5 to 15 weight percent.

10. A process as claimed in claim 1 substantially as hereinbefore described in each of the Examples and with reference to the accompanying drawing.

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Relevant Technical Fields		Search Examiner A KERRY
(i) UK CI (Ed.N)	C1P: PA, PE, PW	
(ii) Int CI (Ed.6)	A62D: 3/00	
Databases (see below)		Date of completion of Search 29 JUNE 1995
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.		Documents considered relevant following a search in respect of Claims :- 1-10
(ii) ONLINE DATABASES: WPI, CLAIMS		

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- Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.
- A: Document indicating technological background and/or state of the art. &: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
Y	WO 94/03237 A1	(EATECHNOLOGY) see Examples	1 at least
X, Y	EP 0467053 A1	(DEGUSSA) see Claims 1, 2; Examples	X: 1, 4, 5, 6, 8, 9 Y: 1 at least
X	US 4639309 A	see Claims 1-14; Examples	1, 4, 5, 6, 8, 9

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