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HALOGENATED HYDROCARBONS INHIBITED WITH ORGANIC PEROXIDES

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This invention relates to a method of inhibiting the corrosion of halogenated hydrocarbons and aliphatic hydrocarbon solutions of these compounds. More particularly, the invention pertains to inhibiting the corrosion of metals by halogenated hydrocarbons and their aliphatic hydrocarbon solutions by addition thereto of an organic peroxide.

Halogenated hydrocarbons have wide commercial application. However, the corrosiveness of these compounds particularly to iron presents a problem in shipping and storage where metal packaging is highly preferred. The corrosion problem is especially acute where the containers are exposed to these hydrocarbons for periods over 3 days. Numerous corrosion inhibitors have been proposed for halogenated hydrocarbons, especially chlorinated hydrocarbons, but these are not entirely satisfactory for the purpose. The halogenated hydrocarbons will decompose forming hydrogen halide and the function of the numerous inhibitors heretofore used is to react with the acid so formed to neutralize it. Thus, the inhibitor added is continuously being depleted and is necessary to replenish the inhibitor whenever the halogenated hydrocarbons are stored for some time. In normal marketing procedure, halogenated hydrocarbons are stored in tanks or other containers for considerable length of time. It would be very desirable to have an inhibitor which would render the tanks or containers passive to these compounds so that the compounds can be stored without the necessity of periodically replenishing the inhibitor as heretofore required.

It is, therefore, an object of this invention to provide a method for inhibiting the corrosion of metals by halogenated hydrocarbons. A further object is to provide a method for inhibiting the corrosion of metals where the inhibitor is not continuously depleted and where the inhibitor will render the surface exposed to these compositions passive to these compounds.

It has been discovered that the above and other objects may be attained by dissolving a small proportion of an organic peroxide in a halogenated hydrocarbon having not more than 8 carbon atoms or in an aliphatic hydrocarbon solution of a halogenated hydrocarbon having not more than 8 carbon atoms.

When the compositions inhibited according to the invention are placed in contact with iron or other metals, such as copper and aluminum, the peroxide content of the composition will diminish for a week or two and then level off without further loss after that time. If the metal surface is rubbed with an abrasive and again subjected

to the same inhibited solution a similar loss of the peroxide will be obtained as originally. The tests similar to those shown below, and the visual inspection of the samples suggest that the peroxide inhibits the corrosion by forming a protective coating on the metal surface. The protective film may be some type of an oxide coating or some other type of film, such as a reaction product of the organic peroxide and the halogenated aliphatic hydrocarbon or the metal. To obtain the protective action of the peroxides, the presence of a halogen or hydrogen halide is essential. However, if the concentration of the halogen ion or hydrogen halide is initially increased to over around 0.3 weight percent, no corrosion inhibiting action is obtained. The minute amount of the halogen ion or hydrogen halide formed by the normal decomposition of halogenated hydrocarbons is sufficient to activate the protective action of the peroxides.

The organic peroxides which are soluble at least in small proportions in the halogenated hydrocarbons which are normally liquids at room temperature or soluble in small amounts in the solutions of the halogenated hydrocarbons are effective inhibitors. Some of the peroxides are not soluble in halogenated hydrocarbon but are soluble in small proportions in aliphatic hydrocarbon solvent, such as petroleum ethers and gasoline. Since many of the halogenated hydrocarbons are used as solution dissolved in aliphatic hydrocarbons, peroxides which are soluble in these solutions may be used even though the peroxide is not soluble in the halogenated hydrocarbon itself or the halogenated hydrocarbon is normally a solid at room temperatures. Acyl and alkyl peroxides and diperoxides, such as urea peroxide and methylethyl ketone peroxide, may be employed. Benzoyl peroxide and cumene hydroperoxide are preferred due to their availability and effectiveness. Illustrative examples of other peroxides which are effective are acetyl peroxide, succinyl peroxide, p-chlorobenzoyl peroxide, tertbutyl hydroperoxide, tertbutyl peroxide, bis(1-hydroxyheptyl) peroxide, lauryl peroxide, urea peroxide, methyl ethyl ketone peroxide, cyclohexanone peroxide, and other organic peroxygenated materials containing predominately dimethylcyclohexyl hydroperoxide and sold as a tradename item by The Union Oil Company.

The term "organic peroxide," as used herein, includes the hydroperoxides as well as the peroxides and the organic peroxygenated materials, such as "Uniperox." The term "halogenated hydrocarbons," as used herein, means halo carbons and halo hydrocarbons containing as the halogen chlorine, bromine, and a mixture of chlorine and bromine. The term "liquid halogenated hydrocarbon," as used herein, includes halogenated hydrocarbons which are normally liquids at room temperature and aliphatic hydrocarbon solvent solutions of halogenated hydrocarbons which may be normally gases, liquids, or solids at room temperatures.

Liquid halogenated hydrocarbons which will decompose upon standing or in contact with a metal to form a hydrogen halide or have free halogen ions present, such as halogenated aliphatic, cyclic, and aromatic hydrocarbons having not more than 8 carbon atoms, may be thus effectively inhibited by these peroxides, especially halogenated aliphatic hydrocarbons having from 1 to 4 carbon atoms. Examples of the halogenated hydrocarbons which

may be effectively inhibited include: carbon tetrachloride, methyl bromide, 1,2-dibromoethane, 1-bromo-2-chloroethane, 1,2-dibromo-3-chloropropane, 1,2-dichlorobutane, 1,2-dibromobutane, 2-bromopentane, 1,2-dibromohexane, 1-chlorooctane, 3-chloro-2, 2-dimethylpentane, 1,4-dichlorobutene, 1,3-dichloropropene, 3-chloro-2-methyl-1-propene, trichloroethylene, hexachlorocyclopentadiene-1, 3,3-bromo-1-propyne, 1,4-dichloro-2-butyne, mono and trichlorobenzene, monobromobenzene, monochlorotoluene, and chlorocyclohexane, etc.

Small amounts of the organic peroxide are only necessary to be completely effective. The optimum amount will vary with the peroxide used, the percent of active oxygen of the peroxide, and the ratio of the surface of the metal exposed to a given amount of the inhibited solution. The double oxygen of the peroxide molecule is the reactive part of the peroxide and is essential in providing the inhibiting action. Smaller amounts of the more reactive peroxides are necessary to obtain complete protective action than the less reactive ones or those which have partially decomposed due to long standing. Since a protective film is formed, more of the peroxide is necessary where a larger surface is exposed to a fixed amount of the solution in order to build up the film. Generally the amount of the peroxide used is not over 1.5 weight percent, based upon the halogenated hydrocarbon, and preferably from .05 to 0.5 weight percent. In most cases an amount as small as 0.01 weight percent will give complete protection for metal to liquid ratios which are found in ordinary shipping and storage equipment. In storage equipment where the stored solution is used and then fresh solution again added to the tank or container, concentration of the peroxides can be considerably less than 0.01 weight percent and the equipment protected, since by using the inhibited solution the film would gradually build up or be maintained if once established. The presence of too large an amount of the peroxide will destroy the inhibiting action, and thus, concentration of the peroxide over 1.5 weight percent are not ordinarily used. In unusual situations where a large surface is exposed to a small amount of solution, a larger amount of the peroxide may be necessary for the complete protection of the metal; however, in these unusual situations, halogenated hydrocarbons containing 1.5 weight percent of the peroxide will provide considerable protection.

The following series of tests illustrate the film forming behavior of the organic peroxides as used according to the invention.

Several pieces of iron strips obtained from iron shipping drums were placed in a bottle containing 1,4-dichloro-2-butyne to which had been added one weight percent of benzoyl peroxide. The bottle so charged was stored in the dark at room temperature and small amounts of the inhibited dichlorobutyne were withdrawn periodically and analyzed for benzoyl peroxide. The results obtained are shown in the table below.

Length of Time From the Start of Experiment, Days	Weight Percent of Benzoyl Peroxide in Solution	Total Loss of Benzoyl Peroxide Percent
0	1.0	
5	0.80	20
12	0.72	28
19	0.72	28

After 19 days the sample bottle was shaken vigorously so that the metal pieces collided and rubbed together. The sample bottle was again placed in the dark at room temperature and samples of the inhibited dichlorobutyne were withdrawn and analyzed for the peroxide. The results obtained are shown below.

Length of Time From the Start of Experiment, Days	Weight Percent of Benzoyl Peroxide in Solution	Total Loss of Benzoyl Peroxide Percent
26	.58	42
35	.58	42

From the data above it will be noted that after the iron pieces were in the solution for 5 days the peroxide content had decreased about 20 percent and further decreased in 12 days to 28 percent and thereafter remained constant. In 7 days after colliding and rubbing the iron pieces together, the peroxide content decreased to 0.58 percent and then again remained constant.

A sample of the inhibited dichlorobutyne stored for the same period of time without the presence of the iron showed essentially no loss of the peroxide.

To show that the presence of a halogen ion is necessary to obtain the protective action with the peroxide and that a protective film must result, iron test pieces were first placed in different solutions and maintained submerged for one week. These metal pieces were visually inspected and then carefully placed in a solution containing 2.5 pounds of 1,4-dichloro-2-butyne per gallon of a petroleum ether and maintained in this solution for an additional week when the test pieces were removed and inspected visually. The results obtained are given below.

Solution in Which Iron Test Pieces Submerged	Appearance of Iron Test Pieces After Submerged 1 Week in Solution	Appearance of Iron Test Pieces After Transfer and Submerged in the 1,4-dichloro-2-butyne Solution
Petroleum ether	unchanged	corroded.
Petroleum ether plus 0.1 weight percent of benzoyl peroxide.	do	Do.
Petroleum ether plus 0.2 weight percent HCl.	corroded	
Petroleum ether plus 0.2 weight percent HCl and 0.1 weight percent of benzoyl peroxide.	amber coating	not corroded.
The 1,4-dichloro-2-butyne solution to which was added 0.1 weight percent benzoyl peroxide.	do	Do.

The above data indicate that the presence of a halogen ion is necessary to obtain the protective action of the peroxide and that a film is formed which once formed will protect the metal from corrosion even though the metal is exposed to a corrosive halogenated hydrocarbon.

The following examples of the invention are illustrative of the inhibiting action of organic peroxides.

Different organic peroxides at different concentrations were mixed with 1,4-dichloro-2-butyne and placed in bottles. In these tests iron strips were placed in the bottles in a manner such that only half of the metal was covered by the mixtures. The metal strips were of such size that the ratio of the submerged surface area to the volume of the liquid was approximately the same as that existing in a filled standard 5 gallon shipping drum, viz. 4.5 square feet per 0.7 cubic foot of liquid. The bottles were stored in a dark room for 3 months and then the

metal strips were removed and inspected for corrosion. The results obtained are given in the table below.

Inhibitor	Weight Percent of Inhibitor Added	Amount of Corrosion by Visual Inspection
Acetyl peroxide	1.0	None.
Do	0.5	Trace.
p-chlorobenzoyl peroxide	1.0	Do.
Do	0.1	None.
Do	0.01	Slight.
bis(1-hydroxyheptyl) peroxide	0.1	None.
Do	0.05	Trace.
Succinyl peroxide	1.0	Slight.
Do	0.1	Do.
Urea peroxide	0.1	None.
Do	0.01	Trace.
Tert-butyl hydroperoxide	0.1	Slight.
Do	.05	Trace.
Do	.01	None.
Di-tert-butyl peroxide	0.1	Trace.
Do	.01	None.
Lauroyl peroxide	0.1	Trace.
Do	.01	Moderate.
Methyl ethyl ketone peroxide	0.1	None.
Do	.01	Trace.
Benzoyl peroxide	.01	Slight.
dimethylcyclohexyl hydroperoxide	1.0	Do.
Cumene hydroperoxide	0.01	None.
Do	.10	Trace.

Tests similar to above were also run where a petroleum ether solution containing 25 percent of 1,4-dichloro-2-butyne was used in place of halogenated hydrocarbon itself. The results obtained are given below:

Inhibitor	Weight Percent of Inhibitor Based Upon 1,4-dichloro-2-butyne	Amount of Corrosion by Visual Inspection
Acetyl peroxide	0.2	Slight.
p-chlorobenzoyl peroxide	0.2	Do.
bis(1-hydroxyheptyl) peroxide	0.4	Moderate.
Do	0.04	None.
Succinyl peroxide	0.04	Slight.
Tert-butyl hydroperoxide	0.4	Do.
Do	0.2	None.
Do	0.01	Moderate.
Lauroyl peroxide	0.4	None.
Methyl ethyl ketone peroxide	0.4	Slight.
Do	0.04	Moderate.
dimethylcyclohexyl hydroperoxide	0.4	Slight.
Cumene hydroperoxide	0.01	None.
Do	0.1	Trace.

A series of tests was made where iron strips were exposed to different halogenated hydrocarbons inhibited with benzoyl peroxide. The amount of corrosion obtained was compared to that of iron strips exposed to the uninhibited hydrocarbon under the same conditions.

In carrying out these tests, metal strips were placed in bottles containing the hydrocarbons so that ½ of the metal was covered by the solution and ½ of the metal was exposed to the vapor of the hydrocarbons. After 30 days the strips were visually observed for corrosion and pitting. The results obtained are given in the table below.

Halogenated Hydrocarbon	Weight Percent of Benzoyl Peroxide Added	Amount of Corrosion by Visual Inspection
1,2-dibromoethane	0	Severe.
Do	0.01	Trace.
Do	0.10	None.
Do	1.0	Slight.
Carbon tetrachloride	0	Moderate.
Do	.01	None.
1,3-dichloropropene	0	Severe.
Do	0.01	None.
Do	0.05	Do.
Do	1.0	Trace.
1,2-dibromo-3-chloropropane	0	Severe.
Do	0.01	Trace.
Do	0.05	Do.
Do	0.10	Slight.
Ethylene chlorobromide	0	Severe.
Do	0.10	Moderate.
Do	1.0	Trace.
2-bromopentane	0	Moderate.
Do	0.1	None.
1,5-dibromopentane	0	Severe.
Do	.1	Slight.
Trichloroethylene	0.1	None.
Iso-amyl bromide	0	Severe.
Do	0.1	Slight.
Hexachlorocylopentadiene-1,3	0	Moderate.
Do	.1	None.
2-bromotoluence	0	Severe.
Do	.1	Trace.
Monochlorobenzene	0	Slight.
Do	0.1	None.
N-amyl bromide	0	Slight.
Do	0.1	None.
1,2,4- and 1,2,3-trichlorobenzene	0	Trace.
Do	0.1	None.

To show the inhibiting action obtained by using organic peroxides in accordance with the invention, a series of tests was made using different halogenated hydrocarbons and different peroxides. In carrying out these tests, metal strips were placed in bottles containing the halogenated hydrocarbons so that ½ of each strip was covered by the solution and the other half exposed to the vapor of the hydrocarbon. The bottles were stored in a dark room at room temperature. After a period of storage the strips were removed from the bottles and examined for corrosion and pitting. The results obtained are shown in the table below.

Halogenated Hydrocarbon	Inhibitor Used	Amount of Inhibitor Used Wt. Percent	Kind of Test Pieces	Length of Time Test Pieces Exposed to Halogenated Hydrocarbon, months	Visual Inspection After Exposure
3-bromo-1-propene	none	0	iron	4⅓	severe corrosion.
Do	benzoyl peroxide	0.1	do	4⅓	no corrosion.
Carbon tetrachloride	none	0	copper	3	slight corrosion.
Do	none	0	aluminum	3	trace corrosion.
Do	benzoyl peroxide	0.1	copper	3	slight corrosion.
Do	do	0.1	aluminum	3	no corrosion.
Methylchloroform	none	0	copper	3	trace corrosion.
(1,1,1-trichloroethane)	do	0	iron	3	Do.
Do	benzoyl peroxide	0.1	do	3	no corrosion.
Do	do	0.1	copper	3	Do.
1,4-dichloro-2-butyne	none	0	do	4	severe.
Do	do	0	aluminum	4	Do.

Halogenated Hydrocarbon	Inhibitor Used	Amount of Inhibitor Used Wt. Percent	Kind of Test Pieces	Length of Time Test Pieces Exposed to Halogenated Hydrocarbon, months	Visual Inspection After Exposure
1,4-dichloro-2-butyne	tert-butyl hydroperoxide	0.1	copper	4	no corrosion.
Do	do	0.1	aluminum	4	Do.
Trichloroethylene	none	0	copper	3	severe corrosion.
Do	do	0	aluminum	3	Do.
Do	benzoyl peroxide	0.1	copper	3	trace corrosion.
Do	do	0.1	aluminum	3	Do.
Monochlorobenzene	none	0	iron	4½	slight corrosion.
Do	benzoyl peroxide	0.1	do	4½	no corrosion.
Do	tert-butyl hydroperoxide	0.1	do	4½	trace corrosion.
Do	di-tert-butyl peroxide	0.1	do	4½	no corrosion.
1,2,4- and 1,2,3-trichloro benzene	none	0	do	4½	trace corrosion.
Do	benzoyl peroxide	0.1	do	4½	no corrosion.
Do	tert-butyl hydroperoxide	0.1	do	4½	Do.
Do	di-tert-butyl peroxide	0.1	do	4½	Do.
2-bromopentane	none	0	do	4½	severe corrosion.
Do	benzoyl peroxide	0.1	do	4½	no corrosion.
Do	di-tert-butyl peroxide	0.1	do	4½	slight corrosion.

To determine the optimum amount of a particular organic peroxide to use for a particular halogenated hydrocarbon or the aliphatic solution thereof for a given surface area, tests similar to those given in the examples above may be used.

What is claimed is:

1. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by a liquid halogenated hydrocarbon having not more than 8 carbon atoms, which comprises dissolving in said halogenated hydrocarbon a small amount sufficient to inhibit the corrosion of metals of an organic peroxide selected from the group consisting of acetyl peroxide, succinyl peroxide, p-chlorobenzoyl peroxide, tertbutyl hydroperoxide, tertbutyl peroxide, bis(1-hydroxyheptyl) peroxide, lauryl peroxide, urea peroxide, methyl ethyl ketone peroxide, cyclohexanone peroxide, and dimethylcyclohexyl hydroperoxide.

2. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by a liquid halogenated hydrocarbon having not more than 8 carbon atoms, which comprises dissolving in said halogenated hydrocarbon up to 1.5 weight percent of an organic peroxide selected from the group consisting of acetyl peroxide, succinyl peroxide, p-chlorobenzoyl peroxide, tertbutyl hydroperoxide, tertbutyl peroxide, bis(1-hydroxyheptyl) peroxide, lauryl peroxide, urea peroxide, methyl ethyl ketone peroxide, cyclohexanone peroxide, and dimethylcyclohexyl hydroperoxide.

3. A method according to claim 2 wherein the liquid halogenated hydrocarbon is an aliphatic halogenated hydrocarbon having from 1 to 4 carbon atoms.

4. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by a halogenated aliphatic hydrocarbon having from 1 to 4 carbon atoms, which comprises dissolving in said halogenated hydrocarbon from .01 to 1.5 weight percent of benzoyl peroxide.

5. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by 1,4-dichloro-2-butyne, which comprises dissolving in said 1,4-dichloro-2-butyne from 0.01 to 1.5 weight percent of benzoyl peroxide.

6. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by 1,4-dichloro-2-butyne, which comprises dissolving in said 1,4-dichloro-2-butyne from 0.05 to 0.5 weight percent of benzoyl peroxide.

7. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by trichloroethylene, which comprises dissolving in said trichloroethylene from 0.01 to 1.5 weight percent of benzoyl peroxide.

8. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by trichloroethylene, which comprises dissolving in said trichloroethylene from 0.05 to 0.5 weight percent of benzoyl peroxide.

9. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by carbon tetrachloride, which comprises dissolving in said carbon tetrachloride from 0.01 to 1.5 weight percent of benzoyl peroxide.

10. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by carbon tetrachloride, which comprises dissolving in said carbon tetrachloride from 0.05 to 0.5 weight percent of benzoyl peroxide.

11. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by a halogenated aliphatic hydrocarbon having from 1 to 4 carbon atoms, which comprises dissolving in said halogenated aliphatic hydrocarbon from 0.01 to 1.5 weight percent of cumene hydroperoxide.

12. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper,

and ferrous metals by 1,4-dichloro-2-butyne, which comprises dissolving in said 1,4-dichloro-2-butyne from 0.01 to 1.5 weight percent of cumene hydroperoxide.

13. A method of inhibiting the corrosion of a metal selected from the group consisting of aluminum, copper, and ferrous metals by 1,4-dichloro-2-butyne, which comprises dissolving in said 1,4-dichloro-2-butyne from 0.01 to 1.5 weight percent of tert-butyl peroxide.

14. In the storage of a liquid halogenated hydrocarbon having not more than 8 carbon atoms in a metal container selected from the group consisting of aluminum, copper, and ferrous metals, the method of inhibiting the corrosion of the container, which comprises dissolving in the liquid halogenated hydrocarbon not more than 1.5 weight percent of an organic peroxide selected from the group consisting of acetyl peroxide, succinyl peroxide, p-chlorobenzoyl peroxide, tertbutyl hydroperoxide, tert-butyl peroxide, bis(1-hydroxyheptyl) peroxide, lauryl peroxide, urea peroxide, methyl ethyl ketone peroxide, cyclohexanone peroxide, and dimethylcyclohexyl hydroperoxide.

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