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(54) A process for the decontamination of apparatus or other materials contaminated by PCB or other toxic and noxious substances.

(57) A process for the decontamination of apparatus or other materials being contaminated with PCB or other toxic and noxious substances, comprises introducing the contaminated apparatus or material into an autoclave provided with a condenser, charging a liquid solvent to the autoclave to fill it up, applying an ultrasonic charge to the autoclave containing the liquid solvent, removing the dissolved contaminant-containing solvent from the autoclave while producing a vacuum, admitting solvent vapors to the autoclave until they reach the top part of the autoclave where the solvent vapors condense and commence to drop off, stopping the solvent vapor admission and repeating the above steps a few cycles.

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A PROCESS FOR THE DECONTAMINATION OF APPARATUS OR OTHER MATERIALS CONTAMINATED BY PCB OR OTHER TOXIC AND NOXIOUS SUBSTANCES.

This invention relates to a process for decontaminating apparatus, particularly electrical apparatus, contaminated by toxic and noxious substances.

Included among noxious contaminants are arsenic compounds, chlorinated compounds, etc., but especially polychlorobiphenyls and dioxin.

As is known, polychlorobiphenyl (PCB) has physical and chemical properties which make it very suitable for a large range of applications. In general, aromatic chlorinated compounds possess very good chemical and dielectric properties and heat stability. In particular, polychlorobiphenyls are very stable, in general chemically inert, compounds and they do not react under normal conditions, so that only when in presence of reagents and under extreme reactive conditions they give rise to the formation of new compounds.

Accordingly, PCB was used as an electro-insulating fluid for transformers and condensers, as an industrial fluid for use in coolants for machine operations, in hydraulic systems and vacuum pumps. It is also utilizable as a flame retardant, heat transfer agent and plasticizer.

Unfortunately, some of the properties of PCB that

contribute to its spreading range of applications are also involved in sanitary and ecologic problems recently abscribed to the use of polychlorobiphenyls. PCB are a class of compounds which, even though present in small amounts, are very toxic towards living cells and they produce systematic toxic effects. Comparatively recent research work has shown PCB as being a possible carcinogen and inducing neoplastic changes in mice.

PCB accumulates in aliments owing to its solubility in fatty tissues and its resistance to chemical degradation. Basically, the problems with BCB are that PCB is soluble in fats, is stored in animal lipids and tends to be concentrated in foods in high quantities. Moreover, resistance of PCB to thermal, chemical and biological degradation has contributed to its accumulation, particularly in industrial environments. The very low biodegradation rates and the high resistance to metabolic changes of PCB are causes for ecologic and pollution problems, so that measures have to be taken for elimination thereof. The system only used for eliminating PCB is incineration but incinerators are very expensive and cause further problems to arise. PCB is usually destroyed by incineration at high temperatures, say in excess of 1100°C with long residence times in the incinerators being required. The ordinary incinerators, as used for eliminating organic matters,

normally tend to vaporize PCB rather than converting it to CO_2, water and HCl. Obviously, other toxic and objectionable substances exist which are very hard to eliminate and materials contaminated thereby require likewise special measures for elimination thereof.

Thus, there is a need for other methods of disposal of apparatus, particularly electrical apparatus, when contaminated by PCB and other contaminating substances. For example, most of them are presently buried into pits or caverns.

Accordingly, a different decontamination system for such apparatus has to be found which also should permit reutilization thereof without involving any dangers to the persons who have to manipulate them, or to the environment.

Most recently proposed processes for the decontamination of apparatus contaminated with PCB and other toxic andnoxious substances have provided for consecutive washings with liquid solvent at atmospheric pressure to dissolve as high an amount of contaminant as possible in the liquid solvent, the contaminant being then eliminated and the solvent recovered. In the following, the term 'contaminant' is intended to include PCB and all other toxic and noxious substances such as dioxin, arsenic compounds, etc..

However, the above processes have not proven

satisfactory in that, as already said, the involved contaminant is a chemical compound hard to dissolve, and this is especially so when apparatus to be decontaminated have parts to which access by solvent is difficult.

Other processes are also known which provide for washing the apparatus with solvent, the washing being effected in a vapor phase and under vacuum. These processes have proven satisfactory in that they succeed in removing contaminant from an apparatus to bring it down to an amount less than that accepted by ecological defense authorities. However, a disadvantage of these processes is the time they require for the decontamination of an apparatus, which time is in any case, under best operating conditions, of the order of not less than 48h.

Accordingly, an object of this invention is to obviate also this latter disadvantage by providing a process for the decontamination of apparatus contaminated with toxic and noxious substances which requires a very reduced time over that involved in said other processes, while retaining efficiency of these latter.

Another object of this invention is to provide a process for the decontamination of apparatus which enables recovery of the solvent to be achieved in an automatic cycle without requiring any integrating distillation.

More specifically, the process according to this

invention for the decontamination of apparatus being contaminated by toxic and noxious substances, is characterized in that it comprises :

- introducing the apparatus to be decontaminated into an autoclave provided at the top with a condenser and closed to tightness,
- charging a liquid solvent into the autoclave until filling it up,
- applying a ultrasonic discharge to the autoclave containing the liquid solvent,
- withdrawing the dissolved contaminant-containing solvent from the autoclave so producing a vacuum simultaneously,
- admitting solvent vapors to the autoclave until they reach the top part of the autoclave where the solvent vapors are condensed and begin to drop off,
- stopping the admission of solvent vapors and repeating the above steps for a few cycles.

Advantageously, the liquid solvent is introduced into the autoclave at room temperature.

Preferably, the solvent vapors admitted to the autoclave subsequent to the step of discharging the liquid solvent and simultaneously producing a vacuum, are at a temperature of minus 100°C, more preferably of 40° to 80°C.

This method permits an apparatus to be decontaminated

in a matter of a few hours, the apparatus being decontaminated to a residual contaminant content of less than 50 ppm.

The invention will now be described in full details in connection with a preferred embodiment thereof shown by way of a non restrictive example in the accompanying drawing, wherein the single figure diagrammatically shows a plant for carrying out the process of the invention.

Referring now to the drawing, there is illustrated a plant that comprises an autoclave A having a condenser C at its upper part, the condenser C forming a top wall for said autoclave. Provided in this top wall is a check valve V6 permitting the air in the autoclave to pass out thereof. An apparatus to be decontaminated, such for example as an electric transformer generally designated at T, is introduced into the autoclave by the aid of a basket D.

An orifice E is provided in the bottom of the autoclave and communicates the autoclave with an outlet pipe U branching into three pipe legs R1, R2, R8.

The pipe leg R1 is connected via a valve V1 and a circulating pump P1 to a pure liquid solvent tank SL, the pipe leg R2 is connected via a valve V2 and a circulating pump P2 to a tank SR for collecting the solvent having the contaminant dissolved therein, while the pipe leg R8 leads to discharge via a valve V8.

The collecting tank SR is connected through a pipe 43 and associated pump P3, to a distillation column Z which is designed for the distillation of the contaminant-containing solvent and from which pure solvent fractions in the form of vapors are supplied through a pipe R4, a pump P4 and a three-way valve V4, to either the condenser CO via a pipe R5, or the inlet G to autoclave A via a pipe R6. The pure solvent vapors condensed in condenser CO are supplied to the pure solvent tank SL through pipe R7 and pump P7. A valve V5 permits the residues of distillation to be discharged.

Mounted on the outside of autoclave A is an ultrasonic generator US which operates to cause a short ultrasonic discharge to pass through the autoclave walls with the purpose of enhancing solubility of contaminant in the solvent and ability of the solvent to penetrate porous materials.

Operation of the plant is very simple.

Once the transformer T has been introduced in the autoclave A, the autoclave A is closed to tightness and supply of pure liquid solvent from tank SL to the bottom of autoclave A commences to take place through pipe branch R1 and tube U via circulating pump P1 and valve V1, the valves V2 and V8 being closed. Upon the liquid solvent coming into contact with the transformer contaminated by toxic and noxious substances, the solvent commences to

dissolve said substance. When the solvent has reached the top wall of autoclave A, valve V1 is closed and a ultrasonic discharge is effected from ultrasonic generator US whereupon valve V2 is opened so that liquid solvent, with the contaminant dissolved therein, is withdrawn by extracting pump P2 to be conveyed to receiving tank SR. During this extraction of solvent from autoclave, a vacuum is produced therein due to the autoclave being thoroughly closed to tightness. Once the liquid solvent has been drained off the autoclave A, valve V2 is closed and thereafter valve V4 is opened to permit a stream of hot (50° - 80°C) solvent vapors from distiller Z to be admitted to the autoclave via the pipe R6. The solvent vapors flow upwardly and upon reaching the top of autoclave they commence to condense under effect of condenser C to fall down in the form of droplets. At this time, a signal is issued from a level indicator ML and causes valve V4 to be operated so as to to permit solvent vapors to enter the condenser CO whereupon condensed pure liquid solvent formed in this condenser is supplied back to tank SL through pipe R7 and pump P5. The solvent vapors injected into the autoclave act on the treated apparatus in such a manner as to remove contaminant particles from the most hidden interstices of said apparatus. At this time, valve VI is reopened to admit again fresh liquid solvent to the autoclave

via the circulating pump P1.

The fresh liquid solvent entering the autoclave causes the solvent vapors still contained therein to condense and this condensate is mixed with the liquid solvent which is rising to fill the autoclave A.

The procedure described above is repeated for a two-three cycles until the amount of contaminant on the apparatus or the material is reduced to below 50 ppm. The time for performing this process of decontamination is about 10h, which is far below that required by the prior art decontamination processes.

The most suitable solvents for use in the process of this invention are, in general, the chlorinated compounds of paraffinic or olefinic hydrocarbons which have a high dissolving power towards the above mentioned contaminants, in particular use being made of perchloroethylene for the olefinic chlorinated hydrocarbons and of 1,1,1-trichloroethane for the paraffinic chlorinated hydrocarbons.

Recovery of these solvents is quite easy to obtain so that the plant can be expected to be operating on a thoroughly automatic cycle.

To this end, a control station can be provided which is designed to govern all of the decontaminating and other related operations in a predetermined automatic sequence such that a very reduced personnel is required for

operation of the plant.

Furthermore, with the process of the invention the apparatus or the material to be decontaminated is always immersed in the solvent.

Of particular importance in this respect is the ultrasonic discharge whereby a pulsating movement is transmitted to the liquid solvent to cause it to penetrate more and more deep the inaccessible recesses or interstices in the apparatus or material to be treated, such that, upon extracting solvent from the autoclave the extracted solvent already contains contaminant to a large amount.

It is to be noted that the expression "other materials" in this context is intended to include, in addition to apparatus, also, for example, a PCB- or dioxin-contaminated soil which will be thoroughly reclaimed by this process.

From the above, it will be appreciated that the process of the invention offers a number of advantages over the prior art processes, the most significant advantages residing in that :

- the time of treatment is substantially reduced due to the alternate use of liquid-phase and vapor-phase solvent-extraction steps,
- recovery of the solvent is achieved on an automatic cycle-base without requiring any integrating process of distillation, the removed contaminant being collected

immediately,

- decontamination of apparatus or materials is achieved to a drastic extent due to the action of the ultrasonic discharge which is used as an integrating and basic technique of the inventive process to cause the liquid solvent to penetrate the most inaccessible interstices or recesses of the material to be decontaminated,
- a vacuum is produced by merely draining the autoclave.

Although a preferred embodiment of the invention has been disclosed herein above, it is to be intended that changes thereto, such as might readily occur to one skilled in the art, are possibile without departing from the spirit and scope of the invention.

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CLAIMS

1. A process for the decontamination of apparatus or other materials contaminated by toxic and noxious substances, in particular PCB and dioxin, characterized in that it comprises :-

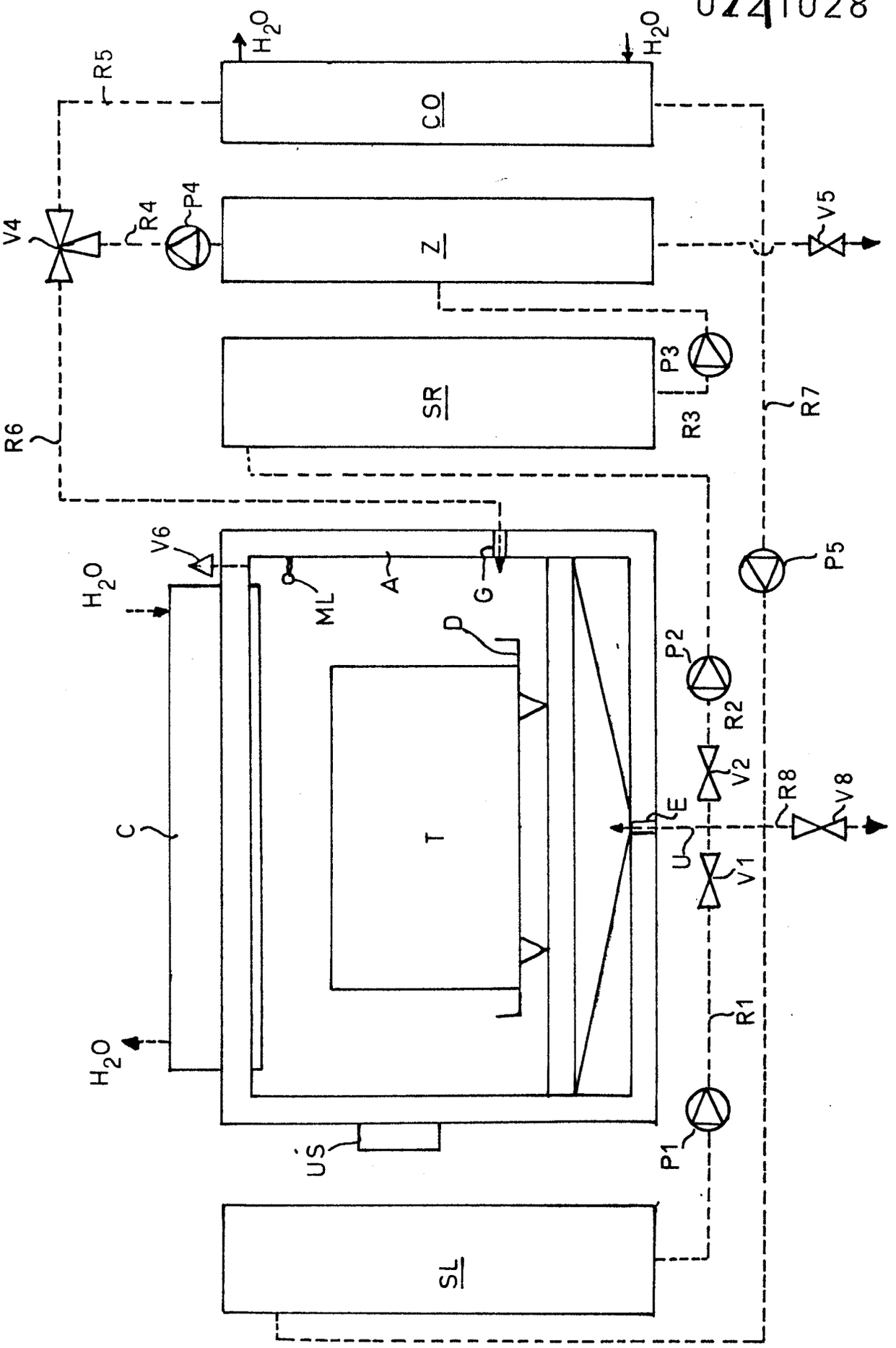
- introducing the apparatus to be decontaminated into an autoclave which is provided at its top with a condenser and which is tightly closed,
- admitting a liquid solvent to the autoclave to fill it up,
- applying a ultrasonic discharge to the autoclave containing the liquid solvent,
- removing the dissolved contaminant-containing solvent from the autoclave while simultaneously producing a vacuum,
- admitting solvent vapors to the autoclave until the solvent vapors reach the top part of the autoclave where they are condensed and commence to drop off,
- stopping admission of solvent vapors and repeating said steps for a few cycles.

2. The process according to claim 1, wherein the liquid solvent is charged to the autoclave at room temperature.

3. The process according to claim 1, wherein the solvent vapors admitted subsequent to the step of discharging the liquid solvent and simultaneously producing

a vacuum, are at a temperature of less than 100°C, preferably at a temperature in the range of 40° to 80°C.

4. The process according to any of the preceding claims, wherein perchloroethylene or 1,1,1-trichloroethane is used as the solvent.


H2O
H2O
R5
CO
V4
R4
P4
Z
V5
SR
P3
R3
R6
R7
V6
H2O
ML
A
G
P5
P
P2
R2
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EUROPEAN SEARCH REPORT

0221028
Application number

EP 86 83 0132

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)
Y	EP-A-0 098 811 (DECOMAN) * Page 5, line 24 - page 6, line 16; page 7, line 1 - page 8, line 23; claims *	1-4	A 62 D 3/00 B 08 B 3/08 H 01 F 27/14
Y	US-A-3 435 835 (N.L. HOBBS) * Column 2, line 19 - column 3, line 36; claims *	1-4	
A	US-A-4 483 717 (J.H. OLMSTED et al.) * Column 2, line 50 - column 4, line 13; claims *	1-4	
A	DE-A-3 339 048 (N.E.A.) * Claims 1-4; page 10, lines 1-19 *	1,2	
A	US-A-4 425 949 (E.A. ROWE) * Column 3, line 58 - column 5, line 15; claims *	1-4	A 62 D B 08 B H 01 F

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	08-01-1987	FLETCHER A.S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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