Patented May 10, 1932 1,858,022

UNITED STATES PATENT OFFICE

LAWRENCE F. MARTIN AND ARTHUR A. ELSTON, OF MIDLAND, MICHIGAN, ASSIGNORS TO THE DOW CHEMICAL COMPANY, OF MIDLAND, MICHIGAN, A CORPORATION OF MICHIGAN

METHOD OF PREVENTING THE DECOMPOSITION OF CARBON TETRACHLORIDE AND PRODUCT THEREOF

No Drawing. Application filed May 3, 1929, Serial No. 360,310. Renewed March 7, 1931.

The present invention is concerned with the prevention of the decomposition of halogenated aliphatic hydrocarbons by means of the addition thereto of certain substances which, when present in only relatively small amount, have the property of inhibiting such decomposition. More particularly, it is concerned with the preservation of chlorinated or brominated derivatives of the saturated or unsaturated aliphatic series of hydrocarbons which have a tendency to decompose under the influence of air, moisture, heat or light, or a combination of such factors, with the consequent formation of corrosive chloro- or bromo-compounds. Examples of such halogenated hydrocarbons are carbon tetrachloride, CCl_4, chloroform, $CHCl_3$, trichlorethylene, C_2HCl_3, tetrachlorethylene, C_2Cl_4, and the like.

A source of trouble connected with the use of the aforementioned halogenated hydrocarbons is the corrosion of metal surfaces exposed thereto, either in the liquid, gaseous or combined phases, and especially in the presence of water. The problem may be subdivided into two principal factors, (1) corrosion of metal containers with which the liquid comes in contact and (2) deterioration of the fluid itself, due to the presence of decomposition products. Of the aforementioned factors influencing the decomposition of halogenated aliphatic hydrocarbons, i. e., air, moisture, light and heat, moisture plays the greatest part in the present problem, the others being of lesser importance. If water is absent, the corrosion of metallic surfaces produced as a result of the action of the decomposition products of the halogenated hydrocarbon, e. g. carbon tetrachloride, is negligible.

It is known that certain compounds, such as benzaldehyde, tend to prevent corrosion of metals by carbon tetrachloride, as shown by Ferguson in U. S. Patent 1,151,255, thus making the carbon tetrachloride more suitable for use in metallic fire-extinguisher containers. We have now discovered that in the presence of considerable moisture decomposition of carbon tetrachloride or like halogenated aliphatic hydrocarbon may be inhibited, or, at least, largely prevented by the addition thereto of a hydrogenated aromatic hydrocarbon, such a cyclohexane. It is known that cyclohexane forms an azeotropic mixture with carbon tetrachloride, hence the former is carried along with the latter when the mixture is subjected to distillation. Such formation of a constant boiling mixture is particularly advantageous in the present case because no material separation of the effective inhibitory agent occurs when the mixture is distilled for the purpose of purification after use, e. g. in dry-cleaning. Furthermore, the protective or preservative effect is exerted in the vapor phase to an equal degree as in the liquid phase. To the accomplishment of the foregoing and related ends, the invention, then, consists of the steps and new products hereinafter fully described and particularly pointed out in the claims, the following description setting forth but several of the various ways in which the principle of the invention may be employed.

Of various preservative compounds that we have tested, we have found cyclohexane to be the most effective in reducing the decomposition of carbon tetrachloride in the presence of moisture. The following detailed examples will serve to demonstrate the beneficial effect of the admixture of the former with the latter compounds for reducing the corrosion of metals exposed to the action of the mixture when water is present.

Example

In a set of comparative tests, strips of lead and nickel of known weight were suspended above the surface of the liquid boiling under reflux for a period of ten days, the metal surfaces being exposed to the vapors and re-

fluxing liquid continuously. In one series the liquid employed consisted of carbon tetrachloride to which was added 10 per cent by volume of water, while in another a mixture was used consisting of approximately 81 per cent carbon tetrachloride and 19 per cent cyclohexane by volume to which was added 10 per cent water. The extent of corrosion was determined by the loss in weight of the metal strips, as shown in the following table:—

Metal	Loss in weight, grams (100 cm.²) day	
	CCl_4+10% H_2O	(81% CCl_4+19% C_6H_{12}) +10% H_2O
Nickel	0.0057	0.0013
Lead	0.0157	0.0011

Inspection of the above table shows conclusively that the presence of cyclohexane has the effect of greatly reducing the corrosion of the metallic samples under the conditions of the tests. It, therefore, becomes apparent that decomposition of the carbon tetrachloride due to the action of water has been repressed or prevented to a corresponding degree by the addition thereto of a minor proportion of cyclohexane. Thereby a simple means is afforded of limiting or preventing the deleterious action of water upon carbon tetrachloride.

The present method has not only the advantages of ease of application and cheapness along with attainment of preservative results, but the use for the purpose in question of a material forming an azeotropic solution with carbon tetrachloride is especially desirable because such material is not separated from the mixture in case repurification thereof by distillation becomes necessary. Regardless of such contingency the two components of the mixture are maintained at all times in approximately their original proportions.

We have found that the extent to which the decomposition of carbon tetrachloride is repressed or inhibited varies somewhat with the amount of preservative added. However, when the cyclohexane is present in from five to forty per cent by volume of the mixture, the decomposition is inhibited sufficiently for practical use. Although cyclohexane by itself is inflammable, the above mixture is non-inflammable, and is outside of the limits within which combustion can be spontaneously maintained.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. The method of preventing the decomposition of halogenated aliphatic hydrocarbons which comprises adding thereto cyclohexane.

2. The method of preventing the decomposition of halogenated aliphatic hydrocarbons which comprises adding thereto cyclohexane in amount corresponding to from five to forty per cent by volume of the resultant mixture.

3. The method of preventing the decomposition of carbon tetrachloride which comprises adding thereto cyclohexane.

4. The method of preventing the decomposition of carbon tetrachloride which comprises adding thereto cyclohexane in amount corresponding to from five to forty per cent by volume of the resultant mixture.

5. As a composition of matter, a halogenated aliphatic hydrocarbon having dissolved therein cyclohexane.

6. As a composition of matter, a halogenated aliphatic hydrocarbon having dissolved therein cyclohexane in amount from five to forty per cent by volume of the resultant mixture.

7. As a composition of matter, carbon tetrachloride having dissolved therein cyclohexane.

8. As a composition of matter, carbon tetrachloride having dissolved therein cyclohexane in amount from five to forty per cent by volume of the resultant mixture.

9. The method of preventing the decomposition of a chlorinated methane which comprises adding thereto cyclohexane.

10. As a composition of matter, a chlorinated methane having dissolved therein cyclohexane.

11. As a composition of matter, chloroform having dissolved therein cyclohexane.

Signed by us this 27 day of April, 1929.

LAWRENCE F. MARTIN.
ARTHUR A. ELSTON.