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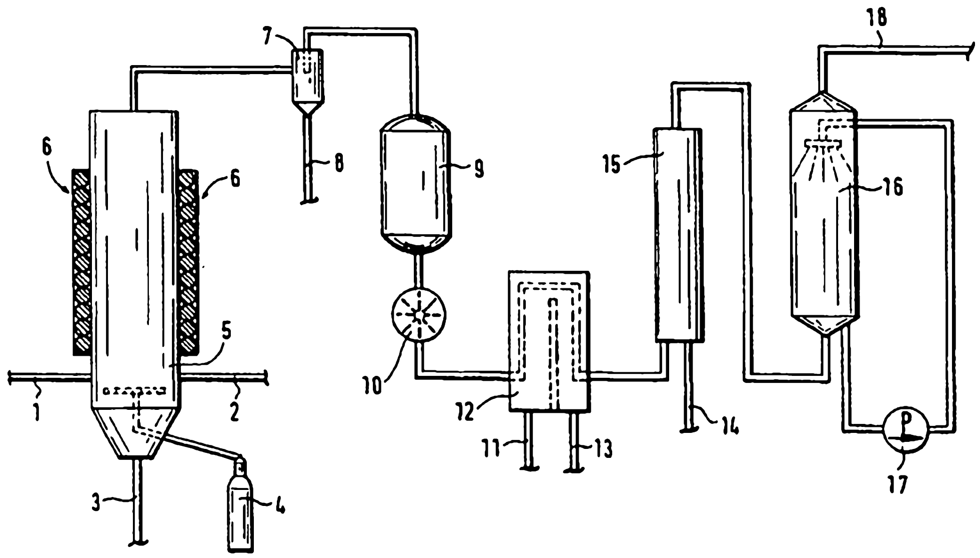
Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.

(54) Title: METHOD FOR ELIMINATING HALOGENATED AND NON HALOGENATED WASTE

(54) Bezeichnung: VERFAHREN ZUR ENTSORGUNG VON HALOGENIERTEN UND NICHT HALOGENIERTEN ABFALLSTOFFEN



(57) Abstract

Disclosed is a method for eliminating halogenated and non halogenated waste, whereby waste is reacted with products containing metal oxide in an oxygen-free medium at temperatures ranging from 800 °C to 1100 °C.

(57) Zusammenfassung

Verfahren zur Entsorgung halogenierter und nicht halogenierter Abfallstoffe, wobei die Abfallstoffe mit metalloxidhaltigen Produkten unter Ausschluß von Sauerstoff bei Temperaturen von 800 °C bis 1100 °C umgesetzt werden.

PROCESS FOR DISPOSING OF HALOGENATED AND NON-HALOGENATED WASTE SUBSTANCES

The present invention relates to a process for disposing of halogenated and non-halogenated waste substances.

Substituted, in particular halogenated hydrocarbons, such as are present for example in carbon tetrachloride, chloroform, methylene chloride, tetra- and trichloroethylene, tetrachloroethane, PCB etc., but also in PVC or polyvinylidene chloride, are a more or less problematical toxic or special waste following use, which has to be disposed of.

Substances with a strong toxic effect on the environment and man, such as halogenated compounds, in particular polyhalogenated substances such as PCBs or TCDD/TCDF (dioxins/furans) cannot be automatically recycled and have to be disposed of in an environmentally friendly manner.

The disposal takes place either by dumping or by incineration on the high seas or else on land in high-temperature furnaces with an excess of air.

The energy requirement is in many cases not inconsiderable, since not only do the substances to be disposed of have to be vaporised and heated to the required decomposition temperature, but enormous amounts of air also have to be heated up. In so doing either, as with incineration on the high seas, pollution of the atmosphere and the risk of acid rain have to be allowed for, or extremely expensive plants are required for keeping the air clean.

There is known from DE-A-33 13 889 a process or an apparatus for disposing of toxic and special waste, in which the toxic waste substances are mixed with an electrically conductive material, in particular in the form of iron powder and/or coke, and are brought in an induction furnace to the decomposition temperature of the toxic and/or special waste to be eliminated.

US-A-4 435 379 discloses a process for decomposing chlorinated hydrocarbons with metal oxides with the aim of converting all carbon atoms into carbon monoxide. It is a question here of providing elemental chlorine for the conversion of hydrogen groups into HCl. The overall ratio of chlorine to hydrogen groups must be at least 1 : 1 here, in order to be able to produce metal chloride.

US-A-4 587 116 discloses a similar process, in which nitrogen-containing waste substances can also be disposed of. The heating likewise takes place from the outside and not from the inside.

EP-0 306 540 discloses a process for recovering energy from substituted hydrocarbons such as are present e.g. as CCl_4, $CHCl_3$, $C_2H_2Cl_4$, PCB, PVC, polyvinylidene chloride etc. in pure or bound form. In this process the waste material is decomposed thermally in an inductively heated reactor in the presence of a barely treatable metal oxide and an electrically conductive material, for example electrode coke or electrographite, and in contact with water vapour at temperatures of between 800 and 1 100 °C. A portion of the metal oxide that corresponds to the chloride content of the waste materials is there converted into volatile metal chloride. A portion of the liberated carbon is converted into carbon monoxide and the portion of the carbon not reacting on the metal oxide is converted to water gas ($CO + H_2$) with the aid of a stoichiometric amount of water vapour.

It is the object of the present invention to develop a process which makes it possible to dispose of various halogenated and non-halogenated carbon-containing waste materials in an environmentally friendly manner.

This object is achieved according to the invention by a process for disposing of halogenated and non-halogenated carbon containing waste materials in which the halogenated and non-halogenated waste materials are reacted with metal oxide-containing products with the exclusion of oxygen at temperatures of 800°C to 1100°C. It must be emphasised in particular that carbon dioxide is added during the process.

The process described here can be used for the environmentally neutral recycling of halogenated and non-halogenated waste materials.

The volume of the wastes used is largely reduced, so that as few residues as possible remain and as large a quantity as possible of metals/metal compounds is obtained. As positive an energy balance as possible is aimed at during the reaction.

In a preferred embodiment of the process, carbon-containing halogenated waste materials are reacted.

Furthermore the reactor can also be supplied with carbon in the form of graphite and/or coal.

In a preferred manner a halogenatable metal oxide-containing product is used as a metal oxide-containing educt.

In a specific embodiment variant of the process according to the invention products which contain CaO, TiO_2, SiO_2, Al_2O_3 and/or Fe_2O_3 or a mixture thereof are used as halogenatable, metal oxide-containing reactants.

Various metal-oxide containing waste materials, such as silicon-containing residues from the metal-working industry, filter dusts, flue ashes, wind-blown sands, waste dumps, galvanic sludges, slags, slate residues etc., can also serve as reactants. Simple quartz, which consists about 98% of silicon dioxide (SiO_2), is the simplest possible material which can be use for the conversion.

All of the above-mentioned materials are characterised by the fact that they contain a relatively high content of halogenatable metal oxides (CaO, SiO_2, TiO_2, Al_2O_3, Fe_2O_3 etc..

This has the resultant advantage that materials containing metal oxides not treatable with economic agents to date now acquire a useful application.

Solvents such as carbon tetrachloride, chloroform, methylene chloride, tetra- and trichloroethylene, tetrachloroethane, coolants or refrigerants, PCB, pesticides, fungicides and herbicides, halogenated plastics such as PVC can be used as halogenated waste materials.

A portion of the metal oxide that corresponds to the chlorine content of the waste materials is converted into metal chloride by the above-mentioned process. Ecologically and economically useful metal chlorides are obtained, wherein silicon and titanium tetrachloride ($SiCl_4$, $TiCl_4$,) represent particularly preferred products.

Other materials such as spent oils, lubricants, fats, paints, dyes, tars, waxes, plastics, coolants and solvents, brake fluid or similar non-halogenated substances and materials can also be disposed of.

The reaction or conversion products preferably formed thermodynamically under these process parameters are hydrogen (H_2), which primarily occurs in gaseous form, together with smaller volumes in percentage terms of methane (CH_4).

The formation of environmentally dangerous or environmentally polluting, gaseous substances such as carbon monoxide (CO), as well as the carbon dioxide (CO_2) known as a so-called greenhouse gas, is, under the preferred reaction conditions, negligibly small. Only at temperatures above 1100°C can CO or CO_2 be formed by chemical decomposition processes.

The conversion takes place in a fluidised bed reactor. The latter can be constructed either from special ceramics, silicon carbide (SiC) or specially alloyed steels.

The reactor can be brought to the required operating temperatures either by the use of electric heating elements (e.g. heating half-shells) or by the use of an induction heater. The temperatures required for the conversion lie in the range from 800°C to 1100°C. The reaction itself takes place with the exclusion of oxygen. Carbon dioxide (CO_2) is used as the fluidising gas.

The halogenated compounds are decomposed into their simplest constituents by the high temperatures. In the case of chlorinated hydrocarbons, hydrogen chloride, hydrogen, alkanes and chlorine gas are formed. The chlorine gas and the hydrogen chloride serve as chlorinating agents for the metal oxide-containing products or wastes. Products of this chlorinating reaction are the thermodynamically preferred metal chlorides.

In addition to the chlorides, hydrogen and carbon monoxide are formed, which can be used as a synthesis gas either for the obtaining of electrical energy or for other chemical syntheses, for example the methanol synthesis.

$$2\,H_2 + CO = CH_3OH$$

Reaction equation 1

The carbon dioxide (CO_2) used as the fluidising gas is converted completely to carbon monoxide (CO) by reaction with the carbon of the decomposed hydrocarbons and by an additional coal or graphite charge in the top part of the reactor.

The so-called BOUDOUARD reaction is referred to in this context:

$$CO_2 + C = 2\,CO$$

Reaction equation 2

The formation of environmentally harmful compounds such as dioxins, furans or e.g. phosgene ($COCl_2$) is extremely improbable under the prevailing reaction conditions.

All the halogenated metal compounds produced are present initially in gaseous form. Depending on the starting material, solid, i.e. crystalline metal compounds can be obtained by cooling to room temperature, or else liquid metal compounds by condensation at low temperatures.

The degree of purity of these compounds is around 96% and can be further improved e.g. by a fractionating distillation, also called rectification.

Various embodiments of the invention will now be described below by means of the attached figures, where

Fig. 1 shows a diagram of the plant for disposing of halogenated waste materials.

In the diagrammatic flow-chart of the process, as shown in Fig. 1, a feed line 1 for the halogenated waste materials, a feed line 2 for metal oxide-containing products, and a line 3 for the discharge of unconverted materials 3 can be seen. A fluidising gas (CO_2) is blown into the fluidised bed reactor 5 via a feed unit 4.

The reactor 5 is heated by means of a reactor heater 6 to a temperature of between 800°C and 1100°C, so that a reaction between the halogenated waste materials and the metal oxide-containing materials takes place in the reactor. The products formed are separated in a solids trap 7, and the solid metal chlorides formed, in particular $AlCl_3$ and $FeCl_3$, are discharged via a line 8. The remaining gases are purified by an activated carbon filter 9 and then compressed by a fan 10. The gases are then cooled in a cooling tank 12, which comprises a coolant inlet 11 and a coolant outlet 13, so that the remaining metal chlorides are separated out. $SiCl_4$ is mainly involved here.

The gases are then fed to a condenser 15 and subjected to an alkaline gas scrubbing in a gas scrubbing column 16. The column 16 possesses a circulating pump 17 for the scrubbing fluid. The remaining synthesis gas, a mixture of CO and H_2, is discharged through the line 18 in the upper part of the gas scrubbing column 16.

The disposal of perchloroethylene (C_2Cl_4) and vinyl chloride (C_2H_3Cl, a monomer of polyvinyl chloride) as halogenated waste materials may be cited as an example of practical application. The conversion takes place with slate wastes from slate production as the metal oxide-containing product.

<u>Table 1</u>: Slate analysis from Martelange, Belgian-Luxembourg border region

Compound	Share in per cent (% w/w)
SiO_2	59.1
Al_2O_3	19.8
Fe_2O_3	8.2
Na_2O	2.5
CaO	2.4
K_2O	3.3
MgO	3.2
FeS_2	0.5
C	1

Prior to the processing the slate wastes are reduced in size by means of a jaw crusher. Mean grain sizes in the range from 3 – 8 mm are advantageous.

Application example 1: Disposal of vinyl chloride

The process engineering layout of the plant corresponds to the layout that has also been used for the disposal of perchloroethylene (PER). The underlying chemical reactions are described below.

During the reacting of vinyl chloride (C_2H_3Cl), as a monomer of polyvinyl chloride (PVC), with slate wastes the following chemical reactions occur, for example:

$$SiO_2 + 4\ C_2H_3Cl + 6\ CO_2 = SiCl_4 + 6\ H_2 + 14\ CO$$

Reaction equation 3

$$Al_2O_3 + 6\ C_2H_3Cl + 9\ CO_2 = 2\ AlCl_3 + 9\ H_2 + 21\ CO$$

Reaction equation 4

$$Fe_2O_3 + 6\ C_2H_3Cl + 9\ CO_2 = 2\ FeCl_3 + 9\ H_2 + 21\ CO$$

Reaction equation 5

There is therefore obtained as the total reaction equation:

$$SiO_2 + Al_2O_3 + Fe_2O_3 + 16\ C_2H_3Cl + 24\ CO_2 =$$
$$SiCl_4 + 2\ AlCl_3 + 2\ FeCl_3 + 24\ H_2 + 56\ CO$$

Reaction equation 6

The process engineering separation of the aluminium and the iron chloride ($AlCl_3$, $FeCl_3$) takes place on the one hand by centrifugal force deposition in a cyclone and on the other by deposition in special filters. The separation of the silicon tetrachloride takes place in the manner already described.

It is obvious from reaction equation 6 that in addition to the metal chlorides a synthesis gas consisting of carbon monoxide and hydrogen is formed. The ratio between hydrogen and carbon monoxide is 1 : 2.3. A so-called synthesis gas is spoken of here, which has many technical uses.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for disposing of halogenated and non-halogenated carbon-containing waste materials, wherein the waste materials are reacted with metal-oxide containing products with the exclusion of oxygen at temperatures of 800°C to 1100°C, and carbon dioxide is added during the process.

2. Process according to claim 1, characterised in that carbon is added during the process.

3. Process according to claim 2, characterised in that graphite and/or coal is used as carbon.

4. Process according to any one of the previous claims, characterised in that halogenatable metal oxide-containing products are used as a metal oxide-containing educt.

5. Process according to claim 4, characterised in that products which containing TiO_2, SiO_2, Al_2O_3, CaO and/or Fe_2O_3 or a mixture thereof are used as halogenatable metal oxide-containing materials.

6. Process according to any one of the preceding claims, characterised in that solvents, tetrachloroethane, coolants, refrigerants, PCB, pesticides, fungicides, herbicides or halogenated plastics are used as halogenated waste materials.

7. Process according to claim 6, characterised in that the solvent is carbon tetrachloride, chloroform, methylene chloride, tetra- or trichloroethylene.

8. Process according to claim 6 or claim 7, characterised in that the halogenated plastic is PVC.

9. Process according to any one of the preceding claims, characterised in that a portion of the metal oxide that corresponds to the chlorine content of the waste materials is converted into metal chloride.

10. Process according to any one of claims 1 to 9, characterised in that spent oils, lubricants, fats, paints, dyes, tars, waxes, plastics, coolants and solvents, brake fluid or similar non-halogenated substances and materials are used as non-halogenated waste materials.

11. Process for disposing of halogenated and non-halogenated carbon-containing waste materials, substantially as hereinbefore described with reference to the example and/or drawing.

Dated this 5th day of March 2002
PAC HOLDING S.A.
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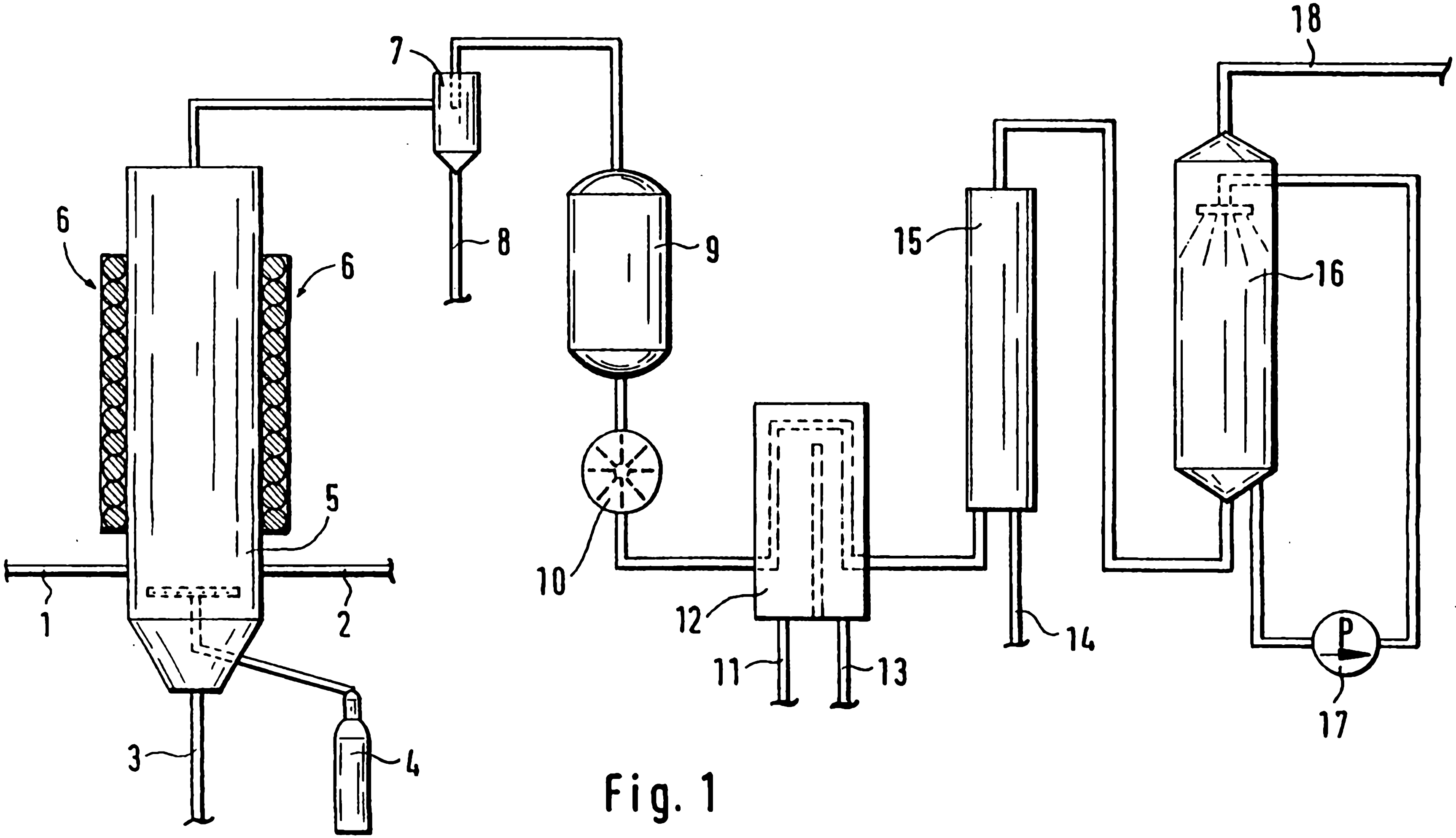

Fig. 1