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STABILIZATION OF CHLORINATED HYDROCARBONS WITH CARBOXYLIC ACID ESTERS OF ACETYLENIC ALCOHOLS

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This invention relates to inhibiting the decomposition of tetrachloroethylene catalyzed by light, air, heat, moisture, and metal surfaces and more particularly relates to a composition of matter consisting essentially of tetrachloroethylene and stabilizing amounts of an acetylenic ester.

It has heretofore been known that tetrachloroethylene (perchloroethylene) of a high degree of purity and containing only minute amounts of saturated, or other unsaturated, lower aliphatic chloro-hydrocarbons is very inert to the action of air, light, heat, moisture, and metal surfaces with which it comes into contact during storage and commercial use. However, the obtaining of such high purity tetrachloroethylene in commercial production is not generally feasible and it has been found that the impure material normally encountered in commerce decomposes when in contact with the substances noted above. Hence, means other than purification for preventing or inhibiting the decomposition of tetrachloroethylene and the lower chlorinated aliphatic hydrocarbons generally associated therewith must be had.

It is generally believed that tetrachloroethylene exposed to air, light, heat, moisture, etc., decomposes, especially in the presence of moisture, principally by way of oxidative attack at the double bond involving a series of steps in which the ultimate products include phosgene, trichloroacetic acid, and hydrogen chloride. It is also believed that the oxidative attack is catalyzed by light and by the products of oxidation, as a result of which, oxidative decomposition once initiated is self-catalyzing and self-sustaining. Other chloro-hydrocarbons generally associated with crude commercial tetrachloroethylene also are subject to oxidative attack and decompose to some of the same products as those formed by the oxidation of tetrachloroethylene, and at a somewhat accelerated rate, as compared to the oxidation of tetrachloroethylene. These products are then available to catalyze the decomposition of the tetrachloroethylene. For example, tetrachloroethylene obtained commercially from the crude products of chlorination and chlorinolysis of lower aliphatic hydrocarbons may contain small but appreciable amounts of saturated and unsaturated chlorinated hydrocarbons, such as dichloroethylene, trichloroethylene, trichloroethane, unsymmetrical tetrachloroethane, pentachloroethane, and the like. These lower chloro-hydrocarbons in themselves are relatively innocuous in solvent extraction processes in which the tetrachloroethylene is used, but the oxidation decomposition products thereof corrode metal surfaces with which a body of tetrachloroethylene containing them comes into contact. These less stable chloro-hydrocarbons are believed to be the principal initial source of chloro oxygen-containing impurities, such as phosgene, chloroacetic acid, trichloroacetic acid, and the like, in the tetrachloroethylene, which impurities catalyze decomposition of the tetrachloroethylene.

The problem, therefore, is principally one of inhibiting the initiation of the oxidation of the chloro-hydrocarbons commonly associated with commercial tetrachloroeth-

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ylene, as well as inhibiting the oxidation of tetrachloroethylene itself.

One of the objects of the present invention is to provide means for inhibiting oxidation of tetrachloroethylene and lower aliphatic chloro-hydrocarbons generally associated therewith during exposure to air, light, heat, moisture, and metal surfaces.

Many materials are known to be useful for the purpose of stabilizing chlorinated hydrocarbons, particularly, tetrachloroethylene, and, in general, they may be regarded as satisfactory in that they effect stabilization sufficiently adequately, as determined by well-known tests, for most of the major uses of chlorinated solvents. However, the needs of industry for improved solvents meeting the requirements of specified operations is expanding constantly; hence, the quest continues for new stabilizers adapted to diverse uses.

In many instances of stabilizing chlorinated solvents, it has been found desirable to employ a pair of stabilizing ingredients, one for the general purpose of stabilizing the solvent against the effects of air, heat and moisture and another for the purpose of stabilizing against decomposition under the influence of light. This is because various stabilizers are to some extent deficient in their ability to effect the desired degree of light-stability. Accordingly, materials such as benzaldehyde, thymol, isoeugenol, ethyl alcohol, butyl alcohol, turpentine, benzene, toluene resorcinol, aniline, ethyl alcohol, quinol, hydroquinone monomethyl and monoethyl ethers have been employed in conjunction with the general-purpose stabilizers. Of this group, isoeugenol has been found to be unusually effective and it is especially effective when employed in combination with the new general-purpose stabilizers of this invention.

A further object of this invention, therefore, is to provide a new stabilizing composition of matter and a new solvent composition including the new stabilizing composition which will be especially stable under the influences of all of the several decomposing effects, and, particularly, the effect of light.

These and other objects will be apparent to those skilled in the art from the discussion hereinafter.

Unstabilized chlorinated solvents, as obtained from the producer, including tetrachloroethylene, may be either in relatively pure or impure condition. For the most part, the purity of such tetrachloroethylene depends upon its age, that is, the length of time it has stood unstabilized after production without particular effort being made to prevent decomposition. Accordingly, the relatively impure solvent is found to be of limited utility for many industrial needs, although further decomposition may be satisfactorily inhibited by using the stabilizers of this invention. On the other hand, some solvent is relatively fresh and is correspondingly pure and useable; such solvent requires only stabilization against further decomposition in order to be satisfactory for a number of its uses.

Where the initial percentage impurity is not tolerable, the solvent requires pre-treatment of a nature such that the major portion or substantially all of the impurities are removed, prior to the addition of stabilizers so as to provide a material having a good initial level of acceptability for industrial needs. As noted above, some solvent may not require such pre-treatment; however, those skilled in the art will understand that preferably, a solvent containing undesirable impurities is treated for the removal of any impurities prior to stabilization. Such purification may be effected as hereinafter taught.

The present invention is described primarily in relation to solvent materials of relatively high initial purity. It should be understood, however, that the invention is not limited in applicability to substantially pure solvents but,

rather, insofar as effecting stabilization against further decomposition is concerned, the present invention is effective substantially equally, in an impure or pure solvent.

It has been found that where the crude tetrachloroethylene, particularly that obtained from commercial processes involving the chlorinolysis of lower hydrocarbons or hydrocarbon chlorides, or the chlorination and simultaneous dehydrochlorination of hydrocarbon chlorides, such as ethylene dichloride, or of unsaturated hydrocarbons, such as acetylene, ethylene, and the like, contains appreciable amounts of lower chlorinated aliphatic hydrocarbons other than tetrachloroethylene as impurities, such crude product may initially be purified by well-known means, such as by contact with an aqueous solution of an inorganic base or a high boiling point organic base in order to destroy the major portion of volatile acids and acid-forming impurities, and then combined with an acetylenic ester, decomposition of the tetrachloroethylene and other lower chlorinated aliphatic hydrocarbons is inhibited under the most adverse conditions of storage and commercial use.

In general, the present invention is directed to a composition comprising essentially tetrachloroethylene and stabilizing amounts of esters of certain mono or dihydric alcohols characterized by the presence of a triple bond. Further, the invention is directed to such a composition including an additional ingredient effective to exert stabilizing action against the influences of light. It will be understood that the invention is not limited to a particular light stabilizer and that any of the well-known light stabilizers may be employed. Preferably, however, the invention contemplates the use of isoeugenol in combination with the new general-purpose stabilizers.

The new class of general-purpose stabilizers noted immediately above, namely, acetylenic esters, have been found particularly effective in stabilizing tetrachloroethylene contaminated with minor amounts of other lower aliphatic chlorohydrocarbons, both in the liquid and in the vapor phase. For the most part the stabilizing effect has been found to be most pronounced and prolonged where pre-treatments which destroy the greater part of the chloro-acids and acid chlorides have been resorted to prior to the addition of the stabilizing acetylenic ester.

The initial treatment of the crude tetrachloroethylene may include adding an organic base of the amine type and having a boiling point higher than tetrachloroethylene, for example, aniline or morpholine, in an amount from approximately 0.2–2.0% by weight to the crude product, and fractionally distilling the crude mass to recover substantially all of the tetrachloroethylene as an intermediate fraction in the distillation; additional treatments may include washing the tetrachloroethylene fraction with a solution of an inorganic base, such as an alkali metal or alkaline earth metal base, for example, sodium hydroxide, sodium carbonate, calcium hydroxide, magnesium bicarbonate, and the like, drying the washed product and distilling the dried product to recover a more highly refined tetrachloroethylene fraction. The purpose in using an amine, such as aniline, is to allow for the reaction of such amine with acid chloride products contained in the crude product whereby an anilide or analogous compound may form during distillation and the undesired impurity is retained in the distillation residue. The purpose of washing the effluent from the initial distillation with an alkali metal or alkaline earth metal base is to remove the more volatile of the acid chloride impurities, such as hydrogen chloride, phosgene, and the like, which may not have reacted with the amine.

The crude product may also be washed initially with a solution of an inorganic base, such as those noted above, dried, and combined with an amine having a boiling point substantially higher than tetrachloroethylene, generally in an amount from 0.2–2.0% by weight, and the mixture thus obtained distilled as described above in order to recover

the purified tetrachloroethylene substantially free from chloro oxygen-containing impurities.

Where such impurities as hydrogen chloride, phosgene, chloro-acids, and the like, are known to be extremely low in the crude product, this material may be combined with an amine, such as aniline, as noted hereinabove, and subjected to fractional distillation to recover the substantially pure tetrachloroethylene without the necessity of resorting to the treatment with a solution of an inorganic base. Moreover, the dilute alkaline wash may be omitted even where the chloro oxygen-containing compounds are present in appreciable quantities in the crude product, but it has been found that the amount of organic amine consumed and the volume of distillation residue accumulated is excessive.

After any one of the above-described initial treatments, the recovered tetrachloroethylene may be combined with a stabilizing amount of an acetylenic ester as noted above, for example, in an amount from 0.01–1.0% by weight of tetrachloroethylene, preferably, however, from 0.2–0.3% where the above pre-treatments or their equivalent have been used. The extremes within the above-noted broad range are preferred where the amount of chloro-hydrocarbon impurities associated with the tetrachloroethylene is unusually high or unusually low, while the amounts within the intermediate preferred range are generally sufficiently effective where the purified tetrachloroethylene contains not more than about 1–3% of the lower chlorinated aliphatic hydrocarbon impurities consisting essentially of trichloroethylene, the most common impurity obtained in commercial production.

The beneficial effects of the present invention may also be realized where tetrachloroethylene has been purified in a commercial operation and stabilized either with a high boiling point stabilizer, i.e., a stabilizer such as one of the amine or of the ether type having a higher boiling point than that of tetrachloroethylene, or with stabilizers which are more volatile than tetrachloroethylene, by removing such stabilizer as by chemical reaction, azeotropic distillation, or the like; the thus-treated mass is then fractionally distilled to recover the tetrachloroethylene fraction, which may be combined with an acetylenic ester, as described above, in an amount sufficient to effect stabilization, whereby the tetrachloroethylene is rendered especially suitable, due to its stability, for degreasing or dry cleaning operations.

The benefits which may be derived from this invention may be had by employing any one of a large number of acetylenic esters. For convenience in indicating the exemplary compounds that are suitable the various acids and alcohols which may be combined to provide an ester product are set forth separately.

It is contemplated that for the purpose of forming acetylenic esters for use according to this invention either mono or dihydric alcohols containing a triple bond wherein the hydroxyl groups of the compound are secured to carbon atoms which are substituted by three other substituents may be employed. Of this class of alcohols, both straight and branched chain compounds are suitable and, within the range expressed in the previous sentence, the relative position of the triple bond and the hydroxyl groups is not pertinent.

Of the straight chain mono-hydric compounds, there may be mentioned propargyl alcohol, propargyl carbinol, methyl acetylenyl carbinol, ethyl acetylenyl carbinol, 2-butyne-1-ol, and higher homologues of this series, including the octyl and nonyl substituted compounds, as well as aryl substituted compounds. Of the branched chain mono-hydric compounds may be mentioned dimethyl acetylenyl carbinol and higher homologues, such as diethyl, dibutyl, diamyl and similar substituted compounds, including those having two different substitutes, such as methyl, ethyl acetylenyl carbinol, and the like. Of special use in this group are methyl butynol and methyl pentynol, and of particular interest of the isomers of

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these compounds are respectively 2-methyl-3-butyne-2-ol and 3-methyl-1-pentyne-3-ol. Any readily available diol may be employed, especially attractive examples being 2,5-dimethyl-3-hexyne-2,5-diol, 3,6-dimethyl-4-octyne-3,6-diol, 3,6-dimethyl-4-octyne-3,6-diol, and 3,5-dimethyl-1-hexyne-3-ol.

Suitable acids which may be reacted with the aforementioned alcohols to provide the new stabilizers of the invention may be either acyclic or cyclic. They may be mono or dicarboxylic, and either saturated or unsaturated acids. Also, substituted forms of these various acids may be employed. It is contemplated that such acids may contain as many as ten or more carbon atoms. Preferably, and in general, more suitable acids are the lower molecular weight acids, particularly those numbering about six or less carbon atoms. The selection of the acid as to molecular weight in a great many instances of contemplated use for the stabilized solvent is quite agreeably in relation to the boiling point of the resulting ester that is produced. Thus, if an end product of a specified boiling point, or one boiling within a particular range, is desired, the acid might well be selected after having determined the alcohol to be included in the reaction. For example, if a high boiling alcohol is selected for esterification and it requires only a small alteration in boiling point upwardly to a preferred figure, a low molecular weight acid probably would be chosen. Sometimes it is quite difficult to procure particular desired chemical compounds in quantities that are needed for industrial operations. On the other hand, it may be possible to obtain a homologue of the desired material or a closely related chemical in large quantity. It will be seen that in this event, the present invention permits the use of such substitute chemicals and the realization of the improved result of the invention substantially without regard to the availability of particular chemicals. In the present instance, it is to be expected that such difficulty would most likely arise in obtaining particular ones of the alcohols heretofore enumerated since organic acids are generally very readily available in any quantity desired.

More particularly illustrative of the acids which are suitable for use in the present invention there may be mentioned such acids as formic, acetic, propionic, butyric, valeric, oleic hexanoic, acrylic, maleic, vinylacetic, oxalic, succinic, malonic, glutaric, fumaric, glycollic, lactic, malic, benzoic, oxybenzoic, salicylic, toluic, tolylic, phthalic, xylic, and resorcylic acids. Also, cyclic acids that are only partially unsaturated and cyclic acids wholly saturated may be employed, for example, cyclohexenoic and cyclohexanoic acids and their various substituted forms are suitable. In addition to the more common unsaturated acyclic acids enumerated above, acetylenic acids are also suitable, for example, propiolic acids and its various homologues and derivatives may be employed.

Those skilled in the art will appreciate that while all of the esters derivable from the above-mentioned alcohols and acids, and particularly the specifically mentioned alcohols and acids will be useful in the practice of the present invention, those esters having boiling points in the same general range as that of tetrachlorethylene (B.P. 119–122° C.) will be especially desirable as they may be expected to have the property of going into the vapor phase with the solvent and returning with it to the liquid phase. This is especially significant in vapor phase metal degreasing operations, as well as in the dry cleaning industry where solvents commonly are recovered by distillation and reused. It will be recognized that certain esters are outstanding in this property, for example, propargyl formate (B.P. 105–109° C.), propargyl acetate (B.P. 124–125° C.), 3-butyne-2-ol-acetate (B.P. 124–126° C.) and 3-methyl-3-butyne-2-ol-acetate (B.P. 133–135° C.). In general, esters boiling in the range of about 100–145° C. are to be preferred.

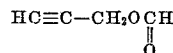
In order that no difficulty will be encountered in practicing the present invention, it is desired to illustrate

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methods for preparing some of the esters contemplated for use in the invention:

FORMIC ACID ESTER OF PROPARGYL ALCOHOL

- 5 A mixture of 56 g. of propargyl alcohol and 46 g. anhydrous formic acid is heated to boiling and while still boiling 30 g. powdered calcium chloride is added, and allowed to stand at room temperature for several hours. The liquid turns dark brown almost immediately.
- 10 The formic acid-propargyl alcohol-calcium chloride solution appears unchanged after standing. The liquid portion is decanted and distilled at atmospheric pressure. All of the liquid except a small amount of tar distills over between 87–100° C., yielding about 75.3 grams.
- 15 The condensate is cooled in ice, diluted with two volumes of ether, washed with four portions dilute NaHCO₃, dried over CaCl₂, the ether distilled off over a water bath, then the remainder distilled at atmospheric pressure through a Vigreux column. All distillate collected distills over from 103.5–105.0° C. Analysis of the products reveal it to be propargyl formate, i.e.,



25 ACETIC ACID ESTER OF PROPARGYL ALCOHOL

- A rapidly-stirred mixture of 72.9 g. (75 ml.) propargyl alcohol in 225 ml. water is cooled to –20° C. in a methanol-dry ice bath and to the resulting slurry is added 51 g. acetic anhydride and 57 ml. of 35% NaOH solution. Stirring is continued while the reaction mixture is allowed to warm to room temperature. The mixture is then extracted with four portions (100, 50, 50, 50 ml.) of ether and the ether extract extracted with two portions of water. The ether solution is dried over calcium chloride and the ether distilled off over a water bath. The remainder is distilled through a modified Vigreux column at atmospheric pressure and the fraction at between 124°–125° C. is collected and analyzed. It is found to be propargyl acetate.

BENZOIC ACID ESTER OF PROPARGYL ALCOHOL

- A rapidly-stirred mixture of 75 ml. propargyl alcohol in 225 ml. water is cooled to –20° C. in a methanol-dry ice bath. To this is added 70 g. benzoyl chloride and 57 ml. of 35% aqueous NaOH. The mixture is allowed to warm to room temperature, is then extracted with four portions of diethyl ether and the ethereal solution extracted twice with water. It is then dried over calcium chloride, the ether removed by distillation and the remainder distilled at about 45 mm. through a Vigreux column. Four fractions are collected, the first two being discarded and the latter two collected at 138°–140° F. and retained for analysis. The material is found to be propargyl benzoate.

In order that those skilled in the art may better understand the present invention and in what manner the same may be carried into effect, specific examples are provided below.

- 60 In all examples, stability is tested in accordance with the following procedure:

- One hundred mls. of the tetrachloroethylene to be tested for stability are placed in a 300-ml. flask equipped with a ground glass joint. A copper strip 2.0 x 7.5 x 0.005 cm., which has been washed with concentrated hydrochloric acid, water, dried and weighed, is placed in the flask. Next, 0.2 ml. of water is added. The flask is attached to a small Soxhlet extractor equipped with a bottom ground glass joint and a top ground glass joint.
- 70 A bulb type condenser with a bottom ground glass joint is attached to the Soxhlet. An acid washed, weighed copper strip (2.0 x 7.5 x 0.005 cm.) is placed in the Soxhlet, and another acid washed and weighed copper strip of the same size is placed in the bottom part of the condenser, so that the condensing tetrachloroethylene

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condenses on the strip. The water scrubber (containing 150–200 mls. H_2O) absorbs any HCl that does not react with the copper during the stability run. To prevent the sucking back of water, two filter flasks, so arranged that water is pushed from one flask to the other with changes in pressure, are employed. The flask containing the tetrachloroethylene is heated on a heater controlled to adjust the boiling rate so that the Soxhlet extractor empties every 8–10 minutes. A 100-watt bulb is placed one inch from the vapor line of the Soxhlet extractor to furnish light for the photochemical oxidation. The stability test is run for 72 hours.

The aggregate loss in weight of the copper strips is a measure of the stability of the tetrachloroethylene tested.

In general, material which shows a 45 mg. aggregate loss in weight in the 3 copper strips over the period of the test is acceptable for dry cleaning purposes. (National Institute of Cleaning and Dyeing, Perchloroethylene (Drycleaning), Tentative Standard 3–50). 18 mg. loss is closer to industry standards, however, but naturally the more stable the material, the better.

In all of the following exemplary material, 100 ml. portions of samples are employed to which 0.25% by weight of the new stabilizers is added. Where isoeugenol is specified, the portion employed is 0.01% by weight.

Example I

For this example, two 100-ml. samples of unstabilized tetrachloroethylene obtained from substantially current production are employed. This material, due to its age of about two weeks, contains a significant quantity of impurity; nevertheless, the effectiveness of the stabilizer is demonstrated as follows:

Sample	Total Loss in Weight of 3 Cu Strips
Containing propargyl formate.....	about 27.0 mg.
Control (unstabilized).....	more than 100 mg.

Example II

A similar sample tested identically with the above but containing 0.01% by weight isoeugenol in addition to propargyl formate loses only about 24.4 mg.

Example III

The stock tetrachloroethylene of Example I is stabilized with propargyl acetate with the following test results:

Sample	Total Loss in Weight of 3 Cu Strips
Containing propargyl acetate.....	about 17.0 mg.
Control stabilized with a standard known stabilizer (including special light-stabilizer).	about 18.1 mg.

Example IV

A sample similar in all respects to that of Example III except that isoeugenol is present as a light stabilizer is prepared and tested concurrently with the Example III samples. The total loss of three copper strips is about 15.5 mg.

Example V

Employing the tetrachloroethylene source of Example I further aged by about one week, the following results are obtained under identical test procedure:

Sample	Total Loss in Weight of 3 Cu Strips
Containing propargyl benzoate.....	about 10.0 mg.
Control containing a standard known stabilizer (including special light-stabilizer).	about 61.6 mg.

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Example VI

Tests which are run on the same stock material as that of Example V and concurrently therewith reveal the following results:

Sample	Total Loss in Weight of 3 Cu Strips
Containing 2-butyne-1,4-diol-diacetate.....	about 15.0 mg.

Example VII

Tests which are run on the same stock material as that of Example V and concurrently therewith reveal the following results:

Sample	Total Loss in Weight of 3 Cu Strips
Containing 2-butyne-1,4-diol-diacetate isoeugenol.....	about 13.3 mg.

Example VIII

Tests which are run on the same stock material as that of Example V and concurrently therewith reveal the following results:

Sample	Total Loss in Weight of 3 Cu Strips
Containing propargyl benzoate isoeugenol.....	about 8.3 mg.

Example IX

Tests employing the same stock material as in Example V, but a few days further aged reveal the following results:

Sample	Total Loss in Weight of 3 Cu Strips
Containing 3-methyl-1-butyne-3-ol-acetate.....	about 35.0 mg.
Control containing standard known stabilizer (including light stabilizer).	about 65.0 mg.

Example X

Tests employing the same stock material as in Example IX and run concurrently therewith reveal the following results:

Sample	Total Loss in Weight of 3 Cu Strips
Containing 3-methyl-1-butyne-3-ol-acetate isoeugenol..	about 31.9 mg.

Example XI

Tests which are run on the same stock material as that of Example IX and concurrently therewith reveal the following results:

Sample	Total Loss in Weight of 3 Cu Strips
Containing 2-butyne-1,4-diol-dibenzoate.....	about 16.0 mg.

Example XII

Tests which are run on the same stock material as that of Example IX and concurrently therewith reveal the following results:

Sample	Total Loss in Weight of 3 Cu Strips
Containing 2-butyne-1,4-diol-dibenzoate isoeugenol.....	about 14.4 mg.

While the invention has been described in terms of its use in connection with tetrachloroethylene, it is desired to point out that it is not to be thus limited. The invention extends to the stabilization of other lower chlorinated aliphatic hydrocarbons, either saturated or unsaturated, such as dichloroethylene, trichloroethylene, trichloroethane, pentachloroethane, chloroform, carbon tetrachloride and the like, in which a similar stability problem is encountered. In fact, it will be noted that the origin of the problem in connection with the tetrachloroethylene is in part attributable to the presence of such less stable chlorohydrocarbons and, as mentioned above, the new stabilizers of the invention effectively prevent their decomposition.

While there have been described various embodiments of the invention, the products described are not intended to be understood as limiting the scope of the invention as it is realized that changes therewithin are possible and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A composition of matter comprising a lower mo-

lecular weight chlorinated hydrocarbon and a stabilizing amount of a carboxylic acid ester of an acetylenic alcohol.

2. A composition of matter comprising a lower molecular weight chlorinated hydrocarbon and a stabilizing amount of a carboxylic acid ester of an acetylenic alcohol, the boiling point of which ester is within about 20° C. of the boiling point of the said chlorinated hydrocarbon.

3. A composition of matter as claimed in claim 1 which includes a light stabilizer.

4. A composition of matter as claimed in claim 1 which includes isoeugenol as a light stabilizer.

5. A composition of matter as claimed in claim 2 which includes isoeugenol as a light stabilizer.

6. A composition of matter comprising tetrachloroethylene and a stabilizing amount of a carboxylic acid ester of an acetylenic alcohol.

7. A composition of matter comprising tetrachloroethylene and a stabilizing amount of a carboxylic acid ester of an acetylenic alcohol, the boiling point of which ester falls within the range of about 100° to about 150° C.

8. A composition of matter as claimed in claim 6 which includes a light stabilizer.

9. A composition of matter as claimed in claim 6 which includes an effective amount of isoeugenol as a light stabilizer.

10. A composition of matter as claimed in claim 7 which includes an effective amount of isoeugenol as a light stabilizer.

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