

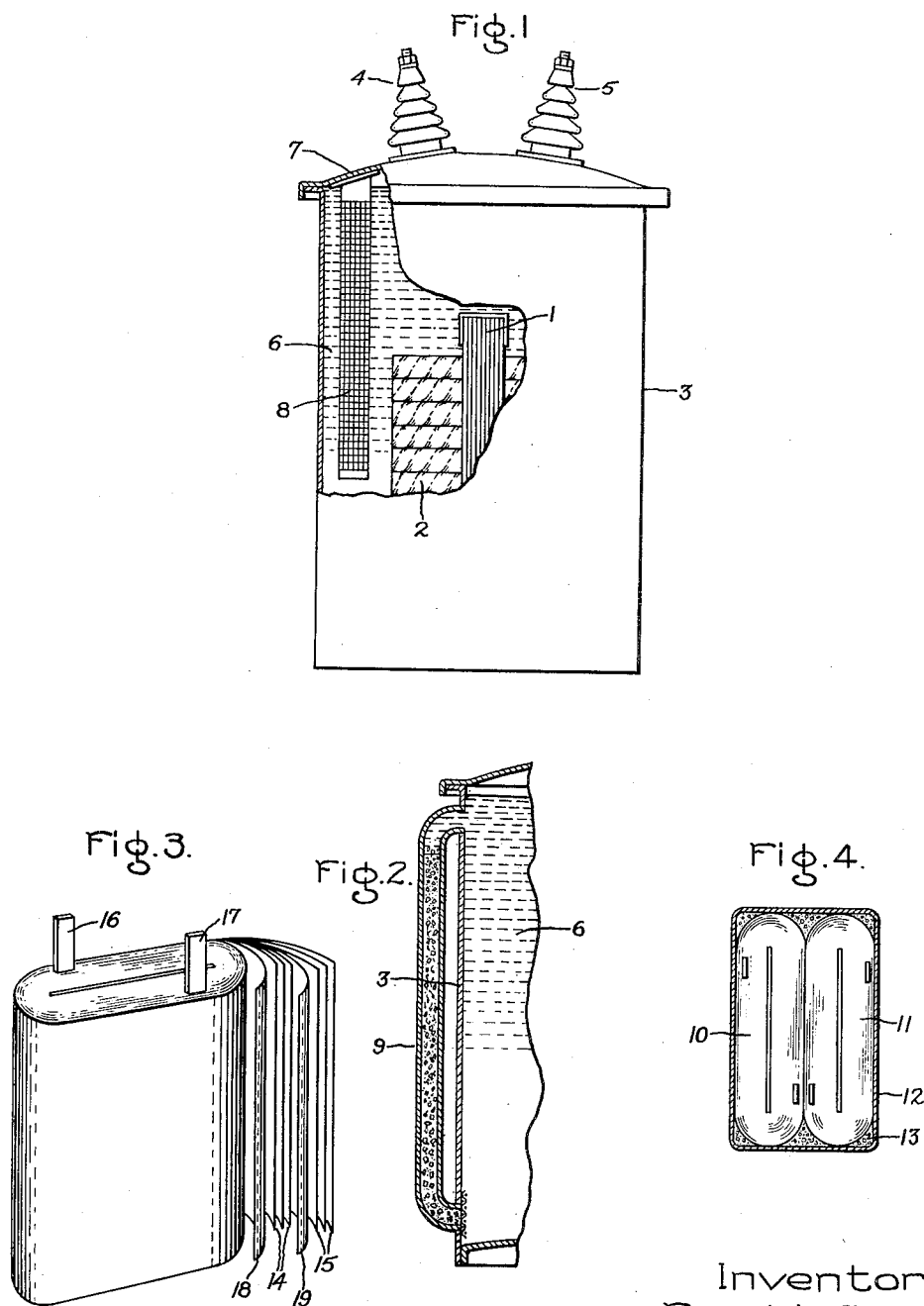
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STABILIZATION OF HALOGENATED HYDROCARBONS

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STABILIZATION OF HALOGENATED
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The present invention relates to electrical devices, as, for example, transformers, capacitors, regulators, bushings, and the like, which contain liquid halogenated aromatic hydrocarbons as insulating and dielectric media.

Insulating and dielectric compositions comprising halogenated aromatic compounds have many desirable properties. They are stable chemically under ordinary operating conditions. However, experience has shown that such compounds, and particularly the halogenated mononuclear compounds, are subject to some deterioration during use in electrical devices. Deterioration becomes evident by decrease of resistivity at elevated temperatures, say at 100° C. and upward. It is the object of my present invention to decrease or entirely avoid such deterioration.

I have discovered that halogenated aryl compounds, and even compositions consisting entirely of chlorinated mononuclear aromatic hydrocarbons, may be given adequate stability by contact therewith of an oxygenous compound of aluminum. By the term "oxygenous compound" I mean to include only inorganic compound of the oxide and hydroxide type.

My invention comprises halogenated aryl hydrocarbon in combination with oxide, hydroxide, or other suitable oxygenous aluminum compound, including corundum, gibbsite, diaspore and bauxite; my invention includes also electrical devices containing such combination in operative relation to cooperating electrical conductors charged with different potentials.

My invention is illustrated by the accompanying drawing in which Fig. 1 illustrates a transformer provided with a foraminous receptacle containing a quantity of stabilizer; Fig. 2 shows a modified structure in which the stabilizer is placed in a tubular side chamber; and Figs. 3 and 4 illustrate capacitors embodying my invention.

Referring to the drawing, there is shown in Fig. 1 somewhat conventionally, illustrative of an embodiment of my invention, a transformer comprising a core 1 and electrical windings 2, contained in a tank 3 and provided with external terminals 4, 5, as usual. The tank also contains a quantity 6 of insulating liquid consisting wholly or in part of aromatic halogenated hydrocarbon. Suspended from the tank cover 7 is a foraminous receptacle 8 consisting of wire mesh, spun glass, cellulosic fabric, or other suitable material, and containing a quantity of suitable oxygenous compound of aluminum which functions as a stabilizer by its contact with the halogenated hydrocarbon.

In the modification of Fig. 2 in which only a part of the transformer tank 3 is shown, the oxygenous aluminum compound is contained in the tubular side chamber 9 which is in communication at both ends with the main tank. A slow cir-

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ulation of the halogenated hydrocarbon liquid 6 occurs through the chamber 9 where the circulating liquid comes into contact with the aluminum compound.

5 Approximately one-fourth pound of aluminum oxide, bauxite, or the like, is provided per gallon of halogenated aromatic hydrocarbon liquid. This amount of stabilizer (about 2 per cent by weight) is illustrative but not critical. Greater and lesser amounts have been found to be of practical utility.

In the preparation of the stabilizer of my invention, a selected aluminum compound may be heated to a temperature in the range of about 350 to 500° C. in order to remove all moisture and to produce a substantially dry solid. In order to promote efficient circulation of the halogenated hydrocarbon through the stabilizer, the aluminum compound preferably should be of a size retained by about 8 to 16 mesh. This size is not critical as material of 30 to 60 mesh has been found to be of practical utility. To utilize material of materially finer mesh, as for example 80 to 100 mesh or finer, special precautions are necessary to insure liquid flow over or through the stabilizer without the material being taken up in liquid suspension. In one form of my invention, the oxygenous aluminum compound is pressed into porous plates or cylinders through which the liquid flows. Rods which are hung in the liquid to obtain intimate contact may be used. Intimate contact between the stabilizer and the halogenated aromatic compound is an important requisite.

15 The following example illustrates the efficiency of a retarder comprising an oxygenous aluminum in transformers containing trichlorobenzene as the cooling and dielectric medium. Commercial five kilowatt transformers (which will be referred to as the first set) were dried in the usual manner and then filled with trichlorobenzene. Upon being placed in the transformer, the resistivity of the trichlorobenzene decreased rapidly. After having been in the transformer for 24 hours, the resistivity was 30×10^9 ohms-centimeter at 100° C. The dielectric strength was 40 kilovolts when tested at 25° C. using the method D-117 of the American Society for Testing Materials. The dielectric loss of the transformers of this first set averaged about two watts immediately after filling with trichlorobenzene. After one month's operation at normal voltage, and under restricted conditions of heat dissipation resulting in a liquid temperature of 80° C., the dielectric loss had risen to 15 watts. The transformers of this first set, when operated under the described conditions, continued to rise in dielectric loss with continued operation and reached dielectric losses as high as 30 watts. The transformers of this set failed in approximately six months.

When a quantity of aluminum oxide was pro-

vided in contact with the trichlorbenzene in a similar second set of transformers, no such dielectric deterioration was observed. Despite continuous operation at about 80° C., the dielectric loss in the second set of transformers containing the retarder was maintained at approximately two watts with no sign of increase in dielectric loss or any other deterioration. Even when operated at normal voltage with a liquid temperature of 80° C. for more than a year, the second set of transformers showed no evidence of dielectric or chemical deterioration.

The advantages of the present invention are further illustrated by the behavior of trichlorbenzene when aged at 100° C. in closed containers under conditions which simulate transformer operation. In the presence of aluminum oxide, the resistivity of the trichlorbenzene is maintained at high and satisfactory values. Trichlorbenzene before being aged had a resistivity of 1410×10^9 ohms-centimeter at 100° C. In the following tabulation the 100° C. resistivity of the trichlorbenzene was measured after one week of aging at 100° C.:

	Ohms-cm.
Trichlorbenzene only	20×10^9
Trichlorbenzene with aluminum oxide	3950×10^9

In the presence of aluminum hydroxide, the resistivity of trichlorbenzene is increased.

When aged in the presence of transformer structural materials, dielectric deterioration of the halogenated aromatic compounds is more severe. Resin-bonded, paper-laminated cylinders and plates are commonly used in transformer construction. Such materials are recognized to lead to rapid dielectric deterioration of halogenated aromatic dielectric liquids in which they are immersed. When immersed in trichlorbenzene in the presence of aluminum oxide, as already described, the dielectric deterioration is substantially reduced and the resistivity is maintained at safe and commercially practical values. In the following tabulation, the resistivity at 100° C. of the trichlorbenzene is given after the liquid had been heated in sealed containers for one week in contact with laminated plates, commercially known as Herkolite, which consist of paper laminae bonded with a phenolic type resin:

	Ohms-cm.
Trichlorbenzene only	4.4×10^9
Trichlorbenzene with aluminum oxide	965×10^9

My invention also is applicable to the stabilization of halogenated polynuclear hydrocarbon, as, for example, chlorinated diphenyl.

When pentachlor diphenyl is aged at 100° C. in closed containers as above-described, the resistivity is decreased after about one week to about one-half of its original value, continued aging at 100° C. producing further decrease. When aluminum hydroxide is present, the resistivity increases during the 100° C. aging. The advantage resulting from the use of the aluminum hydroxide is illustrated in the following tabulation:

	Pentachlor diphenyl only	Pentachlor diphenyl with aluminum hydroxide
Original resistivity tested at 100° C.	$6,300 \times 10^9$	$6,300 \times 10^9$
Tested after 1 week aging at 100° C.	3,140	$10,200 \times 10^9$
Tested after 2 weeks aging at 100° C.	1,180	$23,500 \times 10^9$

In like manner, my invention is applicable to mixtures of halogenated polynuclear and mononuclear hydrocarbons functioning as insulating or dielectric media. Such a liquid composition may consist, for example, of a solution of 60 per cent chlordiphenyl (chlorinated to contain 60 per cent chlorine) and 40 per cent trichlorbenzene. When this composition is aged for one week at 100° C., the resistivity falls to approximately 450×10^9 ohms-centimeter when measured at 100° C. In the presence of the resin-bonded, paper-laminated paper, the resistivity falls to approximately 60×10^9 ohms-centimeter. When, however, such a composition is in contact with aluminum oxide, the resistivity is maintained at a high value. The resistivities obtained are approximately 3500×10^9 and 2000×10^9 ohms-centimeter respectively.

A composition used for the impregnation of capacitors consists by weight of about 75 parts of pentachlor and 25 parts of trichlorbenzene. The composition may contain about .5 per cent anthraquinone or one per cent monochlor anthraquinone, or one per cent of dichlor anthraquinone. When such mixture is aged at 100° C., the resistivity drops from an initial value of about 2670×10^9 ohms-centimeter to about 212×10^9 ohms-centimeter. In the presence of aluminum hydroxide, $\text{Al}(\text{OH})_3$, the resistivity actually increases under the same conditions to 3690×10^9 ohms-centimeter. It is particularly desirable to maintain the resistivity of capacitors for the direct current field as high as possible. For this reason an oxygenous aluminum compound is maintained in contact with halogenated capacitor impregnants in accordance with my invention. In accordance with one form of my invention, the oxygenous compound of aluminum, such as aluminum oxide or hydroxide, may be placed in the spaces surrounding the capacitor winding. For this purpose the material should be finely divided, preferably 30-60 mesh. I have found it desirable to pack the material as with a vibrator. Because of its excellent heat conductivity, the presence of the oxygenous aluminum compound does not adversely affect the heat dissipation characteristics of the capacitor. This embodiment of my invention is illustrated by Fig. 4 which shows in cross-section a capacitor in which the capacitor rolls 16, 17 are contained in a casing 12. The aluminum oxide or hydroxide is packed around the rolls as indicated at 13. In another embodiment of my invention, the dielectric paper spacer between the armatures is loaded with the finely divided oxygenous aluminum compound during the manufacture of the paper. The aluminum compound thus acts as a filler in the paper. Fig. 3 shows a capacitor assembly partly unrolled, the paper spacers charged with oxygenous compound of aluminum being indicated at 14, 15. The terminals 16, 17 make contact with the armatures 18, 19. With either mode of application, I have found that the desired stabilization of the halogenated impregnant is obtained.

The deterioration of halogenated hydrocarbons has been attributed to chemical deterioration with the formation of hydrogen halide. When the liquid is composed of chlorinated paraffin hydrocarbon and the like, the formation of hydrogen chloride during operation at temperatures above room temperature is recognized. When the liquid cooling and insulating medium of a transformer is composed of chlorinated aromatic hydrocarbons, experience has shown that

during the normal operation of the transformers the formation of hydrogen chloride does not occur. When the trichlorbenzene is heated at 100° C. in the presence of soda lime or zinc oxide, which are efficient neutralizers of hydrogen chloride, the resistivity of the trichlorbenzene is not maintained at the high value resulting from the presence of oxygenous compounds of aluminum. The formation of hydrogen chloride and its neutralization, therefore, can not be the basis of the efficient stabilizing effect of an oxygenous aluminum stabilizer.

Another observation based on commercial experience in the manufacture of transformers and capacitors filled with chlorinated aromatic hydrocarbon liquid is that the resistivity drops rapidly because of its great solvency on the dielectric solid materials necessarily used in the construction of the transformer or capacitor. Evidence obtained indicates that an oxygenous aluminum stabilizer does not owe its efficiency to the removal of dissolved contaminants. Activated carbon when present in chlorinated compounds of benzene or polyphenyl during an aging run at 100° C., as already described, is not capable of maintaining the liquid resistivity at its high and efficient value as demonstrated for aluminum oxide. It is only in the presence of an oxygenous aluminum stabilizer that the chlorinated hydrocarbons are maintained at their high and commercially satisfactory dielectric value.

Not only chlorinated benzene and polyphenyl, but other halogenated compounds, including in particular fluorinated compounds of benzene and its alkyl derivatives, may be associated advantageously in an electric device with an oxygen compound of aluminum. Included among such alkyl derivatives are the methyl, ethyl, propyl benzenes, dimethyl benzene, methyl-ethyl benzene, and the like.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. An insulating and dielectric composition comprising, in combination, liquid halogenated aromatic hydrocarbon and a change of a compound selected from the class consisting of aluminum hydroxide and aluminum oxide sufficient in amount to prevent decrease of resistivity of said composition.

2. An insulating and dielectric composition comprising in combination liquid chlorinated mononuclear hydrocarbon and a sufficient quantity of a compound selected from the class consisting of aluminum hydroxide and aluminum oxide to prevent substantial rise of power factor.

3. An insulating medium consisting of trichlorbenzene and an effective quantity of a compound selected from the class consisting of aluminum hydroxide and aluminum oxide in contact therewith, to prevent material decrease of electrical conductivity at elevated temperature.

4. An insulating and cooling composition consisting of a liquid mixture of trichlorbenzene and chlorinated diphenyl and about two per cent by weight of aluminum oxide in contact with said mixture.

5. The method of retarding the depreciation of dielectric and insulating properties of liquid halogenated aromatic hydrocarbons under conditions ordinarily resulting in deterioration which consists in maintaining a charge of a compound selected from the class consisting of aluminum hydroxide and aluminum oxide in contact with such hydrocarbon under such conditions.

6. An electric device including in combination cooperating conductors normally charged with different potentials, insulating means therefor consisting of liquid halogenated aromatic hydrocarbon and a sufficient quantity of a compound selected from the class consisting of aluminum hydroxide and aluminum oxide in contact with said halogenated hydrocarbon to prevent decrease of resistivity of said hydrocarbon.

7. An electric capacitor including the combination of cooperating armatures a dielectric medium therebetween consisting of liquid chlorinated aromatic hydrocarbon and a quantity of a compound selected from the class consisting of aluminum hydroxide and aluminum oxide in contact with said chlorinated hydrocarbon.

8. The method of treating an insulating composition consisting substantially solely of liquid chlorinated aromatic hydrocarbon which consists in maintaining said composition in contact with granular aluminum hydroxide sufficient in quantity to prevent decrease of resistivity at temperatures in the range of about 80 to 100° C.

9. An electric capacitor comprising the combination of a container, capacitor elements disposed therein and comprising cooperating armatures, a dielectric paper spacer between said armatures and a dielectric impregnant consisting of halogenated aromatic hydrocarbon and a quantity of a compound selected from the class consisting of aluminum hydroxide and aluminum oxide in said container in contact with said hydrocarbon.

10. An electric capacitor comprising the combination of a container, capacitor elements disposed therein and comprising cooperating armatures, a dielectric paper spacer between said armatures and a dielectric impregnant consisting of a liquid chlorinated benzene compound and a quantity of a compound selected from the class consisting of aluminum hydroxide and aluminum oxide in said container in contact with said benzene compound.

11. An electric capacitor comprising the combination of a container, capacitor elements disposed therein and comprising cooperating armatures, a dielectric paper spacer between said armatures and a dielectric impregnant consisting of a liquid chlorinated diphenyl compound and a quantity of aluminum oxide in said container in contact with said diphenyl compound.

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