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TRICHLOROETHYLENE STABILIZED WITH PROPARGYL ALCOHOL AND PYRROLE

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This invention relates to a composition of matter comprising trichloroethylene and an inhibitor mixture to prevent it from decomposing and attacking metals.

Trichloroethylene ($\text{CHCl}_2\text{CCl}_2$) is used in industry mainly as a solvent for cleaning metal articles, especially by the vapor-degreasing process. In this service, it may come into contact at elevated temperature with most of the common metals, and also with lubricants, sulfurized cutting oils, buffing compounds, and other agents used in metal working. Under these severe conditions, the normal slight decomposition of trichloroethylene when in contact with metal, particularly when moisture is present, is greatly increased. The trichloroethylene may discolor badly over a period of weeks and also develop acidity sufficient to attack reactive metals such as aluminum and iron.

To offset this behavior, it is conventional to add to the trichloroethylene one or more inhibiting agents, usually unsaturated hydrocarbons or organic nitrogen bases. Many of these agents are of considerable help, but none used heretofore has been more than partly effective.

It is therefore the principal object of this invention to provide an inhibiting composition which is far more effective in stabilizing trichloroethylene during storage, shipment, and use than any heretofore employed.

The inhibiting compositions of the invention consist essentially of a lower acetylenic alcohol and a lesser but substantial proportion of a pyrrole having less than 8 carbon atoms per molecule. Further advantage is realized by also including a minor but appreciable proportion of an organic nitrogen base having a substantial vapor pressure at the boiling temperature of trichloroethylene. A minor proportion of the inhibiting composition, usually less than one percent, is dissolved in the trichloroethylene to be stabilized.

In the new compositions, the lower acetylenic alcohol is one containing less than six carbon atoms per molecule. Propargyl alcohol is preferred both because of its more ready availability and, for some conditions, greater effectiveness. However, any of the other lower acetylenic alcohols may be used, e. g. butyn-1-ol-3 (methyl ethynyl carbinol), butyn-2-ol-1 (propynyl carbinol), and methyl-3-buten-1-ol-3 (dimethyl ethynyl carbinol). The proportion of propargyl alcohol, or other acetylenic alcohol, required in stabilizing trichloroethylene according to the invention is in general from about 0.005 to 1.0 percent, preferably 0.05 to 0.5 percent (all proportions given herein are by weight).

In addition to the acetylenic alcohol, the new inhibiting compositions contain a pyrrole having less than 8 carbon atoms per molecule. The term "a pyrrole" as used herein means pyrrole itself and homologs of pyrrole, containing the pyrrole nucleus.

Pyrrole itself is entirely satisfactory and is usually preferred. However, homologs such as the N-lower alkyl pyrroles, e. g. N-methyl pyrrole and N-ethyl pyrrole, and such as 2-methyl pyrrole, 2,5-dimethyl pyrrole, may also be employed. The proportion of pyrrole or pyr-

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role homolog needed for stabilizing trichloroethylene is in general from 0.005 to 0.1 percent, preferably 0.01 to 0.05 percent.

Trichloroethylene stabilized with an acetylenic alcohol and a pyrrole according to the invention undergoes little or no decomposition or tendency to become acidic on storage in metal containers. It likewise shows very little tendency to attack metals, even when the trichloroethylene is at the boiling point and the metal is iron, aluminum, or any of the common aluminum-base alloys. In addition, the inhibitor mixture is largely effective in preventing attack of metal by the condensing vapors of stabilized trichloroethylene, as in a vapor degreaser. Moreover, the inhibiting effect is not lost as the trichloroethylene evaporates, the unevaporated residue being still stabilized. Likewise, trichloroethylene is stabilized by the inhibitor mixtures of the invention even when mixed with other chlorohydrocarbons or other diluents which may be added.

It has been observed, however, that trichloroethylene stabilized with an acetylenic alcohol and a pyrrole, when stored over periods of several months in ordinary black iron drums, occasionally tends to develop discoloration. Such discoloration, attributable at least in part to the presence of the pyrrole, is of no moment for many uses of the trichloroethylene. However, the discoloration may be minimized or even eliminated, and the stabilized trichloroethylene maintained clear, by dissolving therein a small proportion of an organic nitrogen base having a substantial vapor pressure at the boiling temperature of trichloroethylene. This base appears to restrain any tendency of the pyrrole component to cause discoloration, and may also contribute something toward the stability of the trichloroethylene itself. Any of a wide range of organic nitrogen bases may be used, although in general a lower aliphatic amine, i. e. a monoamino hydrocarbon having no more than six carbon atoms per molecule, is preferred, e. g. n-propyl amine, n-butyl amine, isopropyl amine, diisopropyl amine, etc. Diisopropyl amine has proved extraordinarily effective, even in minute proportions. The proportion of diisopropyl amine or other nitrogen base required is in general from 0.0005 to 0.1 percent, with 0.0005 to 0.01 percent usually being preferred.

For most purposes, the inhibiting agents according to the invention are individually dissolved in the proper amounts in the trichloroethylene soon after it is manufactured. However, it is entirely feasible to make up separately a concentrate consisting essentially of the acetylenic alcohol, the pyrrole, and optionally also the organic base, in appropriate relative proportions, and then add this concentrate to the trichloroethylene, either at once or at some later time when severe exposure is expected. Such a concentrate may also be used to replenish the inhibitor in a stabilized trichloroethylene which may show signs of incipient instability due to long use or storage.

The following examples will illustrate the invention.

Example 1

To evaluate the effectiveness of various additives as inhibitors for the decomposition of trichloroethylene, an accelerated laboratory test was established. In each test, a 200 ml. sample of the trichloroethylene composition and 10 ml. of water were introduced into a glass flask fitted with a long reflux condenser. Five gram portions of iron, copper, zinc, and aluminum, each in the form of coarse powder, were also placed in the flask. In addition, strips of each metal in sheet form were placed in the condenser in position to contact vapor and refluxing liquid. The whole was then heated at a reflux temperature with vigorous boiling for a period of six

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days. The acidity of the trichloroethylene, expressed as parts per million, and the concentration of inorganic chloride, in parts per million Cl, were determined by titration at the start and at the end of each test.

As a blank determination, a sample of industrial grade trichloroethylene (containing about 0.15 percent carbon tetrachloride as the major chlorohydrocarbon impurity) and containing no inhibitor was subjected to the test. Before the test the acidity was 230 p. p. m., and the chloride about 2 p. p. m. At the end of the test, the acidity was 494 p. p. m., and the chloride was 675 p. p. m.

In a test according to the invention, there were added to the same sample of trichloroethylene 0.1 percent of propargyl alcohol, 0.05 percent of pyrrole, and 0.0015 percent diisopropylamine. Before the test, the material was slightly alkaline (7 p. p. m.). After the test, the acidity was 93 p. p. m., and the chloride was 149 p. p. m. It will thus be seen that even under the extreme conditions of the test the decomposition of the stabilized trichloroethylene was only a small fraction of that of the uninhibited material.

The addition of 0.1 percent of dioxane to the composition of the invention as an additional stabilizer did not appreciably affect the results.

When the pyrrole was omitted, but the propargyl alcohol retained, the degree of inhibition during the test was small.

Example 2

The test of of Example 1 was repeated using 0.05 percent propargyl alcohol and 0.025 percent pyrrole. The results were virtually identical with those in that example.

In a further test, using 0.1 percent propargyl alcohol, 0.025 percent pyrrole, and 0.0015 percent diisopropylamine, at the end of the six days the acidity of the stabilized trichloroethylene was 86 p. p. m. and the chloride was 123 p. p. m.

The stabilizing compositions of the invention are broadly effective in stabilizing trichloroethylene from various sources. In the past, trichloroethylene made by the alkali dehydrochlorination of the product of the chlorina-

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tion of acetylene has presented a different stabilization problem from that of trichloroethylene made by high-temperature chlorinolysis of ethane and ethylene. Both such grades of trichloroethylene are satisfactorily stabilized by the compositions described above. Further, trichloroethylene stabilized according to the invention meets standard specifications for trichloroethylene, i. e. the inhibitors do not affect the grading of trichloroethylene, as has often been the case heretofore.

What is claimed is:

1. Trichloroethylene containing from 0.005 to 1.0 percent of propargyl alcohol and from 0.005 to 0.1 percent pyrrole.

2. A composition of matter, consisting essentially of trichloroethylene having dissolved therein propargyl alcohol, pyrrole, and an organic nitrogen base having a substantial vapor pressure at the boiling temperature of trichloroethylene in a minor proportion sufficient to inhibit decomposition of the trichloroethylene when in contact with metal.

3. Trichloroethylene stabilized with from 0.005 to 1.0 percent of propargyl alcohol, from 0.005 to 0.1 percent pyrrole, and from 0.0005 to 0.1 percent of a lower aliphatic amine.

4. Trichloroethylene stabilized with from 0.05 to 0.5 percent of propargyl alcohol, from 0.01 to 0.05 percent pyrrole, and 0.0005 to 0.01 percent diisopropyl amine.

5. A method of inhibiting the decomposition of trichloroethylene during contact with one of the metals aluminum and iron which comprises maintaining dissolved therein from 0.005 to 1.0 percent of propargyl alcohol and from 0.005 to 0.1 percent pyrrole.

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