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STABILIZATION OF CHLORINATED HYDROCARBONS WITH 2,5-DIMETHYL-1,5-HEXADIENE-3-YNE AND SYNERGISTIC MIXTURES CONTAINING SAME

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This invention relates to the stabilization of chlorinated hydrocarbons, more particularly, it relates to the stabilization of chlorinated hydrocarbon solvents against degradation when exposed to heat, light, and air; and it comprises a method of effecting such stabilization.

The term "stabilization," in its various forms, as used in this specification and the appended claims, is intended to refer to the inhibition of the decomposition reaction and/or the alleviation of the deleterious effects of decomposition products.

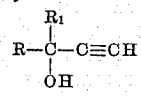
The chlorinated hydrocarbons are widely used, among other things, as solvents in degreasing metallic articles, extracting caffein from coffee, and in dry cleaning. The principal shortcoming of chlorinated hydrocarbons is their tendency to undergo degradation by oxidation, hydrolysis, or pyrolysis when exposed to light, air, or elevated temperatures or upon long term storage. Upon degradation, various chloride derivatives of the solvents are formed which hydrolyze in the presence of moisture to produce hydrochloric acid and organic acids. It is believed that these acid substances are responsible for the corrosion of metals with which the chlorinated hydrocarbon solvent comes into contact. The acid substances formed are also detrimental to both fabrics and dyestuffs. While many organic chemical additives have been suggested as stabilizers for chlorinated hydrocarbons there is still a great need for improving the stability of chlorinated hydrocarbons. To be of greatest value, a stabilizer or stabilizer system should inhibit the degradation of the solvent under most conditions of application, act as a scavenger for whatever objectionable degradation products that are formed, and inhibit metal corrosion.

It is an object of the present invention to provide a chlorinated hydrocarbon solvent having improved stability. An additional object is to provide a mixture of stabilizing materials which will exert a synergistic effect one with the other so that chlorinated hydrocarbon solvents are more effectively stabilized with the mixture than with either stabilizing material alone. A further object is to provide an improved process for stabilizing chlorinated hydrocarbons. Other objects will in part appear in, and in part be obvious from, the following detailed description.

According to the present invention, it has now been discovered that 2,5-dimethyl-1,5-hexadiene-3-yne (hereinafter referred to by its common name, diisopropenyl acetylene) is particularly effective as a stabilizer for chlorinated hydrocarbons. Diisopropenyl acetylene has been found to be especially suitable for inhibiting metal induced degradation of chlorinated hydrocarbons.

It has also been found that certain combinations of diisopropenyl acetylene with other materials exert a stabilizing action upon chlorinated hydrocarbons which is greater than additive with respect to the effect exerted by its components separately. Thus, combinations of diisopropenyl acetylene with a phenolic antioxidant, such as 2,6-di-tert-butyl-para-cresol, thymol and resorcinol, or

with a tertiary acetylenic monohydric alcohol, such as 3-methyl-1-pentyn-3-ol, 2-methyl-3-butyn-2-ol and the like, have been found to display synergistic stabilizing properties. Diisopropenyl acetylene has been found particularly effective in combination with tertiary acetylenic alcohols represented by the formula



wherein R is an alkyl group containing from 1 through 6 carbon atoms and R_1 may be an alkyl, aryl, alkaryl, or cycloalkyl radical. The following compounds are representative tertiary acetylenic monohydric alcohols encompassed by the foregoing formula and found suitable for use in combination with diisopropenyl acetylene:

2-methyl-3-butyn-2-ol
3-methyl-1-pentyn-3-ol
3-methyl-1-nonyn-3-ol
3,5-dimethyl-1-hexyn-3-ol
2-phenyl-3-butyn-2-ol

The use of tertiary acetylenic monohydric alcohols as stabilizers for chlorinated hydrocarbon solvents is more fully described and disclosed in the copending application of Warren C. Ellis, Jr., and Morton W. Leeds, Serial No. 408,978, filed on February 8, 1954.

In addition to the synergistic stabilizing activity noted for the foregoing combinations of materials, it has also been found that chlorinated hydrocarbons stabilized with diisopropenyl acetylene or combinations of materials containing same may be employed for a wider variety of uses and under more extreme conditions without fear of the formation of objectionable amounts of acid products. Furthermore, the combination of stabilizer materials not only unexpectedly improves the anti-corrosive properties of chlorinated hydrocarbons stabilized therewith, but also effectively acts as a scavenger for any objectionable degradation products that are formed.

While the amount of diisopropenyl acetylene or diisopropenyl acetylene containing mixture added to the chlorohydrocarbon solvent will depend upon the particular solvent to be stabilized, the intended use of the solvent composition, and the degree of stability desired, generally, the total amount of the stabilizer, whether alone or in combination with another stabilizing material, added to the chlorinated solvent may range from as low as about 0.05 percent to about 1.0 percent by weight. When combinations of diisopropenyl acetylene and another material are employed as the stabilizing mixture, any suitable proportion of diisopropenyl acetylene to other stabilizer may be used. For example, the ratio of diisopropenyl acetylene to other stabilizing material may vary from 1:10 to 10:1.

When operating in accordance with this invention, the stabilizing materials may simply be mixed together to form a composition adapted to be subsequently added to or admixed with the chlorinated hydrocarbon solvent to be stabilized, or each of the stabilizer materials to be used may be individually added to or admixed with the chlorohydrocarbon solvent. For certain applications of the chlorinated hydrocarbon solvents it may be desirable to add still other stabilizing substances, such as alkaline reacting materials.

While the use of diisopropenyl acetylene or combinations of stabilizers containing diisopropenyl acetylene has been found to be especially suitable for the stabilization of trichloroethylene and perchloroethylene, the mixture may also be used to stabilize other chlorohydrocarbons such as methylene chloride, methyl chloroform, ethylene dichloride, trichloroethane, vinylidine chloride, vinyl chloride and the like.

The following table will illustrate the unexpected stabilizing effects obtainable by employing diisopropenyl acetylene alone, or in combination with other additives for the stabilization of chlorinated hydrocarbons. In each case the stabilizer system was added, in the amounts indicated, to 150 ml. of trichloroethylene containing 7.5 ml. of water and 4 grams each of finely divided aluminum (8–20 mesh), iron (40 mesh), zinc (40 mesh) and fine copper turnings. The water and finely divided metals were added to accelerate solvent decomposition. The trichloroethylene employed had previously been purified by passing it through a column packed with alumina. Cleaned metal specimens, measuring 2" x ½" x 1/16", of each of iron, copper, zinc, and aluminum were suspended at three different locations: (1) half in and half out of the liquid, (2) in the boiling vapors, and (3) halfway immersed in the condensate. After refluxing the solvent mixture for 144 hours, the metal specimens were removed. Those specimens which were in the liquid phase were rinsed into the flask. The metal specimens were visually examined for corrosion, and rated for corrosion on an arbitrary scale from 1 to 10, the numeral 1 indicating minimum corrosion and 10 indicating maximum corrosion. The trichloroethylene solvent mixture was filtered. Approximately 50 ml. of 0.1N sodium hydroxide solution and enough water were added to the filtrate to make the final volume 500 ml. The final mixture was shaken and permitted to settle into an aqueous and an organic layer. Samples of the water layer were analyzed for total acidity by back titration of the base, and for chloride ion by electrometric titration. The figure, $\Delta Cl^- \times 10^3$ moles, appearing in the table represents the amount of Cl^- ion formed during the test, or the difference in concentration between that Cl^- ion present at the start of the test and that which was present after the test was completed. Similarly, $\Delta H^+ \times 10^3$ moles is the amount of H^+ ion formed during the test. The various tests were performed in duplicate and the results recorded in the following table are an average of these duplicate runs. Percents given are percent by weight.

Table

Stabilizer System	Total Corrosion Rating for All Metals	$\Delta Cl^- \times 10^3$ Moles	$\Delta H^+ \times 10^3$ Moles
0.1% Diisopropenyl Acetylene	5.0	0.38	0.30
0.2% 3-Methyl-1-pentyn-3-ol	5.5	0.75	0.66
0.009% 2,6-Di-tert-butyl-para-cresol	5.3	0.63	0.63
0.1% Diisopropenyl Acetylene 0.2% 3-Methyl-1-pentyn-3-ol	3.5	0.35	0.23
0.1% Diisopropenyl Acetylene 0.009% 2,6-Di-tert-butyl-para-cresol	3.8	0.35	0.22

Since many different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention should not be limited except as defined in the appended claims.

What is claimed is:

1. A composition of matter comprising a chlorinated hydrocarbon solvent and a small but stabilizing amount of diisopropropenyl acetylene and a stabilizing agent selected from the group consisting of 3-methyl-1-pentyn-3-ol and 2,6-di-tert-butyl-para-cresol.

2. A composition of matter comprising a chlorinated hydrocarbon solvent and a small but stabilizing amount of diisopropenyl acetylene and 3-methyl-1-pentyn-3-ol.

3. A composition of matter comprising a chlorinated hydrocarbon solvent and a small but stabilizing amount of a mixture of diisopropenyl acetylene and 2,6-di-tert-butyl-para-cresol.

4. A composition of matter as defined in claim 1, wherein said chlorinated hydrocarbon solvent is trichloroethylene.

5. A composition of matter comprising a chlorinated hydrocarbon solvent and between about 0.05 to 1.0 percent by weight of diisopropenyl acetylene and a stabilizing agent selected from the group consisting of 3-methyl-1-pentyn-3-ol and 2,6-di-tert-butyl-para-cresol.

6. A process for stabilizing a chlorinated hydrocarbon solvent which comprises incorporating a small but stabilizing amount of diisopropenyl acetylene and a stabilizing agent selected from the group consisting of 3-methyl-1-pentyn-3-ol and 2,6-di-tert-butyl-para-cresol into said chlorinated hydrocarbon solvent.

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