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3,113,154

STABLE METHYLCHLOROFORM COMPOSITIONS

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No Drawing. Filed May 27, 1960, Ser. No. 32,104
13 Claims. (Cl. 260-652.5)

This invention relates to the degreasing of metals. In particular, it relates to stable solvent compositions composed of 1,1,1-trichloroethane containing mixtures of stabilizing additives which prevent metal induced decomposition.

The problem of stabilizing chlorinated aliphatic hydrocarbons—viz., carbon tetrachloride, trichloroethylene, tetrachloroethylene, ethylene dichloride, etc., useful as solvents for degreasing metals has received considerable attention by skillful chemists over many years. It has, however, become increasingly apparent that the discoveries relative to the stabilization of particular chlorinated hydrocarbon solvents are neither applicable nor translatable to the problems of stabilizing other chlorinated hydrocarbon solvents. Even where a successful stabilizing additive has been found for a particular chlorinated hydrocarbon solvent, the stabilized composition still may not meet the rigorous requirements of commercial applications.

Some stabilizing additives thus provide some degree of protection against decomposition of the chlorinated hydrocarbon solvents or against attack upon the metals themselves in liquid and vapor phase but yet do not provide sufficient protection for commercial use. A commercially acceptable stabilizing additive, for example, must also be capable of inhibiting against metal induced decomposition of the chlorinated hydrocarbon solvent under hydrolytic conditions. Often a stabilizer, otherwise acceptable commercially, fails to meet this stringent requirement and when a very small amount of water is introduced into the system severe corrosion of the metal and decomposition of the solvent results. Also, a stabilizing additive otherwise acceptable, is often rejected by the trade because it adds color to the chlorinated hydrocarbon solvent. Cost of the stabilizing additive is another factor which can influence the commercial acceptance of stabilizers.

Insofar as stabilizing 1,1,1-trichloroethane (methylchloroform) is concerned, the problems are even more acute. From the standpoint of metal induced decomposition, 1,1,1-trichloroethane departs drastically from the norm of other chlorinated hydrocarbons. For example, metals, especially aluminum, will last for days or weeks without being attacked by ordinary chlorinated hydrocarbon solvents, but in the presence of 1,1,1-trichloroethane, however, aluminum is vigorously attacked and the 1,1,1-trichloroethane solvent reduced to a blackened or charred mass within minutes. Only a few stabilizers are known which are reasonably effective in inhibiting 1,1,1-trichloroethane against such attack and why these few stabilizers are effective is not known. The mere fact however that a stabilizer will inhibit decomposition of other chlorinated hydrocarbons means absolutely nothing in relation to stabilizing 1,1,1-trichloroethane.

The problem of stabilizing 1,1,1-trichloroethane in the vapor phase is especially acute because even a stabilizer which is useful for stabilization in the liquid phase is useless for stabilizing the vapor phase unless it has suffi-

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cient volatility to stabilize the vapor phase, and yet it cannot have such volatility as to unduly deplete the liquid phase. No commercial vapor phase stabilizer for 1,1,1-trichloroethane is yet known.

It is accordingly an object of this invention to provide stabilized compositions which are highly effective for degreasing aluminum, iron and other metals. A particular object is to provide 1,1,1-trichloroethane solvent compositions which retain chemical passivity during repeated cycles of exposure to metals at processing conditions, and against the degradation influences of moisture, elevated temperature, contact with metals and metal halides, and light. Another object of the present invention is to provide compositions especially suitable for the vapor phase degreasing of aluminum and other metals. A further object is to provide additive compositions especially adapted for use in methyl chloroform as stabilizers therefor.

These and other objects are achieved according to the present invention which comprises forming a stable 1,1,1-trichloroethane solvent composition by dissolving within 1,1,1-trichloroethane a novel mixture of additives in a quantity sufficient to inhibit against decomposition. The stabilizing mixture is one consisting essentially of a dioxolane, a mono-olefin and an amine compound. On the basis of outstanding effectiveness and low cost, the preferred class of stabilizing additives are those wherein the dioxolane compound is a 1,3-dioxolane containing up to two alkyl substituents each having from 1 to 2 carbon atoms, the mono-olefin is an alkene hydrocarbon having from about 6 to about 8 carbon atoms and the amine is a compound selected from a group consisting of alkyl amines containing from about 4 to about 6 carbon atoms, morpholine and pyridine.

In an especially preferred embodiment of this invention the stabilizing mixtures of dioxolane, mono-olefin and amine compounds, added to the 1,1,1-trichloroethane, are preferably 1,3-dioxolane compounds containing up to one alkyl substituent having from 1 to 2 carbon atoms, a mono-olefin which is an alkene hydrocarbon having from about 6 to about 8 carbon atoms and an alkyl amine containing from about 4 to about 6 carbon atoms. These systems have superb stabilizing properties, particularly against iron even under hydrolytic conditions, and even in the stabilization of 1,1,1-trichloroethane in the vapor phase.

An even more highly preferred embodiment in one wherein the stabilizing mixture for 1,1,1-trichloroethane consists essentially of 1,3-dioxolane, diisobutylene, and n-butyl amine. This particular combination of additives shows outstanding stabilizing properties and in the presence of iron does not discolor or cause corrosion of the iron even under severe hydrolytic conditions. In short, on a cost-effectiveness basis this ternary system is particularly outstanding.

In yet another especially preferred embodiment of this invention, the dioxolane, mono-olefin and the amine compounds are blended together to form additive concentrates or corrosion inhibitor compositions. These compositions form homogenous and essentially colorless solutions which can be added rapidly and conveniently to 1,1,1-trichloroethane in all desired proportions. The inhibited 1,1,1-trichloroethane compositions thus formed are highly resistant both to decomposition of the solvent and to corrosion of the metal with which the solvents are placed in contact. In particular, these additive concentrates

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when blended with 1,1,1-trichloroethane form highly useful compositions for degreasing the surfaces of metals. Accordingly, another preferred embodiment of this invention is that of degreasing metal by contacting the surfaces of metal with 1,1,1-trichloroethane while maintaining a stabilizing mixture of a dioxolane, a mono-olefin and an amine dissolved within the 1,1,1-trichloroethane in sufficient quantity to inhibit the 1,1,1-trichloroethane against decomposition.

In accordance with the practice of this invention, 1,1,1-trichloroethane is provided with an additive concentrate composed of a mixture of from about 10 percent to about 75 percent of a dioxolane compound, from about 20 to about 85 percent of a mono-olefin compound and from about 0.1 to about 10 percent of an amine compound, based on the total weight of the additive concentrate or corrosion inhibitor composition. A particularly preferred inhibitor composition is one composed of about 30 to 40 weight percent of a dioxolane compound, from about 55 to 65 weight percent of a mono-olefin compound and from about 1 to 3 weight percent of an amine compound because it provides very high stabilizing benefits under general commercial degreasing conditions. This composition is also available at low cost.

A small amount of this stabilizing mixture, in a quantity sufficient to inhibit the 1,1,1-trichloroethane against decomposition, is added to the 1,1,1-trichloroethane. Generally a minor amount of this stabilizing mixture, suitably about 0.3 to about 15 weight percent (based on the weight of the total inhibited solvent), added to the 1,1,1-trichloroethane solvent forms a highly effective system which resists deteriorating influences such as contact with aluminum—even freshly exposed aluminum surfaces—copper, zinc and other metals, exposure to light and subjection to elevated temperatures. These mixtures are particularly effective in preventing attack upon iron metal, or alloys of iron, which are especially susceptible to attack under hydrolytic conditions. The stabilizing mixtures also form clear and almost colorless solutions which are accepted without prejudice by the trade. This attitude is in sharp contrast to many other situations where stabilizing mixtures are rejected on the basis that they add color to the solvent. A preferred concentration of any of these stabilizing mixtures in 1,1,1-trichloroethane is from about 4 to about 10 weight percent because of the excellent properties of the resulting composition to resist deterioration. A 6 percent concentration is especially preferred because of the excellent properties of the resulting composition to resist deterioration under commercial operating conditions. It will be understood however that the concentrations of the present stabilizers can be varied beyond the ranges given above without loss of most of the benefits of this invention and without departing from the scope of this invention.

It was heretofore discovered by one of my colleagues that these dioxolane compounds when used alone are highly effective stabilizers for 1,1,1-trichloroethane. It has now been discovered that the inhibiting powers of these dioxolane compounds can be even further enhanced by the use of particular mono-olefin and amine compounds. This in indeed unexpected for the latter compounds in themselves, alone or admixed, are poor stabilizers for 1,1,1-trichloroethane. Thus, while the discovery of these dioxolane compounds as inhibitors for 1,1,1-trichloroethane has been of great importance and of significance, dioxolane-1,1,1-trichloroethane systems nevertheless do have one shortcoming. The dioxolane-1,1,1-trichloroethane compositions do leave something to be desired when hydrolytic conditions occur and these compositions are in contact with iron, particularly with certain forms of iron and under extended hydrolytic conditions. The iron, under hydrolytic conditions, does undergo significant corrosion. The corrosion of iron under hydrolytic conditions is considerably and significantly reduced

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by use pursuant to this invention of a dioxolane, mono-olefin and an amine compound in the 1,1,1-trichloroethane solvent. In particular, the value of dioxolane as a vapor phase inhibitor is greatly enhanced by the addition thereto of a mono-olefin and an amine compound.

This invention then is based on the discovery that the value and effectiveness of these dioxolanes as stabilizers, particularly as vapor phase stabilizers, for 1,1,1-trichloroethane can be even further enhanced by the addition thereto of specified mono-olefin and amine compounds. In particular, these stabilizing mixtures considerably enhance the ability of the 1,1,1-trichloroethane to resist deterioration in the presence of iron metal and its alloys. This is true even under severe hydrolytic conditions.

Thus, additive concentrates or inhibitor compositions made up of mixtures of dioxolanes and specified mono-olefin and amine compounds can be formed and added to 1,1,1-trichloroethane and outstanding results achieved. As stated, this is especially true where the stabilized 1,1,1-trichloroethane-dioxolane compositions are used in contact with iron and under hydrolytic conditions. However, the several additive ingredients of the stabilizers of this invention can be blended with the 1,1,1-trichloroethane either individually or in various subcombinations.

The following representative experimental data provide a sound basis for a clear appreciation of this invention. In the demonstration immediately following a stabilized composition of 1,3-dioxolane-1,1,1-trichloroethane is employed with iron under degreasing conditions. Accordingly, to 100 parts by weight of methyl chloroform contained within a reaction vessel were added 3 parts by weight of 1,3-dioxolane. Above the reaction vessel were suspended 2 tared strips of soft iron. The mixture was then continuously refluxed for 67 hours, the vapors condensing upon the strips of iron and pouring back into the vessel. After this time the tared metal strips were dried, cleaned and reweighed. The average weight loss of the two iron strips was 0.14 percent by weight.

To show the benefits derived from the practice of this invention wherein a mono-olefin and an amine compound are used in combination with dioxolane, a mixture of dioxolane and the former compounds was added to 1,1,1-trichloroethane, and a demonstration performed under even more rigorous conditions as in the following example.

EXAMPLE I

To 100 parts by weight of methyl chloroform was added a stabilizing mixture consisting of 2.9 parts by weight 1,3-dioxolane, 5 parts by weight diisobutylene and 0.2 part by weight n-butylamine. Next, four tared strips of iron were suspended above the reaction vessel containing the stabilized solvent. The temperature of the mixture was then raised to boiling and reflux continued for 96 hours. After that time the iron strips were removed from the vicinity of the reactor and examined. The iron appeared completely unaffected and its surface remained bright and clear. The 1,1,1-trichloroethane solvent showed only slight evidence of any discoloration. The average weight loss of the four iron strips was less than 0.02 percent.

EXAMPLE II

The foregoing example was repeated in all details except in this instance four aluminum metal strips were substituted for the iron metal. After refluxing again for 96 hours the four aluminum strips were removed, dried and reweighed. The average weight loss of the four aluminum strips was only 0.015 percent.

The following Table I shows other three-component systems of highly preferred additive concentrates consisting of dioxolane, mono-olefin and amine compounds. These systems of additive concentrates correspond in relative concentrations of components to each other as that of the stabilizing mixture employed in Example I.

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Table I

Example	Dioxolane Compound	Mono-Olefin Compound	Amine Compound
III-----	1,3-dioxolane	Hexene-1	Triethylamine.
IV-----	do	2,3 dimethyl butene-1.	diisopropylamine.
V-----	do	2,4,4-trimethyl pentene-1.	Di-n-propylamine.
VI-----	do	2,4-dimethyl pentene-1.	Hexylamine.

EXAMPLES III-VI

The systems of additive concentrates, II-VI, respectively, are added to 1,1,1-trichloroethane solvent in sufficient quantity to form .03, .05, 1, 2, 4, 5, 6, 10, 12 and 15 percent compositions, respectively. The procedure of Example I is again repeated with each of these compositions. At the termination of each of the runs the 1,1,1-trichloroethane solvent remains essentially colorless and there is no visible evidence of any corrosion.

In the following examples (VII-XXVII), a wide variety of additive concentrates, varying with respect to the individual compounds employed and with respect to their relative proportions to each other, are formed as shown in Table II.

Table II

Example	Dioxolane Compound	Mono-Olefin Compound	Amine Compound
VII-----	10 percent 5-methyl-1,3-dioxolane.	58 percent heptene-1.	5 percent triethylamine.
VIII-----	10 percent 4-methyl-1,3-dioxolane.	80 percent 2,3-dimethyl butene-1.	10 percent n-butylamine.
IX-----	20 percent 2-methyl-1,3-dioxolane.	72 percent 2,3-dimethyl butene-2.	8 percent triethylamine.
X-----	30 percent 2-ethyl-1,3-dioxolane.	64 percent 2-methyl pentene-2(cis).	6 percent diisopropylamine.
XI-----	40 percent 4-methyl-1,3-dioxolane.	56 percent 2-methyl pentene-2 (trans).	4 percent di-n-propylamine.
XII-----	50 percent 4-ethyl-1,3-dioxolane.	47 percent 2,4,4-trimethyl pentene-1.	3 percent ethyl-n-butylamine.
XIII-----	60 percent 5-methyl-1,3-dioxolane.	38 percent 2,3,3-trimethyl pentene-1.	2 percent methyl-n-butylamine.
XIV-----	65 percent 5-ethyl-1,3-dioxolane.	34 percent 2,4-dimethyl pentene-2.	1 percent methyl ethyl propylamine.
XV-----	70 percent 1,3-dioxolane.	29.5 percent heptene-1.	0.5 percent methyl ethyl isopropylamine.
XVI-----	75 percent 1,3-dioxolane.	24.9 percent 2,3,3-trimethyl butene-1.	0.1 percent methyl ethyl-n-propylamine.
XVII-----	70 percent 1,3-dioxolane.	20 percent 2,3,3-trimethyl butene-1.	10 percent methyl ethyl-n-propylamine.

The stabilizing mixtures, or corrosion inhibitor compositions, shown in Examples VII through XVII are added to 1,1,1-trichloroethane to form stabilized 1,1,1-trichloroethane compositions. The corrosion inhibitor compositions are added to the 1,1,1-trichloroethane in sufficient quantity to form 0.3, 0.5, 1, 2, 4, 5, 6, 10, 12 and 15 weight percent compositions of the stabilizing mixtures in 1,1,1-trichloroethane.

Example I is repeated with each of these stabilized 1,1,1-trichloroethane compositions. As in Example I, the solvents show little or no signs of decomposition. The metals also show little or no signs of chemical attack.

When Examples I and II are repeated with each of the compositions of Examples VII through XVII except that the metals are completely immersed within the stabilized 1,1,1-trichloroethane solvent, similar results are obtained.

The corrosion inhibitor compositions of Examples XVIII through XXVI (Table III) are added to 1,1,1-trichloroethane in sufficient quantity of form 0.3, 0.5, 1, 2, 4, 5, 6, 10, 12 and 15 weight percent compositions of the stabilizing mixtures in 1,1,1-trichloroethane. Examples I

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and II are then again repeated with each of these compositions. As in Examples I and II the solvent compositions show little or no signs of decomposition and the metals are essentially unattacked.

Table III

Example	Dioxolane Compound	Mono-Olefin Compound	Amine Compound
XVIII-----	10 percent 2,2-diethyl-1,3-dioxolane.	85 percent 1-hexene.	5 percent ethyl propylamine.
XIX-----	20 percent 1-methyl-2-ethyl-1,3-dioxolane.	76 percent 3-ethyl butene-1.	4 percent ethyl methyl propylamine.
XX-----	30 percent 2,2-dimethyl-1,3-dioxolane.	67 percent 4-ethyl pentene-1.	3 percent dimethylbutylamine.
XXI-----	40 percent 2,4-diethyl-1,3-dioxolane.	58 percent 5-ethylhexene-1.	2 percent n-butylamine.
XXII-----	50 percent 4,4-dimethyl-1,3-dioxolane.	49 percent 2-methyl pentene-2.	1 percent ethyl butylamine.
XXIII-----	60 percent 2-methyl-5-ethyl-1,3-dioxolane.	39.5 percent 2-ethyl-butene-2.	0.5 percent ethyl methyl butylamine.
XXIV-----	65 percent 2-methyl-5-ethyl-1,3-dioxolane.	34.5 percent 2,4,4-trimethyl-pentene-1.	0.3 percent ethylamine.
XXV-----	70 percent 5,5-diethyl-1,3-dioxolane.	23 percent hexene-1.	7 percent n-butylamine.
XXVI-----	75 percent 4,5-diethyl-1,3-dioxolane.	20 percent 2,3,3-trimethyl-butene-1.	5 percent n-butylamine.
XXVII-----	70 percent 4,5-diethyl-1,3-dioxolane.	do	10 percent n-butylamine.

EXAMPLES XXVIII-XXIX

Examples XVIII through XXVII are repeated substituting morpholine and pyridine, respectively, for the amine in each of the examples. Again highly satisfactory corrosion inhibitor compositions are produced for stabilizing 1,1,1-trichloroethane.

In the practice of this invention, a minor concentration of the mixture of components or additive concentrates is added to the 1,1,1-trichloroethane. Any concentration of these compounds will produce some stabilizing effect, and the quantity of the stabilizing mixture to be added is therefore largely contingent upon the use of which the stabilized solvent will be employed. Generally, however, stable compositions consisting essentially of from about 0.3 to about 15 weight percent of the mixture of additives in 1,1,1-trichloroethane are formed. These compositions form highly effective systems which resist the deteriorating influences such as contact with aluminum, iron and other metals, salts of such metals, light, water and elevated temperatures. A preferred concentration of the stabilizing mixture in 1,1,1-trichloroethane is from about 4 to 10 weight percent.

As was stated, a wide variety of dioxolane, mono-olefin and amine compounds are suitable for the practice of this invention.

Nonlimiting examples of the highly preferred dioxolane compounds suitable in the practice of this invention include 1,3-dioxolane, 2-methyl-1,3-dioxolane, 4-methyl-1,3-dioxolane, 5-methyl-1,3-dioxolane, 2-ethyl-1,3-dioxolane, 4-ethyl-1,3-dioxolane, 5-ethyl-1,3-dioxolane, and in general those compounds boiling within a range of from about 50° C. to about 120° C., preferably from about 65° C. to about 85° C., and the like. Other preferred dioxolane compounds include 2,2-dimethyl-1,3-dioxolane, 4,4-dimethyl-1,3-dioxolane, 5,5-dimethyl-1,3-dioxolane, 2,4-dimethyl-1,3-dioxolane, 2,5-dimethyl-1,3-dioxolane, 2,2-diethyl-1,3-dioxolane, 4,4-diethyl-1,3-dioxolane, 5,5-diethyl-1,3-dioxolane, 2,4-diethyl-1,3-dioxolane, 2,5-diethyl-1,3-dioxolane, 2-methyl-2-ethyl-1,3-dioxolane, 2-methyl-4-ethyl-1,3-dioxolane, 2-methyl-5-ethyl-1,3-dioxolane, 2-ethyl-4-methyl-1,3-dioxolane, 2-ethyl-5-methyl-1,3-dioxolane, and the like.

Nonlimiting examples of mono-olefins of this invention include hexene-1, hexene-2, hexene-3, 2,3-dimethyl butene-1, 2,4-dimethyl butene-1, 3,4-dimethyl butene-1, 2,3-dimethyl butene-2, 3-ethyl butene-1, 2-methyl pentene-1, 2-methyl pentene-2, 3-methyl pentene-2, heptene-1, 3-methyl hexene-1, 3,3-dimethyl pentene-2, 3-methyl-3-ethyl butene-1, 3,3-diethyl propene-1, octene-1, octene-3, 2-methyl heptene-1, 2,3-dimethyl hexene-1, 2,4-dimethyl hexene-1, 3-ethyl hexene-2, 2-methyl-3-ethyl pentene-1, 2-methyl-4-ethyl pentene-1, 3,3-diethyl butene-1, 1,1,2-trimethyl butene-2, and in general those compounds boiling within a range of from about 50° C. to about 120° C., preferably from about 65° C. to about 85° C., and the like.

Nonlimiting examples of highly preferred amines are such alkyl amines as butyl amine, diethyl amine, methyl propyl amine, methyl isopropyl amine, methyl butyl amine, ethyl isopropyl amine, ethyl n-propyl amine, methyl diethyl amine, dimethyl propyl amine, amyl amine, methyl amyl amine, ethyl n-butyl amine, triethyl amine, methyl ethyl isopropyl amine, diisopropyl amine, di-n-propyl amine, methyl amyl amine, and in general those compounds boiling within a range of from about 50° C. to about 120° C., preferably from about 65° C. to about 85° C., and the like.

Other highly suitable amines include morpholine, pyridine, and the like.

Having described the invention, what is claimed is:

1. A stable solvent composition for the degreasing of metals, said solvent consisting essentially of 1,1,1-trichloroethane within which is dissolved from about 0.3 to about 15 weight percent of a stabilizing mixture of additives consisting essentially of from about 10 percent to about 75 weight percent dioxolane, from about 20 to about 85 weight percent of mono-olefin and from about 0.1 to about 10 weight percent amine, to inhibit the 1,1,1-trichloroethane against decomposition, said dioxolane being 1,3-dioxolane characterized by containing in the molecule up to two alkyl substituents each having from one to two carbon atoms, said mono-olefin being an alkene hydrocarbon characterized by having from about 6 to about 8 carbon atoms in the molecule and said amines being selected from a group consisting of morpholine, pyridine and alkyl amines characterized by containing in the molecule from about 4 to about 6 carbon atoms.

2. The composition of claim 1 wherein the dioxolane is 1,3-dioxolane.

3. The composition of claim 1 wherein the mono-olefin is diisobutylene.

4. The composition of claim 1 wherein the amine is n-butyl amine.

5. The composition of claim 1 wherein the dioxolane is 1,3-dioxolane, the mono-olefin is diisobutylene and the amine is n-butyl amine.

6. The composition of claim 5 wherein the stabilizing mixture of additives is present within the 1,1,1-trichloroethane at a concentration of from about 4 to about 10 weight percent.

7. The composition of claim 5 wherein the stabilizing mixture of additives is present within the 1,1,1-trichloroethane at a concentration of about 6 weight percent.

8. A 1,1,1-trichloroethane corrosion inhibitor composition composed of a mixture of from about 10 percent to about 75 percent of dioxolane, from about 20 percent to about 85 percent of an alkyl mono-olefin, and from about 0.1 to about 10 percent of an amine, based on the weight of the corrosion inhibitor composition, said dioxolane being 1,3-dioxolane characterized by containing up to two alkyl substituents each having from one to two carbon atoms, said mono-olefin being an alkene hydrocarbon characterized by having from about 6 to about 8 carbon atoms, said amine being selected from a group consisting of morpholine, pyridine and alkyl amines characterized by containing in the molecule from about 4 to about 6 carbon atoms.

9. The composition of claim 1 wherein the stabilizing mixture of additives is present within the 1,1,1-trichloroethane at a concentration of from about 4 to about 10 weight percent.

10. The composition of claim 1 wherein the stabilizing mixture of additives is present within the 1,1,1-trichloroethane at a concentration of about 6 weight percent.

11. The composition of claim 1 wherein the stabilizing mixture dissolved within the 1,1,1-trichloroethane consists essentially of from about 30 to about 40 weight percent of dioxolane, from about 55 to about 65 weight percent mono-olefin and from about 1 to about 3 weight percent amine.

12. The composition of claim 11 wherein the concentration of the stabilizing mixture in 1,1,1-trichloroethane is from about 4 to about 10 weight percent.

13. The composition of claim 11 wherein the concentration of the stabilizing mixture in 1,1,1-trichloroethane is about 6 weight percent.

References Cited in the file of this patent

UNITED STATES PATENTS

1,904,450	Harris	Apr. 18, 1933
2,094,367	Missbach	Sept. 28, 1937
2,371,645	Altchison et al.	Mar. 20, 1945
2,517,894	Larcher	Aug. 8, 1950