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STABILIZATION OF CHLORINATED HYDROCARBONS

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No Drawing. Continuation-in-part of application Ser. No. 566,733, July 21, 1966. This application Mar. 2, 1967, Ser. No. 619,938

Int. Cl. C07c 17/40

U.S. Cl. 260—652.5 8 Claims

ABSTRACT OF THE DISCLOSURE

Lactams having 2 to 7 carbon atoms are effective in stabilizing chlorinated hydrocarbons against decomposition and degradation upon exposure to metals and metal salts. They are especially useful when used together with epoxides and alcohols.

Related applications

This is a continuation-in-part of copending U.S. application Ser. No. 566,733, filed July 21, 1966, now abandoned.

Background of the invention

The chlorinated hydrocarbons, for example trichloroethylene, perchloroethylene and 1,1,1-trichloroethane, are useful in the degreasing of metals such as aluminum, magnesium and iron and of metal alloys, in dry cleaning operations and in other applications where the chlorinated hydrocarbon comes into contact with metals.

Exposure of the chlorinated hydrocarbon to the metal and to the metal chlorides which are frequently formed as a result of this exposure has been found to result in serious degradation or decomposition of the chlorinated hydrocarbon. The metal chlorides, in particular are believed to catalyze the degradation which results in formation of black tars. In this connection 1,1,1-trichloroethane is especially susceptible to degradation by metals and metal salts. Additives, for example amines, alcohols, phenols or the like, have been provided which are effective in varying degrees in minimizing this problem.

To be completely useful in and compatible with operations in which the chlorinated hydrocarbons are used, the additive must have a number of desirable characteristics. It must be soluble in the chlorinated hydrocarbon, so that it is not deposited on the metal or other workpiece with which it comes into contact, upon removal of the chlorinated hydrocarbon. It must not give off noxious fumes and it must not be poisonous. It is helpful if it is compatible with other stabilizers and with oxidation inhibitors for chlorinated hydrocarbons, in order that the particular advantages of such other additives may be compounded into the chlorinated hydrocarbon formulation. Finally, it must be effective in small amounts and be relatively inexpensive so that its commercial use is feasible. Prior stabilizers generally have been deficient in one or more of the above characteristics.

Summary of the invention

I have now found that certain lactams function very effectively in stabilizing chlorinated hydrocarbons, including the difficulty stabilized 1,1,1-trichloroethane, against decomposition and degradation upon exposure of the chlorinated hydrocarbon to metals and metal salts. The lactams which I have found to be effective in this application are those having 2 to 7 carbon atoms, and preferably 3 to 6 carbon atoms, and they are useful in small, stabilizing amounts, generally about 0.05 to 5%, and preferably 0.1 to 1%, by weight of lactam based on the weight of the chlorinated hydrocarbon. These lactams are formulated into the chlorinated hydrocarbon simply by stirring them into the latter.

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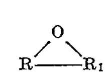
In a particularly preferred embodiment of my invention, an alkylene oxide and/or alcohol is employed with the lactam in the chlorinated hydrocarbon formulation, the alkylene oxide or alcohol being employed in a small, stabilizing amount, normally about 0.05 to 1.0%, and preferably about 0.1 to 0.5% by weight of the alkylene oxide or alcohol based on the weight of the chlorinated hydrocarbon.

Detailed description

The lactams useful in stabilizing chlorinated hydrocarbons in accordance with my invention are those having 2 to 7, and preferably 3 to 6, carbon atoms. They may be single ring compounds, or compounds having two or more rings at least one of which has a lactam grouping, and they may contain unsaturated linkages although normally they are fully saturated. Preferred lactams are the γ-butyrolactam, γ-valerolactam and caprolactam, although other lactams having the above-noted characteristics are also very effective stabilizers for chlorinated hydrocarbons.

The lactams which I have found useful as stabilizers for chlorinated hydrocarbons have boiling points which range up to about 300° C., and are readily soluble in chlorinated hydrocarbons. It is significant also that the lactams are non-toxic, and essentially odorless, and that they form colorless solutions with chlorinated hydrocarbons. Furthermore, various lactams are readily available at moderate cost and they are effective in small amounts in stabilizing the chlorinated hydrocarbons. Also, they are compatible in chlorinated hydrocarbon formulations with other additives which may be employed for particular reasons, for example with para-tert.-butylphenol which functions as an antioxidant, with amines which function as additional acceptors for the hydrogen chloride which is formed upon decomposition of the chlorinated hydrocarbon and the like.

Useful alkylene oxides are those having 3–12 carbon atoms and having a vicinal epoxy group. Preferably they have the formula



in which R and R_1 are divalent aliphatic or alicyclic radicals which may be substituted with an aliphatic, alicyclic or aromatic group and which may have on the aliphatic or alicyclic radical or a substituent thereon one or more epoxy, hydroxy or alkoxy groups. Particularly useful alkylene oxides are glycidol, propylene oxide, 1,2-epoxy butane, cyclohexene oxide and trans 2,3-epoxy butane.

The alcohols useful herein are the aliphatic, alicyclic or aromatic alcohols having 2–8 carbon atoms and having one or more hydroxy groups, and which are free of non-hydroxy substituents having other than carbon and hydrogen atoms. Particularly useful alcohols are ethyl alcohol, n-butyl alcohol, n-amyl alcohol, the secondary and tertiary buty and amyl alcohols, n-propyl alcohol, isopropyl alcohol, cyclohexyl alcohol and the like.

The useful alkylene oxides and alcohols have varying boiling points, and it is possible to formulate mixtures of them with lactams which provide the alkylene oxides in either or both of the liquid chlorinated hydrocarbon and its vapor. The lactams generally boil at reasonably high temperatures and therefore are present in the liquid phase of the chlorinated hydrocarbon. The ability to formulate the chlorinated hydrocarbon with stabilizers which are present in both the liquid and vapor phases of the chlorinated hydrocarbon is particularly useful in cleaning operations such as the degreasing of metals.

My lactams, and my epoxides and alcohols, as indicated are used in small, stabilizing amounts in conjunction with chlorinated hydrocarbons. The numerical amounts given above in which these stabilizing additives are normally used are very useful amounts and are preferred. However, use of more or less of the stabilizing additives may be effective in specific instances and is within the scope of my invention.

Other stabilizers and anti-oxidants for use in chlorinated hydrocarbon formulations with which my lactams are compatible, include the various ethers such as the aromatic, linear and internal ethers, the amines, the lactones, the sulfones, the sulfoxides and other known stabilizers and anti-oxidants. Such known additives are described in the patent and other literature concerned with chlorinated hydrocarbons and in general I employ them in instances where their particular properties are desired. In any event, my lactams are unusually compatible with other stabilizers and anti-oxidants for the chlorinated hydrocarbons and for that reason are particularly desirable in cleaning and other end-use applications.

The chlorinated hydrocarbons which are stabilized with my lactams are exemplified by trichloroethylene, perchloroethylene, methyl chloride, chloroform, carbon tetrachloride, ethyl dichloride, trichloroethane, tetrachloroethane, vinylidene chloride, dichloro-1,2-ethylene, vinyl chloride, butyl chloride and/or dichloro-1,2-propane.

Trichloroethylene, perchloroethylene and 1,1,1-trichloroethane, otherwise called methyl chloroform, are particularly useful chlorinated hydrocarbons, especially for use as solvents in the degreasing of metals such as aluminum. Generally speaking, the unsaturated chlorinated hydrocarbons are affected more adversely by metals and metal salts than are the saturated materials, but the saturated materials frequently become unsaturated upon exposure to conditions in which the solvents are used, for example exposure to elevated temperatures, acids, metals and metal salts, and therefore the use of stabilizers in the formulation is desirable to take care of such in-situ formed unsaturates. In any case, the 1,1,1-trichloroethane is particularly susceptible to decomposition and degradation and difficult to stabilize against the deterious effect of contact with metals and metal salts, but is effectively stabilized with the herein lactams.

The most noticeable effect of decomposition or degradation of the chlorinated hydrocarbon by exposure to metals or metal salts is discoloration. Aluminum chloride, for example, causes formation of black, tarry materials which are highly visible. This provides an excellent means for determining whether a given stabilizer is effective in combination with the chlorinated hydrocarbon, with simple observation of the color of the solution indicating the presence or absence of decomposition.

The following examples are presented by way of illustration of my invention only, and are not to be considered as limiting its scope in any way.

EXAMPLE 1

Control—No stabilizer

A 100 g. sample of unstabilized trichloroethylene and 0.5 g. of anhydrous aluminum chloride were placed in a 250 ml. flask equipped with a reflux condenser and the system was heated to reflux temperature of the trichloroethylene, which was 87° C. Decomposition of the trichloroethylene began rapidly, even before the reflux temperature was reached, and the solution turned black, evidencing extensive trichloroethylene degradation and formation of tars.

EXAMPLE 2

The procedure of Example 1 was followed, with the exception that varying amounts of caprolactam were added to three samples of the trichloroethylene. These amounts were 0.05, 0.1 and 0.2 g. respectively, per 100 g. of trichloroethylene. The trichloroethylene in each case was held at the reflux temperature for 72 hours, and in the case of the sample containing 0.05 g. of caprolactam, a slight discoloration, to a light amber color, of the trichloroethylene resulted. In the case of the samples formulated with 0.1 and 0.2 g. of caprolactam, no discoloration was noted.

EXAMPLE 3

Example 2 was repeated with the exception that γ-butyrolactam was employed in place of the caprolactam. Again, the samples were either water white or only slightly discolored to a pale yellow or amber color after 72 hours at the reflux temperature.

EXAMPLE 4

The procedure of Example 2 was followed again with the exception that γ-valerolactam was employed in place of the caprolactam. This additive was also a highly effective stabilizer, the trichloroethylene containing 0.05 g. of the γ-valerolactam per 100 g. of trichloroethylene being only slighlty discolored, to a pale yellow color, while the other solutions were colorless after 72 hours at reflux.

EXAMPLE 5

The procedure of Example 2 was followed employing caprolactam and treating perchloroethylene in place of the trichloroethylene. Very good results were achieved, the solutions resulting from refluxing for 72 hours being water-white in the case of the sample containing 0.1 and 0.2 g. of caprolactam, and slightly amber-colored when 0.05 g. of caprolactam was employed.

EXAMPLE 6

The procedure of Example 2 was followed employing caprolactam and treating cis- and trans-1,2-dichloroethylene in place of trichloroethylene. Excellent results were achieved, the solutions resulting from refluxing for 72 hours being water-white when 0.1 and 0.2 g. of caprolactam was used and only pale yellow when 0.05 g. of caprolactam was employed.

EXAMPLE 7

Comparative

This example demonstrates the stabilizing effectiveness of the above lactam-stabilizers, by comparing them with a typical trichloroethylene stabilizing system used heretofore. In this example the procedure of Example 2 was followed, with the exception that a mixture of 0.1 g. of N-methyl pyrrole, 0.01 g. of catechol and 0.01 g. of diisobutylene were substituted for the caprolactam employed in Example 2, in an attempt to prevent decomposition of the trichloroethylene. When the solution was heated to reflux over a 5 minute period, decomposition set in rapidly, and by the time the solution reached its reflux temperature the solution had blackened. Addition of 0.1 g. of caprolactam to a trichloroethylene formulation containing the ingredients of this Example 7 resulted in a formulation which showed no separation of ingredients or other evidence of incompatibility and which when heated at its reflux temperature for 72 hours exhibited no discoloration.

EXAMPLE 8

This example demonstrates the effectiveness of my lactam-alkylene oxide stabilization system, specifically caprolactam and glycidol, in aluminum degreasing. To 400 g. of unstabilized trichloroethylene was added 0.05 g. of caprolactam, and 0.1 g. of glycidol. The solution was placed in 500 ml. flask fitted with a Soxhlet extractor and with a condenser. A 7.0060 g. strip of aluminum (5215 5652 H34) was placed in the Soxhlet extractor and into the flask was introduced a 0.4610 g. strip of freshly stripped aluminum turning. Air saturated with water vapor was passed through the solution and the reactor was heated to reflux.

The reflux rate was adjusted so that the cup emptied approximately every 45 minutes. A 150-watt spotlight was shined into the flask while the reaction mixture was refluxed for 48 hours. The solution remained water-white. A 50 g. sample of the trichloroethylene removed after the 48 hour reflux was titrated for acid, which would be formed upon decomposition of the chlorinated hydrocarbon, and no acid was detected. Both the aluminum strip and the aluminum turning were clean, with no loss of weight.

EXAMPLE 9

The procedure of Example 8 was repeated, employing 0.1 g. of caprolactam, and 0.1 g. of n-butanol in place of the 0.1 g. of glycidol. The solution remained water-white and no acid was detected after 48 hours of refluxing. The aluminum strip and aluminum turning were clean and showed no loss of weight.

EXAMPLE 10

While glycidol and n-butanol were shown in Examples 8 and 9, respectively, to be effective additional stabilizers when used with one of my lactam stabilizers in aluminum degreasing, substitution of other alkylene oxides, namely cyclohexane oxide, 1,2-epoxy butane, trans - 2,3 - epoxy butane and propylene oxide for the glycidol, and of other alcohols, namely n-propanol, sec.-butanol, isobutanol, tert.-butanol, isopropanol, n-amyl alcohol, sec.-amyl alcohol and tert.-amyl alcohol for the n-butanol, or use of mixtures of the various alkylene oxides and alcohols results in similarly effective stabilization.

EXAMPLE 11

Control—No stabilizer

A 500 g. sample of unstabilized 1,1,1-trichloroethane was mixed with 0.5 g. of freshly prepared aluminum turnings. The solution and turnings were heated to 65° C. in the presence of strong light. After three minutes of heating, the solution turned black and tarry. A substantial amount of hydrogen chloride gas was evolved and the aluminum turnings were completely dissolved.

EXAMPLE 12

The procedure of Example 11 was followed with the exception that prior to being mixed with the aluminum turnings the 1,1,1-trichloroethane was mixed with 0.2% of caprolactam. In this case the solution remained clear and colorless and the aluminum turnings clean with no loss of weight for 24 hours at 65° C. in the presence of strong light. Furthermore, no free acid was detected by titration.

EXAMPLE 13

A 500 g. sample of unstabilized 1,1,1-trichloroethane was mixed with 0.2% of caprolactam and 0.8% of t-butanol and the solution introduced into a 500 ml. flask equipped with a Soxhlet extractor and condenser. A 7 g. strip of aluminum was placed in the Soxhlet cup together with 0.23 g. of freshly stripped aluminum turning. The reactor was heated to reflux while water-saturated air was passed through the solution.

The reflux rate was adjusted so that the cup emptied every 30 minutes, and a 150-watt spotlight was shined into the flask while refluxing continued for 48 hours. The pale yellow solution remained clear and both the aluminum strip and turnings remained clean with no loss of weight. No free acid was detected by titration.

It is seen from the above examples that the lactams of my invention are particularly effective in stabilizing chlorinated hydrocarbons against the decomposing effect of metal and metal salts. They possess this ability, together with the desired characteristics of being readily soluble in the chlorinated hydrocarbon, of being odorless and non-toxic, of being compatible with additional stabilizing agents and of being useful in very small amounts, and they are available at low cost. They therefore are unusually effective and useful stabilizers for chlorinated hydrocarbons.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims, the invention may be practiced by those skilled in the art, and having the benefit of this disclosure otherwise than as specifically described and exemplified herein.

What is claimed is:

1. A chlorinated hydrocarbon composition containing a small but effective amount, sufficient to stabilize said chlorinated hydrocarbon against degradation by metals and metal salts, of a lactam having 3–7 carbon atoms, said chlorinated hydrocarbon being selected from the group consisting of trichloroethylene, perchlorethylene, 1,1,1-trichloroethane, methyl chloride, chloroform, carbon tetrachloride, trichloroethane, tetrachloroethane, vinylidene chloride, dichloro-1,2-ethylene, vinyl chloride, butyl chloride, dichloro-1,2-propane and mixtures thereof.

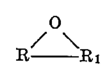
2. The stabilized composition of claim **1** in which the lactam is caprolactam.

3. The stabilized composition of claim **1** in which the lactam is γ-butyrolactam.

4. The stabilized composition of claim **1** in which the lactam is γ-valerolactam.

5. The stabilized composition of claim **1** which contains as an additional stabilizer a small, stabilizing amount of a compound selected from the group consisting of vicinal alkylene oxides having 3–12 carbon atoms and alkanols having 2–8 carbon atoms.

6. The stabilized composition of claim **5** which contains as the additional stabilizer a small, stabilizing amount of a vicinal alkylene oxide having 3–12 carbon atoms.



in which R and R_1 are divalent aliphatic or alicyclic radicals which may be substituted with an aliphatic, alicyclic or atromatic group which may have on the aliphatic or alicyclic radical or a substituent thereon one of more alkylene oxide, hydroxy or alkoxy groups.

7. The stabilized composition of claim **5** in which the alklene oxide is glycidol.

8. The stabilized composition of claim **5** in which the additional stabilizer is an alkanol having 2–8 carbon atoms.

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U.S. Cl. X.R.

252—171, 364, 401

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,496,241 Dated February 17, 1970

Inventor(s) Sidney Berkowitz

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 63, "buty" should read --butyl--.

Column 3, line 45, "deterious" should read --deleterious--.

Column 6, Claim 6, lines 43 to 49 should be deleted.

Column 6, Claim 7, line 52, "alklene" should read --alkylene--.

Signed and sealed this 4th day of May 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents