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⑤④ **Process for dehalogenation of organic halides.**

⑤⑦ Halogenated species such as PCB dissolved in hydrocarbon-based oils such as electrical insulating oils, turbine oils and crankcase oils are dehalogenated by contacting the oil with a fine dispersion of molten sodium particles of which at least 80% are below 10 microns particle size, at a temperature of 100 to 160 °C. The process removes hazardous halogenated species and, after separation of excess sodium suspended solids and, if necessary, water washing, drying, and activated clay treatment, may permit the oil to be re-used.

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PROCESS FOR DEHALOGENATION OF ORGANIC HALIDES

Polychlorinated biphenyls (PCB) have been identified as environmental hazards and possible carcinogens. Therefore the manufacture and sale of these materials in some territories, e.g. North America, is now prohibited. Fluids contaminated in excess of 25 mg/kg with PCB are considered environmentally hazardous and need to be stored until such time as a PCB destruction facility is available. Considerable resources are being expended in the containment and monitoring of PCB and PCB contaminated wastes, both liquid and solid.

Proposed combustion methods for waste disposal will, if adopted, result in the sacrifice of large volumes of oils such as premium quality insulating oils having an economic value. There is thus a need for a process which is capable of selectively destroying PCB in oils such as electrical insulating oils without adversely affecting the important physical and electrical properties of the oil.

This invention relates to a process for the dehalogenation (destruction) of polychlorinated biphenyls and polychlorinated benzenes such as are found in electrical insulating oils contaminated with compounds generically classified as askarels. The process of the invention can

also be used to decontaminate PCB contaminated solid wastes using oil as a solvent and/or for the destruction of concentrated PCB waste liquids by dilution in oil.

5 The process disclosed hereinafter may more generally be applied to the dehalogenation and destruction of organic halides including hazardous halogenated wastes such as organic halide-containing wood preservatives and pesticides.

10 It is known from an article by A.A. Morton et al "Condensation by Sodium Instead of by the Grignard Reaction III. Tertiary Carbinols and Acids" JACS, Soc 53, pages 4028 - 4033 (1931) that chlorobiphenyl may be reacted with metallic sodium, in the form of sodium wire or ribbon, under ice cold conditions or with gentle
15 warming, in the presence of ethyl carbonate or ethyl benzoate, with or without additions of benzene, to obtain low or medium yields of biphenylcarbinols.

20 It is also known from R.L. Menville et al "Determination of Organic Halides with Dispersed Sodium" Anal Chem 31, pages 1901 - 2 (1959) that organic halides may be reacted with "dispersed sodium", (which may be prepared as described in Moeller, T., ed., "Inorganic Synthesis" Vol V, p.6 McGraw Hill, New York, 1957) in solvents such as benzene, toluene, and xylene, to give quantitative yields
25 of water-extractable halides.

It has, however been reported by Pytlewski L.L., et al., Proc. 6th Annual Symposium on Treatment of Hazardous Waste, EPA Report EPA-600/9-80-011 (Sept. 1980) that
30 whereas vigorously stirred solutions of sodium in polyethylene glycol dechlorinate organic chlorides at temperatures above the melting point of liquid sodium (97.28°C), dechlorination does not occur when the

polyethylene glycol is replaced by non-polar, low volatility liquids such as Nujol (a relatively highly viscous non-polar white paraffinic mineral oil of petroleum origin).

- 5 Further it has been reported by Parker D.K., et al.,
Unnumbered Research Report, Goodyear Tire and Rubber Co.,
Akron, Ohio, (August, 1980) that metallic sodium treatment
of heat transfer hydrocarbon oils contaminated by 76 ppm
PCB does not reduce the PCB content below about 49 ppm
10 even after heating for 6 hours unless the mixture is
heated to a temperature of 300°C.

It has now been found that organic halides dissolved in
hydrocarbon-based oils may be effectively dehalogenated at
temperatures ranging from about 100°C up to about 160°C by
15 maintaining the solution under agitation in a mixture with
a fine dispersion of molten sodium particles of which at
least 80% are below 10 microns particle size, whereby the
organic halide groups are reduced to sodium halide.

In the preferred form, the fine dispersion of molten
20 sodium particles is formed by pre-dispersing metallic
sodium under vigorous agitation in a relatively smaller
quantity of a hydrocarbon-based oil the same as or
compatible with the oil to be treated, at a temperature
above the melting point of sodium and preferably in the
25 range 105°C to 160°C, and the pre-dispersion is added to
the bulk of the oil containing the organic halide to be
dehalogenated.

Of particular interest for present purposes is the
treatment of electrical insulating oils contaminated with
30 organic halides. When the present process is applied to
such oils, it has been found that the resulting reaction
mixture, after removal of unreacted sodium, suspended

reaction products and sludges and, if necessary, water-washing, drying and activated clay treatment, has electrical and physical properties which render it re-usable as electrical insulating oil.

- 5 The process is also applicable to other hydrocarbon-based oils such as turbine oils and crankcase oils. In the case of treatment of used crankcase oils, however, the treatment is accompanied by a significant increase in viscosity which renders the application of the process
10 more difficult.

The present invention will now be more fully described, by way of example only, with reference to the accompanying drawings which show schematically one form of apparatus for carrying out the dehalogenation process.

- 15 In order to obtain a satisfactory degree of dehalogenation of the organic halides, it has been found necessary to react the organic halides with a very fine dispersion of molten sodium particles. In this very fine dispersion, at least 80% of the sodium particles should be below 10
20 microns particle size. More preferably, at least 90% of the particles should be below about 10 microns and at least about 65% should be less than 5 microns particle size. These very fine dispersions are best prepared by pre-dispersing sodium at temperatures above its melting
25 point in a relatively smaller volume of the oil to be treated, or an oil compatible therewith and which will not render the eventual product unusable for its intended purpose. The resulting very fine dispersion is then blended with a larger volume of contaminated oil, in order
30 to provide a reaction mixture containing a desired ratio of sodium to reducible organic halide. Attempts to form the fine dispersion directly, by vigorous agitation of sodium metal introduced into the bulk of the oil to be

treated, are subject to the disadvantage that it may be impossible to form a dispersion of the desired degree of fineness without incorporating excessive quantities of sodium into the mixture, and without prolonged agitation at very high shear rates, thus leading to excessive consumption of sodium and wastage of power required for agitation of the bulk of the oil to be treated.

In the preferred form, in order to form the pre-dispersion, lump metallic sodium or liquid metallic sodium is added to dried oil in a quantity sufficient to yield a dispersion containing about 5 to 50% by weight sodium. The use of less than about 5% by weight sodium is usually inefficient, as then greater quantities of the pre-dispersion are required to achieve the desired molar ratios of sodium to reducible halogen, while with quantities of sodium much greater than about 50%, it is difficult to achieve a satisfactory dispersion. Preferably, a weight of sodium sufficient to achieve an about 30% concentration is employed.

The oil in which the pre-dispersion is to be formed may be a fresh, uncontaminated oil, or may be oil which is contaminated with organic halide material. Desirably, in order to avoid excessive wastage of sodium, the oil is substantially dry and, if necessary, it is pre-dried either by heating or by vacuum degassification so that its moisture content is less than about 100 mg/kg. During the formation of the pre-dispersion, the oil is maintained at a temperature above the melting point of liquid sodium, preferably in the range 105°C to 160°C. Below about 105°C, there is increased difficulty in obtaining a satisfactory dispersion, as the sodium particles tend to agglomerate together to form masses and it may not be possible to form a dispersion of the desired particle size range even with prolonged agitation. Temperatures much

above about 160°C are undesirable, as there is an increased tendency for degradation of the oil through thermal cracking and oxidation. Preferably, the dispersion is formed at a temperature of about 120°C.

- 5 The vessel in which the dispersion is formed, and all other vessels and processing equipment subsequently employed in the process with which the metallic-sodium-containing mixtures come into contact, are desirably formed or are lined with materials inert with respect to
10 liquid sodium e.g. mild steel, stainless steel, or glass.

The mixture of sodium and oil is subjected to vigorous agitation for a period sufficient to produce a fine sodium dispersion of the required particle size distribution. The particle size distribution of the resulting dispersion
15 can be readily determined using conventional optical particle counter apparatus, for example a HI-AC (Trade Mark) machine and the conditions of agitation and period of time required to produce the desired particle size distribution can be readily determined in any given case
20 by trial and experiment. By way of example, it may be mentioned that in the case of dispersions containing 5 - 50% by weight sodium, a satisfactory dispersion may be obtained after 10 - 15 minutes agitation in a modified one litre WARING (Trade Mark) blender utilizing a bottom drive
25 four blade impeller operated at 20,000 rpm. Alternatively, a top drive impeller equipped with either a Cowles Dissolver (Trade Mark) head or a Premier Mill Dispersator (Trade Mark) head may be used.

As noted above one preferred class of oils to be treated
30 by the present process are contaminated electrical insulating oils. The properties of oils which are designated as "electrical insulating oils" are well understood by those skilled in the art, and one skilled in

the art can readily determine whether or not a given oil is an electrical insulating oil. For the avoidance of doubt, as used herein the term "electrical insulating oil" refers to mineral electrical insulating oils of petroleum origin for use as insulating and cooling media in electrical power and distribution apparatus such as transformers, regulators, reactors, circuit breakers, switch gear, and attendant equipment.

Desirably, electrical insulating oil should conform to the specifications set out in Table 1, as determined by the relevant ASTM test procedures. Preferably, the oils employed in the present process conform to these specifications.

TABLE 1

15	Dielectric strength (ASTM D 877)	- more than 20 kv (at water content less than 20 mg/kg)
	Relative density at 15°C (ASTM D 1298)	- 0.8 to 0.92
	Pour Point	- -60°C to -10°C
20	Viscosity at 40°C (ASTM D 445)	- 8 to 14 centistokes
	Flash Point (ASTM D 92)	- 140 to 200°C

A further example of a class of oils which may be treated by the present process is turbine oil. These are usually sulfur-free mineral oils of petroleum origin employed as a lubricant medium in steam turbines, electrical generators

and other rotating equipment systems. Preferably, the turbine oils conform to the specifications set out in Table 2.

TABLE 2

5	Pour Point	-40°C to 0°C
	Viscosity at 40°C (ASTM D 445)	25 to 70 centistokes
	Flash Point (ASTM D 92)	180 to 250°C
10	A further example of a class of oils to which the process may be applied is crankcase oil i.e. oil used as internal combustion engine lubricant. Preferably, these conform to the specifications set out in Table 3.	

Table 3

15	Viscosity at 100°C (ASTM D 445)	4 to 20 centistokes
	Viscosity at -18°C (ASTM D 445)	<u>≤</u> 9600 centistokes
	Flash Point (ASTM D 92)	150 to 240°C
20	Pour Point	-50 to -5°C

The dehalogenation of organic halides by fine liquid sodium particles does not occur satisfactorily in silicone-based electrical insulating oils and therefore in
25 the present process hydrocarbon-based oils are employed.

In one example of a process in accordance with the invention, as illustrated in the accompanying drawings, PCB-contaminated electrical insulating oil or other hydrocarbon-based oil to be treated is stored in a storage vessel 10 from which it is transferred by a pump P₁ along a line 11 to an enclosed reactor vessel 12 preferably of steel. The vessel 12 is equipped with a low speed impeller 13, heaters 14, and an exhaust condenser 16. A line 17 is provided connected to a cylinder 18 of nitrogen or other inert gas which is slowly bubbled into the mixture to exclude air and form a blanket of inert gas to reduce losses of the subsequently-introduced sodium through oxidation. The condenser 16 removes organic vapours from the exhaust nitrogen or other inert gas. To avoid excessive production of hydrogen gas on addition of the sodium, and to avoid excessive sodium consumption, the oil in the storage vessel 10 is desirably pre-dried, if necessary, to less than 100 mg/kg water either by heating or by vacuum degassification.

20 With the oil in the vessel being maintained under moderate stirring sufficient to ensure intimate mixing and to prevent settling of the sodium dispersion, the pre-dispersion, prepared as described above is introduced into the reactor through a line 19.

25 Before the introduction of the suspension, the oil contained within the reactor vessel 12 is heated to a temperature in the range of 100 - 160°C. At temperatures below 100°C, the reaction times needed for substantially complete reduction of the organic halide groups to sodium halide tend to be excessively long, and there is a risk of the liquid sodium particles tending to agglomerate together to form agglomerated masses. It is important that the dispersion of sodium particles should remain in the form of dispersed particles of fine particle size, as

with particles of greater size, the reaction is much less effective. Without wishing to be bound by any theory, it is believed that the reduction in the rate and efficiency of the dehalogenation process with particles of increased size is due to the coating of such large particles by reaction products thus hindering or preventing further reaction. In any event, it is found that with larger sodium particles, for example of 100 microns particle size, the dehalogenation process is much less effective.

10 The use of a dispersion such that at least 80% of the particles are below 10 microns particle size, more preferably with at least about 50% of the particles below about 5 microns particle size, is a highly important factor in obtaining a satisfactory dehalogenation

15 reaction. The oil the reactor vessel should not be heated to temperatures much in excess of about 160°C, as at higher temperatures there is increased risk of degradation of the oil through thermal cracking and oxidation. Preferably, the reaction mixture is maintained at a

20 temperature of about 110°C to about 130°C.

Sufficient of the dispersion is added through the line 19 to the volume of oil contained in the reactor 12 to provide in the reaction mixture a molar ratio of sodium to reducible chlorine in the range about 2:1 to 30:1. Below

25 this range of sodium contents, satisfactory dehalogenation is not likely to be achieved, while contents of sodium higher than the above mentioned range do not appear to add to the effectiveness of the reaction and merely result in excessive consumption of sodium. Preferably, the molar

30 ratio of sodium to reducible halogen is in the range about 4:1 to about 8:1.

Although oil solution containing greater than 10% by weight of dissolved halogenated species can be treated by the present process, greater quantities of the sodium

dispersion need to be added to the oil and this may render it more difficult to maintain intimate mixing of the stirred reaction mixture. It is therefore normally preferred to employ oils containing no more than about 10% by weight dissolved halogenated species. Employing the present process the oil can be substantially wholly dehalogenated to achieve final concentrations of organic halide species of less than about 5 mg/kg, more usually less than about 2 mg/kg within about 15 to 240 minutes. In the preferred form, the dehalogenation is complete in less than about 30 minutes.

On completion of the reaction, the reaction mixture is pumped by a pump P₂ along a line 21 to a solids-liquids separator device, for example a centrifuge C₁. Desirably, a centrifuge capable of maintaining a minimum relative centrifugal force of 210 G at the periphery of the centrifugal plates is employed. At the centrifuge C₁, the solids i.e. unreacted sodium, suspended reaction products and sludges are removed from the oil. The removed solids are passed along a line 22 and are collected in a collection vessel 23. If desired, the solids collected in the vessel 23 may be subjected to a conventional treatment for recovery of metallic sodium therefrom before being disposed of as waste.

The liquids separated at the centrifuge C₁ may be passed along line 25 to a quenching vessel 24 where any remaining traces of sodium are quenched with water introduced through a line 26. If the oil has not cooled sufficiently through its passage through the centrifuge C₁, it is permitted to cool below about 95°C before contact with the water, to avoid excessively vigorous reaction. In the vessel 24, the mixture of oil and water is maintained under agitation by a stirrer 27, and the oil is washed free of any remaining traces of sodium and of soluble

reaction products such as sodium halide and sodium soaps of acidic oil components. The oil and water mixture is pumped by a pump P_3 along a line 28 to a further centrifuge C_2 where the heavier water phase is separated from the oil and collected in a waste water collection vessel 29.

The oil phase may be subjected to further washing stages and in such case is passed successively through a series of washing tanks, similar to the quenching tank 24, where the oil phase is mixed with water, and the oil-water mixture from each tank is passed through a centrifuge similar to the centrifuge C_2 before passing to the subsequent washing tank. A single tank 24 for quenching and washing, and centrifuge C_2 , are sufficient for all washing stages if the oil phase is returned to the washing tank 24 through a return line after passing through centrifuge C_2 . The oil may be washed with a total volume of water approximately equal to that of the volume of the oil, and the washing may be conducted in 3 to 5 separate stages. As shown in the accompanying drawings, the first washing stage in the tank 24 is desirably performed under a blanket of inert gas supplied along line 31 from the inner gas container 18, or may be conducted under copious air flow, to ensure that any hydrogen evolved in the reaction of sodium with water in the tank 24 is diluted to less than the lower explosive limit for hydrogen, more preferably to less than about one-fifth the lower explosive limit. Instead of subjecting the oil-water to centrifugation after each washing stage, the mixture may instead be allowed to settle into distinct oil and water phases and the oil phase pumped off.

The gases evolved from the reactor vessel 12 and the quenching vessel 24 (mainly inert gas containing some

hydrogen) are collected beneath exhaust hoods 32 and may be vented to the atmosphere.

After washing, the oil is passed along line 33 to a storage tank 34. The washed oil is substantially free of halogen and halogenated compounds, but contains some dissolved water. The oil can be dried by pumping it by a pump P₄ along a line 36 and filtering it through blotter type paper in a filter press 37 or by vacuum drying. The dried oil is collected in a vessel 38. If necessary or desirable, the quality of the oil product may be further improved by filtering it through a column of activated clay to remove trace impurities.

The process described above may be modified by eliminating the quenching, water-washing and drying steps, without affecting the quality of the product if the solids separation step is carried out efficiently. In such case, any remaining sodium or suspended solids present in the product can be removed by activated clay treatment.

Some detailed Examples of the present process will now be given.

EXAMPLE 1

Sodium Dispersion Preparation

25 g of lump sodium metal at 23°C is added to the stainless steel mixing bowl of a 1 L capacity Waring Blender containing 300 g of an electrical insulating oil meeting standard specifications for new electrical insulating oil. The oil is at a temperature of 120°C. A nitrogen gas flow of approximately 60 ml/min is established over the oil to provide an inert atmosphere, preventing oxidation of highly reactive sodium and the

mixture is blended for 15 minutes at a controlled temperature of $122.5 \pm 2.5^{\circ}\text{C}$ and impeller speed of 20,000 RPM. The resulting mixture is a uniformly grey dispersion of spherical particles with particle size distributed as shown in Table 4.

The concentration of sodium in oil may be varied from about 5% to about 50% by weight.

TABLE 4

Sodium Particle Distribution Data

10	Particle Diameter Range (μm)	Number Average of Particles in Range (%)
	<3	40
15	3-5	25
	5-9	19
	9-11	12
	11-15	3.4
	15-30	0.6

20 The extreme fineness of the dispersion (65% of particles less than $5 \mu\text{m}$ diameter and 96% less than $11 \mu\text{m}$ diameter) will be noted.

EXAMPLES 2 to 16

Dechlorination of Chlorinated Aromatics with Sodium Dispersion

Freshly prepared sodium dispersion prepared as described
5 in Example 1 is used to dechlorinate several chlorinated
compounds, intimately mixed with insulating oil, in a 1 L
glass reactor consisting of a standard 3-necked flask
equipped with a sealed stirrer, nitrogen gas input/output
connections, four equally spaced 1/2" glass baffles and an
10 electric heating mantle. Reaction conditions and results
for a variety of dechlorinations are given in Table 5.

The results obtained are repeatable and consistent when
using dispersions prepared in the manner disclosed above.
Larger sodium particles, for example 100 μ m particles, are
15 much less effective in promoting dechlorination and
coating of such large particles by reaction products is
suspected. The sodium particle size is thus an important
factor in the efficient dechlorination of PCB by molten
sodium.

20 In example 16, the dechlorination was conducted on an oil
sample containing an oxidation inhibitor, showing that the
presence of oxidation inhibitor does not interfere with
the dechlorination process.

EXAMPLES 17 to 19

25 Dechlorination of PCB and Chlorinated Benzenes with Sodium Dispersion

PCB contaminated insulating oil is treated in a 205 L
reactor system according to the method described above in
detail with reference to the accompanying drawings. Oils

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TABLE 5

DECHLORINATION REACTION PARAMETERS AND RESULTS

Part (a) - Time for total dechlorination at fixed sodium/reducible chlorine mole ratio.

Example Number	Chlorinated Species*	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Sodium/Reducible Chlorine Mole Ratio	Reaction Temperature (°C)	Reaction Time (Minutes)
2	Type D Askarel	620	<2	11/1	160	30
3	"	620	<2	11/1	140	60
4	"	620	<2	11/1	120	120
5	"	620	<2	22/1	160	15
6	"	620	<2	22/1	140	30
7	"	620	<2	22/1	120	60
8	"	620	<2	22/1	100	120

*Type D Askarel contains approximately 70% arochlor 1254 (PCB) and 30% tri and tetrachlorobenzenes by weight.

Part (b) - Employing greater initial concentrations of chlorinated species.

9	Type D Askarel	940	<2	22/1	140	30
10	"	4200	<2	22/1	140	30
11	"	8300	<2	22/1	140	30
12	"	63000	<2	6/1	160	240

TABLE 5 (Cont'd)

Part (c) - Employing various chlorinated species

Example Number	Chlorinated Species*	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Sodium/Reducible Chlorine Mole Ratio	Reaction Temperature (°C)	Reaction Time (Minutes)
13	2, 4-D	390	<2	22/1	140	60
14	2, 4, 5-T	290	<2	22/1	140	60
15	Pentachloro-phenol	440	<2	22/1	140	60

*2, 4-D is 2, 4-dichlorophenoxyacetic acid.
2, 4, 5-T is 2, 4, 5-trichlorophenoxyacetic acid.

Part (d) - Dechlorination of oil containing oxidation inhibitor.

Example Number	Species	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Sodium/Reducible Chlorine Mole Ratio	Reaction Temperature (°C)	Reaction Time (Minutes)
16	Arochlor 1254 DBPC*	530 5000	4 1000	14/1 -	140 -	30 -

DBPC is di-tert-butyl-para-cresol, an oxidation inhibitor.

used are obtained from segregated stocks of PCB contaminated insulating oil from Ontario Hydro storage. These stocks are contaminated with Arochlor 1260 (hexachlorobiphenyl) and polychlorinated benzenes.

- 5 The results of three typical reactions using a batch size of 120 L are given in Table 6. In all cases, PCB and chlorinated benzenes are effectively destroyed in the reaction step. The efficiencies of the dechlorinations are more than twice those of the laboratory scale tests
10 obtained in Examples 2 to 16 and it appears this is because at larger scale operation there is reduced air oxidation of the sodium and more effective contact of reactive sodium with the chlorinated organics.

Oil Reclamation

- 15 To determine the overall effect of the PCB dechlorination reaction, water washing, and clay treatment on oil quantity, standard electrical insulating oil acceptance tests were performed on untreated, PCB-dechlorinated and final clay-treated oils. The oils used in these tests
20 were obtained as follows:

- (1) The untreated oil sample was new insulating oil meeting a standard electrical insulating oil specification (Ontario Hydro specification M-104M-79).
- 25 (2) The PCB dechlorinated oil sample resulted from treatment of 500 mg/kg Type D askarel in untreated oil with sodium followed by water washing and filter drying as described in detail above with reference to
30 the drawings. or by vacuum drying.

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Table 6 - Insulating Oil Dechlorination

Example Number	Reaction Temp (°C)	Reaction Time (minutes)	PCB Content		Askarel (A) Content		Sodium (B) Metal	Na:PCB Ratio	Na:Askarel Ratio	Na:Cl Ratios	
			(mg/kg)	(g)	(mg/kg)	(g)				(by wt)	(molar)
17	140	0	450	47	740	77	179	3.8:1	2.3:1	3.9:1	6.6:1
		30	<2	-	<2	-	-	-	-	-	-
18	140	0	850	89	1420	157	380	4.3:1	2.4:1	4.0:1	6.8:1
		30	<2	-	<2	-	-	-	-	-	-
19	120	0	630	66	1100	116	240	3.9:1	2.1:1	3.4:1	5.8:1
		15	4	-	6	-	-	-	-	-	-
		30	3	-	<5	-	-	-	-	-	-
		45	2	-	<4	-	-	-	-	-	-
		60	2	-	<4	-	-	-	-	-	-
		90	<2	-	<2	-	-	-	-	-	-

(A) - Includes polychlorinated benzenes, trichlorobenzene and tetrachlorobenzene.

(B) - Elemental sodium remaining after allowances have been made for sodium required to react with water and acids in the original oil.

(3) The clay treated oil sample was obtained by agitating 1% by weight Fullers Earth with PCB dechlorinated oil at 70°C using a laboratory bench stirrer for 1 hour.

5 The results for the untreated, PCB-dechlorinated and clay treated oils are compared to new oil acceptance requirements in Table 7. Some of the quality tests were repeated after oxidation stability testing which consisted of subjecting the oil to oxidizing conditions effective to
10 remove oxidation stabilisers from the oil. After PCB dechlorination, the power factor, steam emulsion number, dielectric strength and colour value did not meet the requirements for new oil. Following clay treatment only the colour value failed to meet the new oil requirement.
15 The high colour value is not considered significant since the oil passed the tests for pour point, power factor, dielectric strength, oxidation stability, and steam emulsion number. The final clay treated oil is considered suitable for use in transformers and other electrical
20 equipment requiring an oil meeting standard specifications e.g. Ontario Hydro Specification M-104-M79 and/or CEA Standard C-50.

EXAMPLES 20 and 21

The process generally as described in Example 2 was
25 repeated using PCB-contaminated turbine oil. The results are as indicated in Table 8.

TABLE 7

OIL QUALITY TESTS

Test	Reference (ASTM)	Requirements (Ontario Hydro M104-79)	Untreated Oil Sample	PCB Dechlorinated Sample	Final Clay Treated Oil
Steam Emulsion Number (S)	D1935	Max 60	25	63	59
Water Content (mg/kg)	-	*	36	48	44
PCB Content (mg/kg)	OH Test	2	2	2	2
Power Factor @ 100°C (%)	D924	Max 0.5	0.48	0.64	0.12
Dielectric Strength (kV)	D877	Min 26	32	16	33
Neutralization Number (mg KOH/g)	D974	Max 0.03	0.01	0.01	0.01
Interfacial Tension (mN/m)	D971	Min 35	44	40	48
Relative Density @ 15°C	D1298	Max 0.906	0.861	0.860	0.860
ASTM Colour Value	D1500	Max 1	1.0-	2.0-	1.5+
Pour Point (°C)	OH Test	Max -46	-46	-46	-46
Viscosity @ 37.8°C (mm ² /s)	D445	Max 10	9.0	9.2	9.1
Flash Point (°C)	D92	Min 146	157	157	157
Fire Point (°C)	D92	*	174	168	168
Oxidation Stability	D2440	Pass	Pass	Pass	Pass
<u>Results After Oxidation Stability Test</u>					
Neutralization Number (mg KOH/g)	D974	Max 0.10	0.10	0.01	0.01
Interfacial Tension (mN/m)	D971	Min 20.0	36.5	33.0	38.0
Sludge		Nil	Nil	Nil	Nil
ASTM Colour Value	D1500	*	2.5-	3.5-	2.5+

*Not a requirement for acceptance.

TABLE 8

Initial PCB Content (mg/kg)	Reaction Time (Hours)	Reaction Temperature (°C)	Sodium/Chlorine ratio (mole/mole)	Final PCB Content (mg/kg)
650	1	120	16/1	45
650	1	140	16/1	<2

EXAMPLE 22

The process generally as described in Example 2 was repeated using a PCB-contaminated used crankcase oil. The results are shown in Table 9.

TABLE 9

Initial PCB Content (mg/kg)	Reaction Time (Hours)	Reaction Temperature (°C)	Sodium/Chlorine ratio (mole/mole)	Final PCB Content (mg/kg)
680	1	140	16/1	29

The results show that a significant decrease in the organic halide content was obtained, but the increase in viscosity made it difficult to maintain adequate stirring of the reaction mixture and continue the reaction. Continued reaction using the same equipment, to obtain a product with a reduced PCB content which could be safely

disposed of, could be obtained by using as a diluent other oil less susceptible to an increase in viscosity under the reaction conditions. Alternatively, the reaction could be carried out using equipment such as a roller mill in which continued agitation of the reaction mixture would not be hindered by the viscosity increase.

CLAIMS

1. Process for dehalogenation of organic halides comprising reacting the organic halide dissolved in a hydrocarbon-based oil, at elevated temperature, under agitation, with molten sodium particles characterized in that the reaction is carried out at a temperature in the range 100 to 160°C and that the sodium is in the form of a fine dispersion of particles of which at least 80% of the particles are below 10 microns particle size, whereby substantially all of the organic halide groups are reduced to sodium halide.
2. Process as claimed in claim 1 characterized in that said temperature is about 110°C to about 130°C.
3. Process as claimed in claim 1 or 2 characterized in that the reaction is conducted for a period of from about 10 to 240 minutes.
4. Process as claimed in claim 3 characterized in that said period is less than 30 minutes.
5. Process as claimed in any preceding claim characterized in that the molar ratio of sodium to reducible halogen is from about 2:1 to about 30:1.
6. Process as claimed in claim 5 characterized in that said ratio is from about 4:1 to 8:1.
7. Process as claimed in any preceding claim characterized in that the oil is pre-dried to a water content of less than about 100 mg/kg.
8. Process as claimed in any preceding claim characterized in that the reaction is carried out under an inert gas blanket.
9. Process as claimed in claim 8 characterized in that the inert gas is nitrogen.

10. Process as claimed in any preceding claim characterized by the steps of forming said fine dispersion by pre-dispersing metallic sodium at a temperature above its melting point under vigorous agitation in a relatively smaller quantity of a hydrocarbon-based oil the same as or compatible with the oil containing the organic halide to be dehalogenated, to achieve said fine dispersion, and subsequently blending the fine dispersion with the bulk of the oil containing the organic halide.

11. Process as claimed in claim 10 characterized in that the pre-dispersion is formed at a temperature of about 105°C to about 160°C.

12. Process as claimed in claim 10 or 11 characterized in that the pre-dispersion contains about 5% to about 50% by weight sodium.

13. Process as claimed in any preceding claim characterized in that at least about 50% of the sodium particles in the fine dispersion are below about 5 microns particle size.

14. Process as claimed in any preceding claim characterized in that at least about 90% of the sodium particles in the fine dispersion are below about 10 microns and at least about 65% are less than 5 microns particle size.

15. Process as claimed in any preceding claim characterized in that the organic halide is a chloride.

16. Process as claimed in any preceding claim characterized in that the organic halide is a PCB.

17. Process as claimed in any preceding claim characterized in that the organic halide comprises a halogenated wood preservative or pesticide.

18. Process as claimed in any preceding claim characterized

in that the organic halide is present in the reaction mixture in a concentration of up to about 10% by weight, based on the weight of the mixture.

19. Process as claimed in any preceding claim characterized in that the reaction mixture is subjected to a solids separation step to remove unreacted sodium, suspended reaction products, and sludges, and the oil obtained is recovered.

20. Process as claimed in claim 19 characterized in that said solids separation is conducted by centrifugation.

21. Process as claimed in claim 19 characterized in that the liquid is water washed to remove sodium and water-soluble reaction products and the oil phase is recovered.

22. Process as claimed in claim 21 characterized in that the oil phase is subjected to a drying step.

23. Process as claimed in claim 19, 20 or 22 characterized in that the oil obtained is subsequently purified by treatment with activated clay.

24. Process as claimed in any preceding claim characterized in that the oil having the organic halide dissolved therein is an electrical insulating oil.

25. Process as claimed in claim 24 characterized in that the electrical insulating oil comprises mineral electrical insulating oil of petroleum origin conforming to the following specifications:

Dielectric Strength (ASTM D 877)	more than 20kV (at water content less than 20 mg/kg)
Relative Density at 15°C (ASTM D 1298)	0.80 to 0.92
Pour Point	-60 to -10°C
Viscosity at 40°C (ASTM D 445)	8 to 14 centistokes
Flash Point (ASTM D 92)	140 to 200°C

26. Process as claimed in any preceding claim characterized in that the oil having the organic halide dissolved therein is a turbine oil.

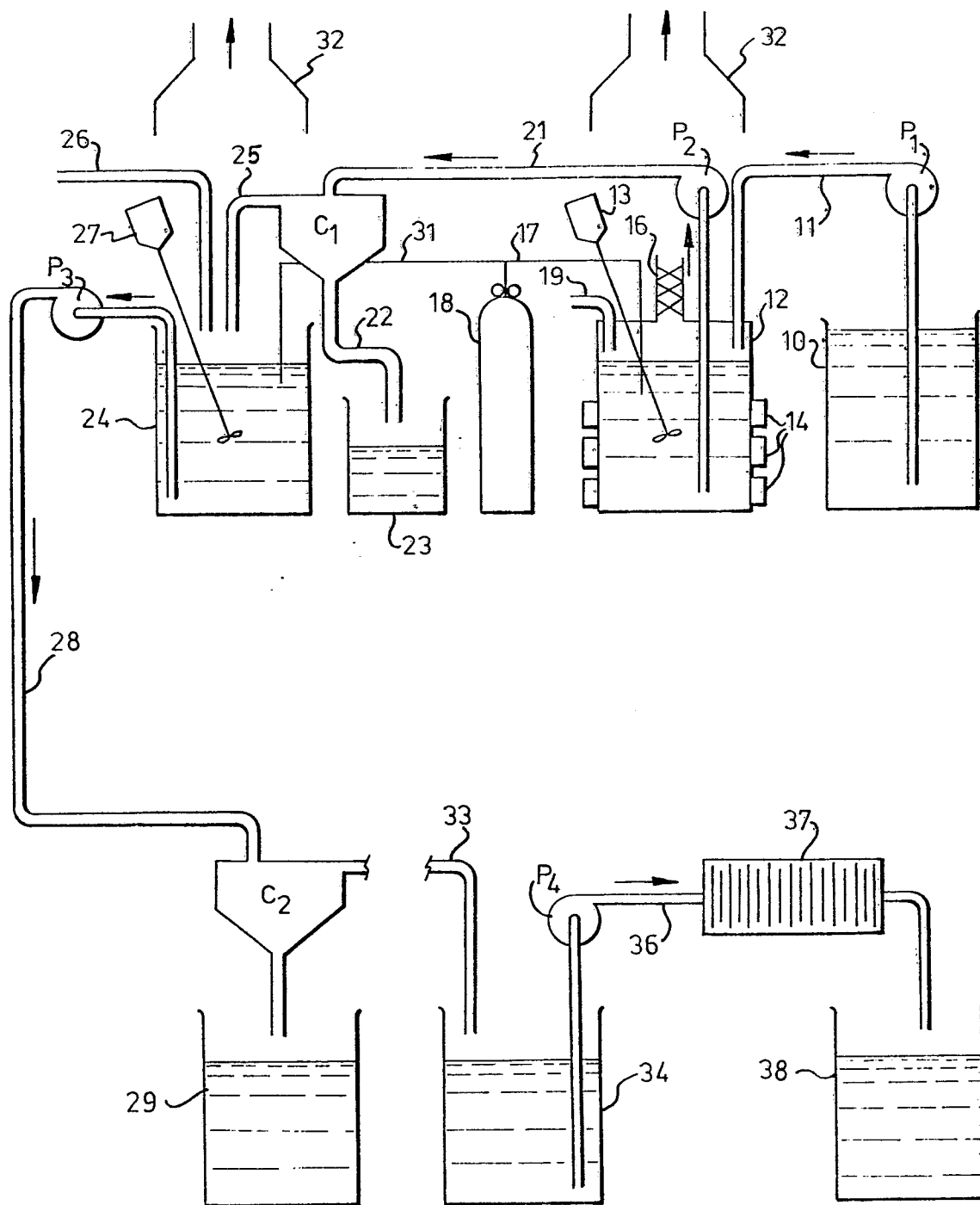
27. Process as claimed in claim 26 characterized in that the turbine oil is substantially sulfur-free and conforms to the following specifications:

Pour Point	-40 to 0°C
Viscosity at 40°C (ASTM D 445)	25 to 70 centistokes
Flash Point (ASTM D 92)	180 to 250°C

28. Process as claimed in any preceding claim characterized in that the oil having the organic halide dissolved therein is a crankcase oil.

29. Process as claimed in claim 28 characterized in that the crankcase oil conforms to the following specifications:

Viscosity at 100°C (ASTM D 445)	4 to 20 centistokes
Viscosity at -18°C (ASTM D 445)	≤9600 centistokes
Flash Point (ASTM D 92)	150 to 240°C
Pour Point	-50 to -5°C





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EUROPEAN SEARCH REPORT

0099951
Application number

EP 82 30 6974

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. ³)
X	GB-A-2 063 908 (SUNOHIO) * Claims 1-5, 8-16; page 1, line 24 - page 2, line 45 *	1-6, 10 -16, 18 -25	C 10 M 11/00
X	GB-A-2 082 625 (SUNOHIO) * Claims 1-6; page 1, line 27 - page 2, line 42 *	1-6, 8 16, 18 25	
X	GB-A-2 017 143 (DEGUSSA) * Claims 1-6 *	1-7	
X	DE-A-2 940 630 (DEGUSSA) * Claims 1,2; pages 10,11, example 1 *	1-7, 10 -14, 19 , 25-29	TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
X	FR-A-2 302 335 (ADOLF SCHMIDS ERBEN A.G.) * Claims 1,6-8; page 8, lines 9-21; page 17, table 9; page 1, lines 1-6 *	1-6, 15 -29	C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-11-1983	Examiner RO TSAERT L.D.C.
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			