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(54) **Destruction of carbonaceous material, and inert solid material formed by reaction of carbonaceous material with sulphur.**

(57) Carbonaceous material, such aspolychlorinated biphenyl, is rendered non-toxic by reaction with sulphur in an inert atmosphere at a temperature of 500 to 1500°C, so as to form an inert solid consisting essentially of carbon and sulphur, and being substantially free of unreacted carbonaceous material.

The resulting solid is an inert, refractory material which is non-flammable, substantially insoluble in all known solvents (including aqua regia) and electrically conductive.

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Destruction of carbonaceous material, and inert solid material formed by reaction of carbonaceous material with sulphur

This invention relates generally to a process for the safe destruction of toxic and hazardous chemicals and for the conversion of such chemicals to a safe inert and useful non-toxic polymer by-product.

BACKGROUND OF THE INVENTION

At the present time, the storage of hazardous and toxic chemicals such as polychlorinated biphenyl may be a very costly procedure to industry. Failures to properly dispose of such toxic chemicals has resulted in long term devastating effects to both local and distant environments. Polychlorinated biphenyl compounds (PCB) have been of great use as an insulating oil in the electrical industry because of its known highly-stable properties under high temperature, but its carcinogenic properties has created difficult long term disposal problems since it is very stable, non-flammable and non-biodegradable. Because of its dangerous effect on the environment when accidentally released, electrical utility companies plan to spend millions of dollars in replacing PCB in capacitors and transformers, but such replacements are, in effect, creating an even more severe problem in the safe disposition of the discarded PCB. A long felt want in the chemical industry has been a safe and reliable process of conversion of such toxic chemicals to inert useful material which will itself have economic value.

STATEMENT OF THE PRIOR ART

The prior art is exemplified by the following patents, (U.S. except where otherwise noted):
3,523,812 3,726,808 3,835,183 3,864,305 2,175,816 3,736,111 3,622,265 3,864,223 74,127,954 (JAPAN)

Such art is generally illustrative of various processes and chemicals in the field of the invention. While such processes and chemicals are usually acceptable for their intended purposes, they have not proven to be satisfactory for the task of reliably converting 100% of a toxic chemical such as polychlorinated Biphenyl (PCB) into a completely inert compound. As a result of the shortcomings of the prior art, typified by the above, there has developed and continues to exist a substantial need for the process of the character described. Despite this need, and the efforts of many individuals and companies to develop such processes, a satisfactory process meeting this need has heretofore been unavailable.

The principal object of this invention is to provide a process of this character which combines simplicity, and reliability together with inexpensiveness of operation and economies resulting from the sale of a useful inert by-product.

SUMMARY OF THE INVENTION

The invention is a chemical process for complete destruction and safe disposition of hazardous organic chemicals and halogen-polymers such as PCB. The invention also resides in the process for production of an inert polymer formed of essentially equal parts of Carbon and Sulfur. The new Carbon-Sulfur polymer has many of the properties of refractory materials and is an inert non-inflammable cross-linked polymer that is insoluble in organic solvents.

PCB and Sulfur is heated, in an atmosphere of Nitrogen at 500 to 1500°C. Waste gases containing sulfides are condensed, scrubbed and recycled. The solids residue when analyzed by a mass spectrometer contains less than one (1) part per million (1ppm) of unreacted polychlorinated biphenyl (PCB).

While the process of the invention will be described in terms of destruction of hazardous PCB, this same process is obviously effective in converting many other hydrocarbon polymers into an inert carbon/sulfide polymer refractory material

Reference will now be made to the accompanying drawing, which is an exemplary embodiment of the process of the invention.

The chemical waste material to be destroyed, an inorganic chemical or an organic chemical which is a halogen compound such as PCB, is added directly into reactor 20 or first heated in preheater 30 and heater 40 before being fed into the reactor 20. Fresh or recycled sulfur is introduced to heated melt tank 50 in which it is held in the melted condition and then fed into high temperature heater and or vaporizer tank 60 to be then fed into reactor 20. An inert gas such as nitrogen is also fed into the reactor 20 to maintain an inert oxygen-free atmosphere. Pressurized nitrogen gas may also be introduced into preheater 30, heater 40, melt tank 50 and high temperature tank 60 and employed to provide a pumping action to drive the waste liquid input and the sulfur into the reactor 20.

Reactor 20 is preferably a rotating screw type oven and heated preferably be electric induction heating coils to maintain a temperature in the range of 500 degrees C. to 1500 degrees C inside the reactor. Within a matter of minutes at this temperature, and in less than 5 minutes, the organic chemical and sulfur or the PCB and sulfur have completely reacted together to produce a black solid material that contains less than 1 part per million of unreacted organic chemical or PCB.

Further heating in the reactor, at the temperature range of 500 to 1500 degrees Celsius produces a black solid polymer product, the analysis of which, by weight, is as follows:

Carbon 49.01 %
Hydrogen 0.67 %
Sulfur 48.79 %
Unreacted PCB < 1 ppm by mass spectrometer

This black solid polymer compound of substantially equal weights of Sulfur and Carbon, I call carbon/sulfur polymer or CSP. Although the exact molecular structure in terms of molar ratios of Sulfur to Carbon has not been established of CSP, the following properties have been demonstrated by actual tests:

When ground to a powder, its appearance resembles carbon black
No observable melting point
Complete absorber of Ultra Violet and Infra-red light spectra
Not soluble in any known solvent
Not affected by Aqua Regia
An excellent electrical conductor

These properties suit the following useful applications:

Filler for non-corrosive coatings
Filler for solar energy absorber devices
Filler in body implants to resist physical changes caused by human biological effects
Electronic resistor and conductive applications
Filler for cements and asphalt.

In particular, the combination of electrical conductive properties, and absorption of infra-red light (radiant heat energy) and inert chemical characteristics are particularly suited for solar energy conversion devices including devices for producing photo-galvanic and thermo-electric conversion.

Uses of the sulfur and carbon composition which is a product of the invention include its utilization as an absorber of other radiant energy, its utilization as a conductor of electricity, its utilization as a refractory material, as well as its utilization as an inert filler material and as a filler in asphalt.

From the standpoint of economy, the process reaction in reactor 20 is largely exothermic at the temperatures above 500 degrees C., and therefor the process supplies much of the necessary energy. Furthermore the current nation-wide ecological emphasis on the use of coal-fired plants and coal gasification results in production of increased quantities of waste Sulfur that may serve as a source of supply to feed my process. Thus my invention may be considered to use up two waste products, PCB and sulfur, to produce a new inert product of economic potential.

As shown in FIG. 1, the vapor products consisting of sulfur vapor, and hydrogen sulfide, carbon di-sulfide, sulfur-chloride gases are fed into a sulfur condenser 70 which recycles condensed sulfur back to the melt tank 50. The remaining gases are then fed into conventional pollution recovery scrubber equipment 80, producing clean effluent gas that may be passed into the atmosphere and conventional chemical intermediates. The solid reaction product of carbon/sulfur polymer is fed into post reactor cooler unit 90, and may be then transferred to appropriate grinding and mixing equipment as desired for further use of the product.

Other by-products of my process include gases of hydrogen sulfide (H_2S), carbon disulfide (CS_2) and sulfur chloride ($S_x Cl_y$) which may be recovered and removed from the effluent by conventional methods. Sulfur vapors are also recovered and condensed and recycled through the process. The organic chemical to be disposed of is normally fed into the reactor at any temperature ranging from ambient to 650 degrees Celsius preferably through a nozzle or distributing spray although in some cases the feed temperature may range to 1100 degrees C. The sulfur is fed into the reactor as a melted liquid at a temperature ranging from about 135 degrees C. to about 450 degrees C. or fed into the reactor as a vapor at temperatures ranging from about 450 degrees C. to 1500 degrees C. through a nozzle or spray nozzle. Pressure of the inert nitrogen gas in the reactor is preferably maintained between 1 and 2 atmospheres.

Estimates of the efficiency and costs of my process indicate that a plant can be constructed at a cost of $26,000,000.00 of a capacity to safely dispose of 24 tons per day of PCB organic such as Westinghouse Company transformer oil "Inerteen 70-30" (ASTM specification D-2283 Type D). The operating costs of such a plant, not including interest and amortization nor credit for sale of by-product, would approximate $.72 per pound of PCB destroyed.

Including interest and amortization, the total costs per pound of PCB destroyed are estimated at $1.50 per pound, on the basis of a three year payout of investment.

It is though that persons skilled in the art to which this invention relates will be able to obtain a clear understanding of the invention after considering the foregoing description in connection with the

accompanying drawing. Therefor, a more lengthy description is deemed unnecessary. It is understood that various changes in shape, size, and arrangement of the elements of this invention as claimed may be resorted to in actual practice, if desired. While the process has been described in terms of conversion of Polychlorinated Biphenyl from a hazardous chemical to a useful inert material, it is equally appropriate for conversion, to an inert material, of other organic chemicals and polymers, including other halogen-hydrocarbon polymers by their reaction with sulfur at temperatures in the indicated range of 500 degrees C to 1500 degrees C

Claims

1. A process of destruction of a carbonaceous material, which comprises heating said carbonaceous material with sulphur in a substantially oxygen-free atmosphere at a temperature in the range 500°C to 1500°C so as to form an inert solid material comprising sulphur and carbon and containing unreacted residues of said carbonaceous material in an amount not exceeding a few parts per million; and separation said solid material from vapour phase material

2, A process according to claim 1, in which the carbonaceous material comprises a halogen compound

3. A process according to claim 2, in which the halogen compound comprises a polychlorinated biphenyl

4. A process according to any of claims 1 to 3, in which the heating is continued for a period of time so as to produce a solid composition consisting of substantially equal proporttions by weight of carbon and sulphur

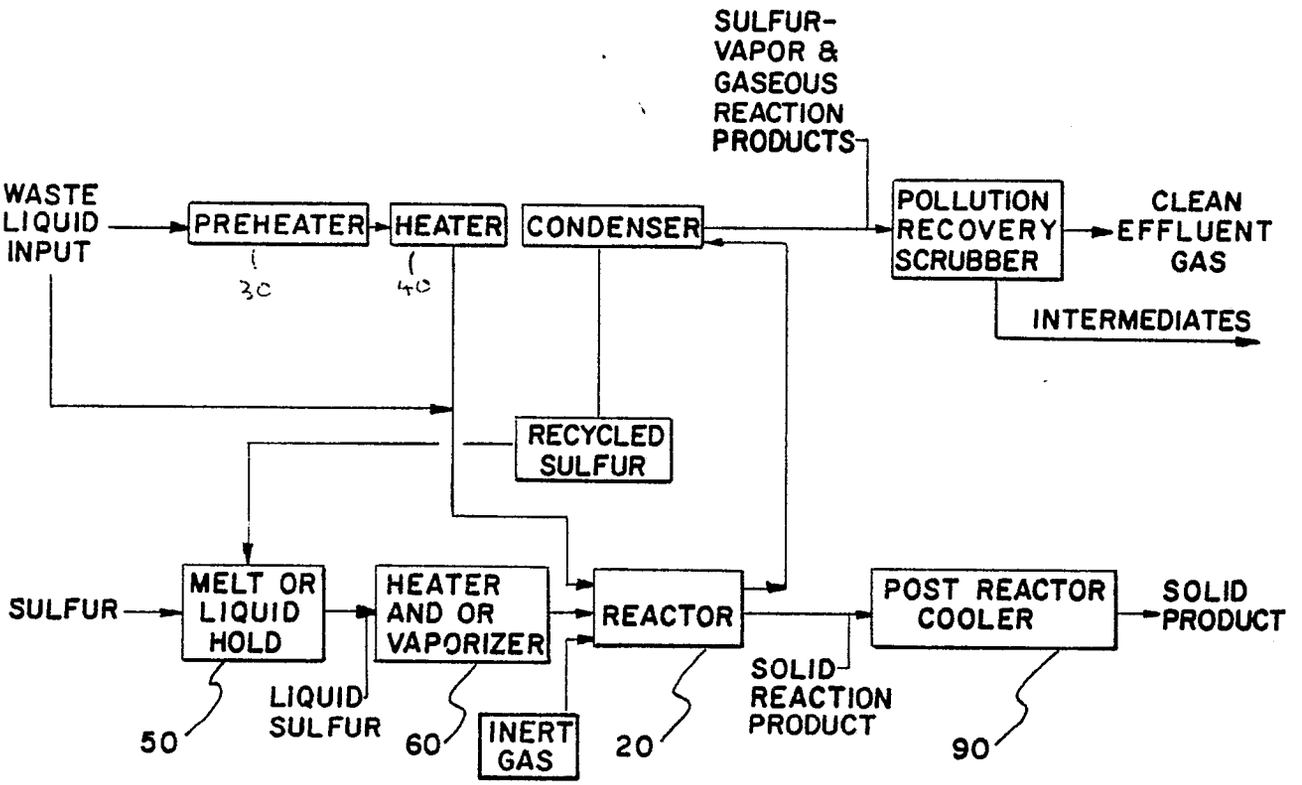
5. A process according to any of claims 1 to 4, wherein said sulphur is fed as a gas at a temperature of about 450°C to 1500°C

6. A process for the substantial destruction of a halogen containing organic material comprising:
supplying said material to a reaction zone under a substantially oxygen-free atmosphere at a temperature ranging from ambient to about 1100°C;
feeding sulphur to said zone at a temperature ranging from about 135°C to 1500°C to form a substantially inert solid reaction product containing carbon and sulphur and gaseous products; and separating said inert solid product from said gaseous products

7. A process according to claim 6, in which the said organic material comprises polychlorinated biphenyl compounds

8. A substantially inert solid material formed by reaction of sulphur with carbonaceous material at an elevated temperature in a relatively oxygen-free atmosphere,
which solid material is comprised of carbon and sulphur in approximate equal proportions by weight, said solid material being characterized as having no observable melting point, by being substantially unaffected by aqua regia, by being electrically conductive, and by containing little or no remaining residue of the said carbonaceous material

9. An inert solid material according to claim 8, in which the carbonaceous material is a polymer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EUROPEAN SEARCH REPORT

Application number
EP 86 30 1671

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
E	US-A-4 581 442 (H.W. ADAMS) * Claims *	1-8	A 62 D 3/00 C 08 G 75/14 C 08 G 83/00
D,A	CHEMICAL ABSTRACTS, vol. 82, no. 23, June 9, 1975, page 553, ref.no. 155718g; Columbus, Ohio, US & JP-A-74 127 954 (MITSUBISHI MONSANTO CHEMICAL CO.) 07-12-1974 * Abstract *	1-5	
D,X		6-8	
A	CENTRAL PATENTS INDEX, Basic Abstracts Journal, Section E, Week E13, March 1982, ref.no. 24635; London, GB & JP-A-82 029 373 (T. ITO) 17-02-1982. * Abstract *	1-8	TECHNICAL FIELDS SEARCHED (Int. Cl.4) A 62 D
A	CHEMICAL ABSTRACTS, vol. 85, no. 11, September 13, 1976, page 515, ref.no. 77762n; Columbus, Ohio, US S. OHAE: "Reaction between diphenyl sulfone and elemental sulfur and detoxication of polychlorinated biphenyls." & GENDAI KAGAKU 1974, 36, 20-7. * Abstract *	1-8	
A	US-A-3 491 046 (J.M. PACHUTA) * Column 1, lines 14-72; column 3, lines 53-63; examples 1-3 *	8	

Place of search	Date of completion of the search	Examiner
The Hague	19-10-1986	FLETCHER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid,

namely claims:

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

X LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,

namely: 1) Claims 1-8(a): When carbonaceous material is as defined in claims 2,3 and 7.

2) Claims 8(b),9: When carbonaceous material is a polymer

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid,

namely claims:

☒ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims,

namely claims: 1-8(a)