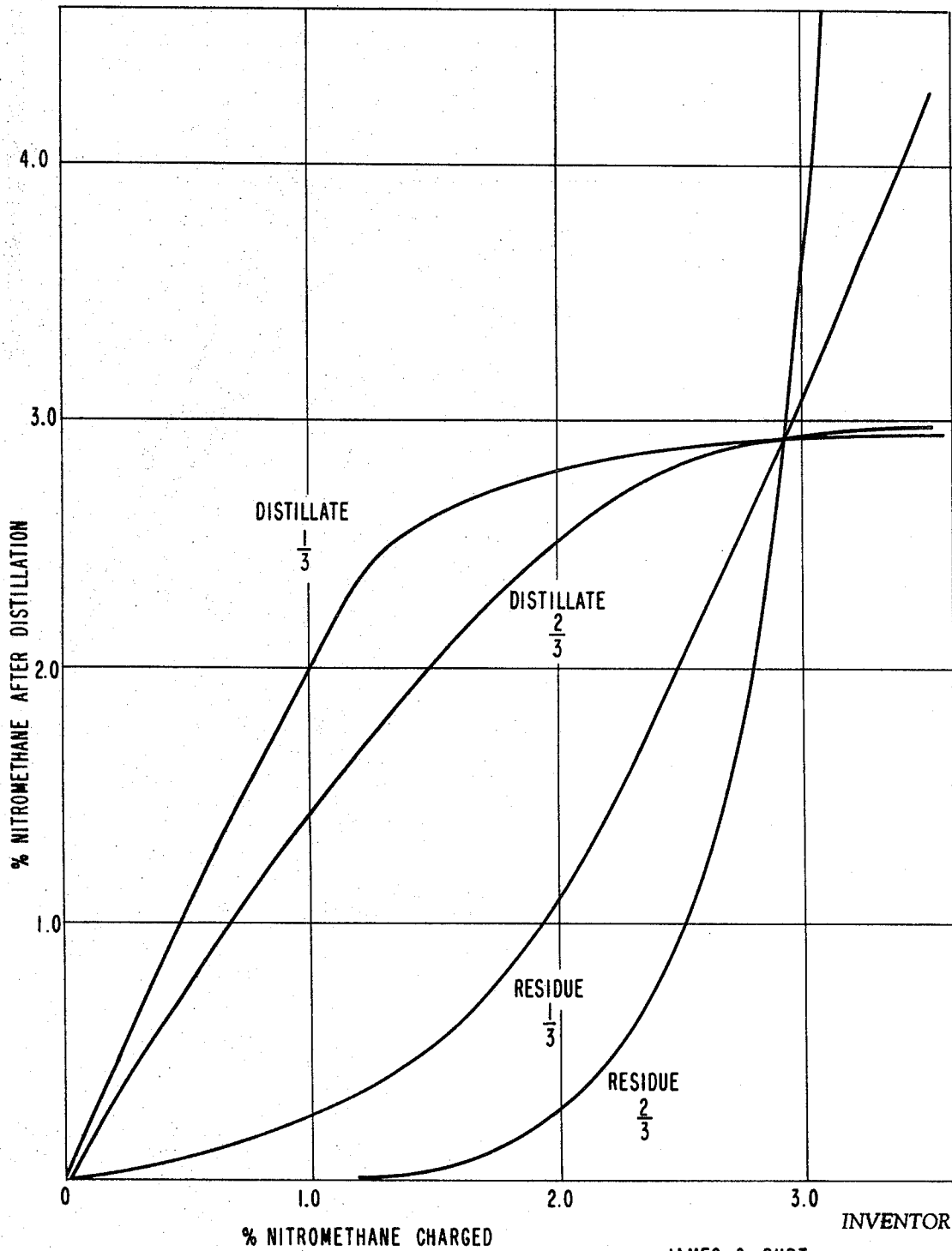


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J. G. BURT
AZEOTROPE OF 1,1,2-TRICHLORO-1,2,3-TRIFLUOROETHANE
AND NITROMETHANE
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BY

Gary A. Samuels

ATTORNEY

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AZEOTROPE OF 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE AND NITROMETHANE

James G. Burt, Oxford, Pa., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del.

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2 Claims

ABSTRACT OF THE DISCLOSURE

An azeotrope of about 97.1 weight percent 1,1,2-trichloro-1,2,2-trifluoroethane and about 2.9 weight percent nitromethane, useful in vapor degreasing and cleaning applications. The presence of nitromethane inhibits reaction of the 1,1,2-trichloro-1,2,2-trifluoroethane with zinc to produce unsaturated halocarbons and inhibits aluminum corrosion as well as stress-corrosion cracking of titanium alloys. Mixtures wherein the nitromethane is present in greater than azeotropic amounts are flammable; while mixtures wherein the nitromethane is much less than azeotropic amounts are not as effective with respect to most of the inhibiting properties of the azeotrope.

BACKGROUND OF THE INVENTION**(1) Field of the invention**

This invention relates to an azeotrope of 1,1,2-trichloro-1,2,2-trifluoroethane and nitromethane, and to its use in vapor-phase degreasing or cleaning.

(2) Description of the prior art

Vapor degreasing and cleaning has found widespread use in industry for degreasing and otherwise cleaning objects, especially intricate parts.

In its simplest form, vapor degreasing or cleaning consists in lowering a room-temperature object to be cleaned into the vapors of a boiling solvent. Vapors condensing on the part provide clean distilled solvent to wash away grease and other contamination. Final evaporation of solvent from the part leaves behind no residue as would be the case where the part was simply washed in liquid solvent.

The solvent is contained in a bath called the boiling sump. Heat is supplied to the sump, usually electrically. A so-called vapor space, relatively free of drafts, in which parts are vapor-rinsed, is provided by extending upward the walls of the sump. The height at which vapors are allowed to rise in the vapor space is controlled by the heat input to the sump and by condensers, generally consisting of water-cooled tubes disposed around the inside periphery of the vapor space walls near the top. Frequently, the condensate from the condenser is collected and passed through a separator to remove co-condensed water before the solvent is returned to the sump.

In more complex variations of the above-described vapor degreasing operation, a so-called clean sump, in addition to the boiling sump, is provided. In this variation, which is more commonly used than is the first-described system, condensate from which co-condensed water has been removed, is directed to a second sump upstream from the boiling sump. Overflow from the clean sump passes over a weir into the boiling sump. Some operators prefer to rinse parts first in the boiling sump or, more usually, in the clean sump before vapor rinsing. Obviously, should the part become warmed to the temperature of the boiling solvent, vapor will no longer condense on the part. In this event, the part is allowed to cool outside the hot vapor zone before vapor rinsing or a spray from the clean sump is provided by means of a pump.

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Heat is ordinarily not provided to the clean sump so that rinsing therein does not overly heat the part and final vapor rinsing is possible without intermediate cooling. Occasionally, through co-distillation of water with water-immiscible solvents, vapor degreasers are also used to dry water-wet articles.

Such vapor degreasers and dryers are well known in the art. For example, Sherliker et al. in U.S. Pat. 3,085,918 disclose a vapor degreaser comprising a boiling sump, a clean sump, a water separator and other ancillary equipment. Sherliker discloses in U.S. Pat. 3,003,347 the drying of water-wet articles in a vapor degreaser by co-distillation of water with boiling chlorinated hydrocarbon solvents containing a cationic surface-active agent.

A number of solvents have been used in vapor degreasers but none of them is ideal. For example, Stoddard solvent, a petroleum distillate, is usually considered unsatisfactory, not only because it is highly flammable but also because, due to its relatively low molecular weight, its vapors tend to diffuse out of the degreaser.

Chlorinated hydrocarbons have also been employed. They are more satisfactory with respect to the deficiencies of the Stoddard solvent; however, they are deficient in other respects. For example, trichloroethylene, 1,1,1-trichloroethane, and tetrachloroethylene are all moderately toxic in acute systemic toxic hazard by inhalation, as rated by Sax. "Dangerous Properties of Industrial Materials," Reinhold Publishing Corporation, New York, N.Y., (1957). Carbon tetrachloride has also been considered for use but is severely toxic. Moreover, the chlorinated solvents tend in use to decompose by hydrolysis or oxidation in the presence of moisture, metals and oxygen to yield acidic materials thus frequently corroding the vapor degreaser and metal parts being cleaned. Despite the above-recited disadvantages, the chlorinated hydrocarbons, especially trichloro- and perchloroethylene, and 1,1,1-trichloroethane have been widely used in degreasing applications by including with them a number of compounds and mixtures of compounds to prevent decomposition of the chlorinated hydrocarbon in use. For example, Bachtel in U.S. Pat. 2,970,113 discloses the inhibition of reaction between 1,1,1-trichloroethane and iron or aluminum, and with mineral oil, with mixtures comprising phosphines or alkyl phosphates. 1,4-dioxane with and without nitromethane. Sims in U.S. Pat. 3,060,125 discloses the stabilization of chlorinated hydrocarbon solvents such as 1,1,1-trichloroethane with a mixture of a nitro aliphatic hydrocarbon such as nitromethane and an aliphatic carboxylic ester such as ethyl acetate. In U.S. Pat. 3,113,155 Sims discloses the mixture of U.S. Pat. 3,060,125 with additionally 1,3-dioxolane and alkyl 1,3-dioxolanes. Sims discloses the use of the latter compositions in degreasing aluminum, copper, and iron in U.S. Pat. 3,113,156. However, in none of these degreasing applications has the chlorinated hydrocarbon been employed with nitromethane alone.

It has been found that the halogenated hydrocarbon 1,1,2-trichloro-1,2,2-trifluoroethane is an effective and non-toxic solvent useful in degreasing applications. However, it attacks reactive metals such as zinc and aluminum and reduces the stress corrosion crack resistance of some titanium alloys. It is of economic consequence that 1,1,2-trichloro-1,2,2-trifluoroethane cannot be used in degreasing applications in which such metals and metal alloys are present. However, with the addition of nitromethane in an amount resulting in azeotropic mixture, it has been found that the reaction with such metals can be effectively inhibited.

A mixture of trichlorotrifluoroethanes and 0.1% to 5% of a mononitroalkane is known (see Kvalnes U.S. Pat. 3,085,116) for use in inhibiting the reaction of 1,1,2-tri-

chloro-1,2,2-trifluoroethane with primary or secondary alcohols; and Eiseman in U.S. Pat. 3,355,391 discloses a degreasing mixture containing trichlorotrifluoroethane which is stabilized with respect to reaction with zinc metal by adding nitromethane and propargyl alcohol. However, both are silent with respect to the recognition of the problem of inhibition of the reaction of the trichlorotrifluoroethane with zinc to produce unsaturated halocarbons and to the problem of inhibiting aluminum corrosion and titanium alloy stress-corrosion cracking. Moreover, neither recognizes that azeotropic proportions of nitromethane with 1,1,2 - trichloro - 1,2,2 - trifluoroethane are most effective in such inhibiting, and neither recognizes that mixtures of 1,1,2-trifluoro-1,2,2-trichloroethane and amounts of nitromethane in excess of azeotropic amounts are flammable. Such flammability is not critical in the uses of the mixtures disclosed by Kvalnes but becomes of great importance in an open system, such as a vapor degreasing or cleaning system.

SUMMARY OF THE INVENTION

The composition of this invention comprises an azeotrope of 97.1 weight percent 1,1,2-trichloro-1,2,2-trifluoroethane and 2.9 weight percent nitromethane.

The invention can also be described as an improved vapor degreasing or cleaning composition wherein the composition comprises a halogenated hydrocarbon and an inhibitor in which the improvement comprises 1,1,2-trichloro-1,2,2-trifluoroethane as the halogenated hydrocarbon and nitromethane as the inhibitor in which the nitromethane is present in an amount of 2.9 weight percent based on the weight of 1,1,2-trichloro-1,2,2-trifluoroethane.

One process aspect of this invention consists of a process for inhibiting the formation of unsaturated halocarbons caused by the reaction of 1,1,2-trichloro-1,2,2-trifluoroethane and zinc which comprises adding nitromethane to the 1,1,2-trichloro-1,2,2-trifluoroethane until the mixture contains 2.9 weight percent nitromethane and 97.1 weight percent 1,1,2-trichloro-1,2,2-trifluoroethane, and contacting the mixture with zinc.

Another process aspect of this invention consists of a process for inhibiting aluminum corrosion or titanium stress-corrosion cracking which comprises adding nitromethane to 1,1,2-trichloro-1,2,2-trifluoroethane until the mixture contains 2.9 weight percent nitromethane and 97.1 weight percent 1,1,2-trichloro-1,2,2-trifluoroethane, and contacting the mixture with aluminum or titanium.

DESCRIPTION OF THE DRAWING

The graph of the drawing shows percent composition of the mixture of 1,1,2-trichloro-1,2,2-trifluoroethane and nitromethane which constitutes the azeotropic proportions.

DESCRIPTION OF THE INVENTION

As stated above, it has now been found that the reaction of 1,1,2-trichloro-1,2,2-trifluoroethane with zinc to produce unsaturated halocarbons can be effectively inhibited both in the liquid and in the vapor phase by addition of small amounts of nitromethane to the solvent, and that the corrosion of aluminum and the decrease in stress-corrosion crack resistance of titanium alloys can be effectively inhibited by the same procedure.

It has further been found that nitromethane forms with 1,1,2-trichloro-1,2,2-trifluoroethane an azeotrope which contains enough nitromethane (2.91 weight percent) to effectively inhibit reaction with the above-mentioned metals in both the vapor and liquid phase and which is nonflammable under all use conditions.

With less than the azeotropic amount of nitromethane, the mixture is not as effective in preventing decrease in stress-corrosion crack resistance in titanium alloys and in amounts greater than the azeotropic amount, nitromethane confers flammability on the evaporating mixture.

The azeotropic mixture can be prepared by adding nitromethane to 1,1,2-trichloro-1,2,2-trifluoroethane until the azeotropic proportions are obtained or by distillation of mixtures of the two compounds having percent compositions outside the azeotropic range. The mixture can then be added directly to a vapor degreasing machine, as shown in some of the following examples.

The examples which follow illustrate the invention in greater detail.

EXAMPLE 1

This example shows the minimum boiling point of the azeotropic mixture of the invention.

The temperature of the vapor over boiling mixtures of 1,1,2 - trichloro - 1,2,2 - trifluoroethane was measured with correction to 760 mm. Hg essentially by the method described by W. Swietoslowski, p. 32, Azeotropy and Polyazeotropy, the Macmillan Company, New York, N.Y., (1963), with the results as shown in the following Table I.

TABLE I

Liquid mixture		
Parts by wt., 1,1,2-trichloro-trifluoroethane	Parts by wt., nitromethane	Vapor temperature (1 atmosphere, ° C.)
100.....	0	47.87
99.5.....	0.5	47.13
99.0.....	1.0	46.95
98.0.....	2.0	46.81
97.0.....	3.0	46.77
96.0.....	4.0	46.78
95.0.....	5.0	46.80
90.0.....	10.0	47.10
60.0.....	40.0	58.8

The table shows that the minimum boiling point of the azeotrope is about 46.77° C.

EXAMPLE 2

This example confirms the existence of the azeotrope of the invention by measuring the percent composition of the distillate of various mixtures of the azeotrope ingredients.

The composition of the azeotrope was further confirmed by distilling various mixtures of nitromethane and 1,1,2-trichloro-1,2,2-trifluoroethane through a 3-foot glass helices-packed fractionating column with a known efficiency of 30 plates. At equilibrium small samples of distillate and residue were analyzed in a calibrated vapor-phase chromatograph after 1/3 and after 2/3 of the sample had been distilled. The results of analyses were plotted in the graph shown in the accompanying drawing which shows the crossover point corresponding to the composition, cited in Example 1, of the azeotrope. In the graph, the percent of nitromethane found in the distillate (e.g., distillate 1/3) and the amount of nitromethane found in the residue (e.g., residue) 1/3 after the distillation are plotted against the percent of nitromethane charged to the mixture.

EXAMPLE 3

This example confirms that the azeotrope of this invention exists in its azeotropic proportions during use in a degreasing operation.

In order to approximate the conditions of recovery of used solvent from a vapor degreaser, a mixture of 7.5 grams of diisocetyl adipate, 17.5 grams of colorless mineral oil, and 225 grams of the azeotropic mixture was distilled in an essentially 1-plate still. The solvent was recovered in 91 wt. percent (205 grams) yield. The recovered solvent was analyzed by gas chromatography yielding the values 97.03 wt. percent, 1,1,2-trichloro-1,2,2-trifluoroethane and 2.97 wt. percent nitromethane.

EXAMPLE 4

This example describes the critical solution temperature of the azeotrope of this invention.

The critical solution temperature, i.e. that temperature below which separation of phases occurs, was determined by cooling mixtures of nitromethane and 1,1,2-trichloro-

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1,2,2-trifluoroethane until cloudiness was observed. The results are shown in the following Table II.

TABLE II

[Miscibility of nitromethane and 1,1,2-trichlorotrifluoroethane]		
Composition		Critical solution temp., °C.
Parts by wt., 1,2,2-trichlorotrifluoroethane	Parts by wt., nitromethane	
97.0-----	3.0	-11.0
95.0-----	5.0	6.8
91.0-----	9.0	23.8

EXAMPLE 5

This example shows the effectiveness of the azeotrope of this invention in inhibiting metal corrosion in the liquid phase, the vapor phase and at the interface.

Pure 1,1,2-trichloro-1,2,2-trifluoroethane, the azeotrope, and a commercial stabilized trichloroethylene sold under the trade name "Triclene" were refluxed separately and continuously in a simple galvanized vapor degreaser consisting of a cylindrical vessel of about 20 inches diameter and 3 feet depth with a water cooled coil installed about 15 inches about the surface of the boiling solvent. In all cases a small amount of water was floated on top of the solvent to approximate co-condensed water in use. Fresh solvent and water were added as needed to replace evaporation losses. The following Table III describes the effect of each solvent upon the galvanized container.

TABLE III.—CORROSION OF A GALVANIZED DEGREASER

Solvent	Days of operation without corrosion	Remarks
1,1,2-trichloro-1,2,2-trifluoroethane.	1	General attack on zinc in the vapor phase.
Stabilized trichloroethylene.....	37	Corrosion at liquid surface and just above.
Azeotrope.....	>100	Terminated without serious corrosion in the liquid and the vapor phase. Some dark spots at liquid surface level.

The composition of the liquid phase was determined by gas chromatography to be 2.65 wt. percent nitromethane and 97.35 wt. percent 1,1,2-trichloro-1,2,2-trifluoroethane after 100 days boiling.

EXAMPLE 6

This example shows the effectiveness of the azeotropic composition of the invention compared with other proportions of the ingredients and with other inhibitors.

The inhibition of corrosion of zinc was further tested by placing a galvanized steel strip in screw capped bottles containing two drops of water, 100 grams of 1,1,2-trichloro-1,2,2-trifluoroethane and nitromethane in the below-indicated concentrations. The closed bottles were stored at 38° C. until corrosion was evident, generally, at the interface and in the vapor phase. Other inhibitors useful in some applications were also tried without evident success. The results of the tests shown in the following Table IV indicate that enduring inhibition is achieved with nitromethane only in concentrations of 2-3 wt. percent.

TABLE IV.—INHIBITION OF CORROSION ON ZINC

Inhibitor	Concentration ¹	Days to first corrosion
None.....		2
Nitromethane.....	3.0	>18
Do.....	2.0	>18
Do.....	1.0	16
Do.....	0.5	5
Do.....	0.2	4
Do.....	0.1	3
Isopropyl vinyl ether.....	2.0	4
Anethole.....	2.0	5
Hexene-1.....	2.0	7
Dioxane.....	2.0	2

¹ Weight percent based on 1,1,2-trichloro-1,2,2-trifluoroethane.

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EXAMPLE 7

The following experiment demonstrates that nitromethane is not depleted by reaction with zinc surfaces in the liquid phase under the conditions of a vapor degreaser. A mixture of 1,1,2-trichloro-1,2,2-trifluoroethane and 0.5 wt. percent water containing a level (1.0 wt. percent) of nitromethane deliberately lower than that of the azeotrope was refluxed for 21 days in the presence of a sample of submerged galvanized window screen corresponding to 10,000 square inches of zinc surface. At the end of this period no visible corrosion had occurred and by gas chromatographic analysis the nitromethane concentration was 1.1 wt. percent.

EXAMPLE 8

Using the method of B. F. Brown, Materials Research and Standards 6, No. 3, 129-133 (March 1966), modified slightly in that the solvent also applied to the specimen at the boiling point, this example shows that 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1,1-trichloroethane, and trichloroethylene promote the stress corrosion cracking of the titanium alloy, Ti-5 Al-2.5 Sn. Table V following shows that 0.75 wt. percent nitromethane is insufficient to prevent notable reduction in fracture toughness, whereas the azeotropic amount of nitromethane is sufficient entirely to prevent such reduction.

TABLE V

Loss of toughness in Ti-5 Al-2.5 Sn alloy

Nitromethane conc. in 1,1,2-trichlorotrifluoroethane, (wt. percent)	Fracture toughness reduction in percent of original
0-----	57
0.75-----	50
2.92-----	0

EXAMPLE 9

In a manner analogous to Example 6, aluminum alloy No. 6061, Al-1.0 Mg-0.6 Si-0.25 Cu-0.25 Cr (Metals Handbook, vol. 1, Amer. Soc. for Metals, 8th edition (1961)), in small samples was exposed to various solvents at 165° F. for 28 days in sealed glass tubes under autogenous pressure in the presence of about 3 wt. percent water based on the solvent weight. The aluminum corroded substantially in all cases except where the solvent was the azeotrope. The percent decomposition of the solvent was estimated by determination of generated chloride ion. The lower limit of chloride ion detection corresponded to one one-thousandth percent solvent decomposition. Table VI describes the results.

TABLE VI

Corrosion of aluminum alloy

(165° F./28 days)

Solvent:	Percent solvent decomposition
1,1,2-trichlorotrifluoroethane-----	0.56.
Azeotrope-----	Not detectable.
Commercial inhibited trichloroethylene-----	0.05.
Commercial inhibited methyl chloroform-----	0.81.

EXAMPLE 10

This example shows the separability and flammability of non-azeotropic proportions of the ingredients.

A mixture of 5 wt. percent and sufficient 1,1,2-trichloro-1,2,2-trifluoroethane to make 100 wt. percent mixture was cooled to 40° F. (4.4° C.), a temperature frequently encountered in a degreaser in practice. A nitromethane-rich layer separated and floated on the top in the water separator. The layer was flammable.

It follows from the data of Example 4 that separation of a nitromethane-rich layer will occur under a variety of conditions above 0° C.

EXAMPLE 11

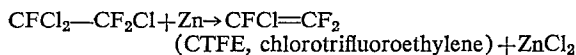
This example shows the flammability of non-azeotropic proportions of the ingredients.

A mixture of 4.3 wt. percent of nitromethane and sufficient 1,1,2-trichloro-1,2,2-trifluoroethane to result in 100 wt. percent mixture was spilled on a concrete floor at room temperature in the presence of a flame. When the mixture was nearly evaporated, the vapors ignited and burned briskly in a blue flame.

The azeotropic mixture is nonflammable. Since it evaporates unchanged in composition, no amount of evaporation can produce flammable vapors. On the other hand, any excess of nitromethane above the azeotropic concentration, no matter how slight, will produce a flammable composition on evaporation. The hazard is especially severe in the case of a slow dripping leak whereby on evaporation of the solvent, residual nitromethane would be concentrated in a small area. Likewise, parts drying in air would produce flammable conditions.

EXAMPLE 12

This example demonstrates that attack on galvanized iron (zinc) by 1,1,2-trichloro-1,2,2-trifluoroethane, under conditions analogous to those of a vapor degreaser (reflux temperature, presence of traces of water and a zinc salt (ZnCl_2)), occurs as follows:



and that nitromethane in azeotropic amount inhibits the reaction completely within the limits of detection of CTFE.

To each of two 500 cc. round-bottom flasks fitted with 5° C. tap water cooled reflux condensers and solid carbon dioxide/acetone-cooled traps attached by means of hoses to the top of the reflux condensers, was charged:

1,1,2-trichloro-1,2,2-trifluoroethane (390 grams)
Galvanized iron (one strip; 1 x 12 cm., two strips about 1.5 x 6 cm.-wts. about 8 grams and about 5 grams respectively. The longer strip extended into the vapor space; the other two were submerged.
Zinc chloride (1 cc. of a solution of 20 grams ZnCl_2 in 100 cc. water).

To flask No. 1 was also added:

Nitromethane (11.4 grams, 2.9 wt. percent).

Both flasks were refluxed for 48 hours after which the metal specimens were removed and the contents of the traps were transferred for analysis to evacuated gas sample bulbs.

The totally immersed metal specimens were unchanged in both flasks. The longer strip in flask 1 was slightly

discolored at the liquid-vapor interface. In flask No. 2, that part of the longer strip in the vapor phase was heavily corroded and was covered with a black granular solid.

The contents of the sample bulbs were analyzed in a model 720 F and M Scientific Corporation gas chromatograph using a 5-meter column packed with 20 wt. percent Dow-Corning DC-200 silicone oil on "Chromosorb" W (Johns-Manville) support. The helium sweep rate was 60 cc./min. The temperature of the column was programmed; 200 sec. at room temperature, then 25° C./min. to 230° C.

1,1,2-trichloro-1,2,2-trifluoroethane was identified by retention time (574 to 596 seconds) in both samples.

Chlorotrifluoroethylene, identified by 214 second retention time, was found in bulb No. 2 in an amount corresponding to 5.53 area percent [area under CTFE peak ÷ sum of the areas under all peaks × 100] in a mixture containing largely air and 1,1,2-trichloro-1,2,2-trifluoroethane. Analysis of the contents of bulb No. 1 showed no compound of retention time about 214 seconds. The estimated sensitivity of the method was such that at least as little as 0.001% chlorotrifluoroethylene would have been detected.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details show and described, for obvious modifications will occur to those skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An azeotrope consisting essentially of 97.1 weight percent 1,1,2-trichloro-1,2,2-trifluoroethane and 2.9 weight percent nitromethane.

2. In the process for cleaning zinc, aluminum or titanium metal articles with 1,1,2-trichloro-1,2,2-trifluoroethane as the solvent, the improvement which consists of adding 2.9 weight percent of nitromethane to the solvent to form an azeotrope mixture therewith, and applying said mixture to the metal whereby corrosion thereof is prevented.

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LEON D. ROSDOL, Primary Examiner

W. E. SCHULZ, Assistant Examiner

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