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⑤④ **Azeotrope-like composition of trichlorotrifluoroethane, ethane, acetone, nitromethane and hexane.**

⑤⑦ **Azeotrope-like compositions comprising of trichlorotrifluoroethane, acetone, nitromethane and hexane are stable and have utility as degreasing agents and as solvents in a variety of industrial cleaning applications.**

DESCRIPTIONAZEOTROPE-LIKE COMPOSITIONS OF TRICHLOROTRIFLUORO-  
ETHANE, ACETONE, NITROMETHANE AND HEXANEField of the Invention

This invention relates to azeotrope-like mixtures of trichlorotrifluoroethane, acetone, nitromethane and hexane. These mixtures are useful in a variety of vapor  
5 degreasing or solvent cleaning applications including defluxing.

BACKGROUND OF THE INVENTION

Vapor degreasing and solvent cleaning with fluorocarbon based solvents have found widespread use in  
10 industry for the degreasing and otherwise cleaning of solid surfaces, especially intricate parts and difficult to remove soils.

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

For difficult to remove soils where elevated temperature is necessary to improve the cleaning action of the solvent, or for large volume assembly line operations where the cleaning of metal parts and assemblies  
25 must be done efficiently and quickly, the conventional operation of a vapor degreaser consists of immersing the part to be cleaned in a sump of boiling solvent which removes the bulk of the soil, thereafter immersing the part in a sump containing freshly distilled solvent near  
30 room temperature, and finally exposing the part to solvent vapors over the boiling sump which condense on the cleaned part. In addition, the part can also be sprayed with distilled solvent before final rinsing.

Vapor degreasers suitable in the above-described operations are well known in the art. For example, Sherliker et al. in U.S. Patent 3,085,918 disclose such suitable vapor degreasers comprising a boiling sump, a  
5 clean sump, a water separator, and other ancillary equipment.

Fluorocarbon solvents, such as trichlorotrifluoroethane, have attained widespread use in recent years as effective, nontoxic, and nonflammable agents useful in  
10 degreasing applications. Trichlorotrifluoroethane in particular has been found to have satisfactory solvent power for greases, oils, waxes and the like. It has therefore found widespread use for cleaning electric motors, compressors, heavy metal parts, delicate pre-  
15 cision metal parts, printed circuit boards, gyroscopes, guidance systems, aerospace and missile hardware, aluminum parts and the like. For certain solvent purposes, however, trichlorotrifluoroethane alone may have insufficient solvent power. Since trichlorotrifluoro-  
20 ethane is non-polar, it does not remove polar contaminants well. Thus, to overcome this deficiency, trichlorotrifluoroethane has been mixed with polar components such as aliphatic alcohols or chlorocarbons such as methylene chloride. As example, U.S. Patent No.  
25 3,881,949 discloses the use of mixtures of 1,1,2-trichloro-1,2,2-trifluoroethane and ethanol as solvents for vapor degreasers.

The art has looked, in particular, towards azeotropic compositions including the desired fluorocarbon  
30 components, such as trichlorotrifluoroethane, which include components which contribute additionally desired characteristics, such as polar functionality, increased solvency power, and stabilizers. Azeotropic compositions are desired because they exhibit a minimum boiling  
35 point and do not fractionate upon boiling. This is desirable because in the previously described vapor degreasing equipment with which these solvents are employed, redistilled material is generated for final

rinse-cleaning. Thus, the vapor degreasing system acts as a still. Unless the solvent composition exhibits a constant boiling point, i.e., is an azeotrope or is azeotrope-like, fractionation will occur and undesirable solvent distribution may act to upset the cleaning and safety of processing. Preferential evaporation of the more volatile components of the solvent mixtures, which would be the case if they were not azeotrope or azeotrope-like, would result in mixtures with changed compositions which may have less desirable properties, such as lower solvency towards soils, less inertness towards metal, plastic or elastomer components, and increased flammability and toxicity.

A number of trichlorotrifluoroethane based azeotrope compositions have been discovered which have been tested and in some cases employed as solvents for miscellaneous vapor degreasing applications. For example, U.S. Pat. No. 2,999,815 discloses the azeotrope of 1,1,2-trichloro-1,2,2-trifluoroethane and acetone; U.S. Pat. No. 3,573,213 discloses the azeotrope of 1,1,2-trichloro-1,2,2-trifluoroethane and nitromethane; U.S. Pat. No. 4,045,366 discloses ternary azeotropic-like mixtures which contain 1,1,2-trichlorotrifluoroethane, nitromethane and acetone; and U.S. Pat. No. 4,279,664 discloses an azeotrope-like composition consisting of trichlorotrifluoroethane, acetone, and hexane.

The art is continually seeking new fluorocarbon based azeotropic mixtures or azeotrope-like mixtures which offer alternatives for new and special applications for vapor degreasing and other cleaning applications.

It is accordingly an object of this invention to provide novel azeotrope-like compositions based on 1,1,2-trichloro-1,2,2-trifluoroethane which have good solvency power and other desirable properties for vapor degreasing and other solvent cleaning applications.

Another object of the invention is to provide novel constant boiling or essentially constant boiling sol-

vents which are liquid at room temperature, will not fractionate under conditions of use and also have the foregoing advantages.

5 A further object is to provide azeotrope-like compositions which are relatively nontoxic and nonflammable both in the liquid phase and the vapor phase.

These and other objects and features of the invention will become more evident from the description which follows.

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#### DESCRIPTION OF THE INVENTION

In accordance with the invention, novel azeotrope-like compositions have been discovered comprising trichlorotrifluoroethane, acetone, nitromethane and hexane, with 1,1,2-trichloro-1,2,2-trifluoroethane being the  
15 trichlorotrifluoroethane of choice. In the invention, the azeotrope-like compositions comprise from 72.7 to 87.8 weight percent of 1,1,2-trichloro-1,2,2-trifluoroethane, from 10.0 to 16.6 weight percent of acetone, from 0.005 to 1.5 weight percent of nitro-  
20 methane, and from 0.2 to 10.6 weight percent of a hexane. In preferred embodiments of the invention, the azeotrope-like compositions comprise from 77.9 to 87.6 weight percent of 1,1,2-trichloro-1,2,2-trifluoroethane; from 10.0 to 14.2 weight percent of acetone; from .05 to  
25 0.9 weight percent of nitromethane, and from 1.0 to 7.9 weight percent of the hexane. Such compositions possess constant or essentially constant boiling points of about 44.0°C at 760 mm Hg. The precise azeotrope composition has not been determined but has been ascertained to be  
30 within the above ranges. Regardless of where the true azeotrope lies, all compositions within the indicated ranges, as well as certain compositions outside the indicated ranges, are azeotrope-like, as defined more particularly below.

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It has been found that these azeotrope-like compositions are stable, safe to use and that the preferred compositions of the invention are nonflammable (exhibit no flash point when tested by the Tag Open Cup test

method - ASTM D1 310-16) and exhibit excellent solvency power. These compositions have been found to be particularly effective when employed in conventional degreasing units for the dissolution of lubricating and machine cutting oils and the cleaning of such oils from solid surfaces.

For the purpose of this discussion, by azeotrope-like composition is intended to mean that the composition behaves like a true azeotrope in terms of its constant boiling characteristics or tendency not to fractionate upon boiling or evaporation. Such composition may or may not be a true azeotrope. Thus, in such compositions, the composition of the vapor formed during boiling or evaporation is identical or substantially identical to the original liquid composition. Hence, during boiling or evaporation, the liquid composition, if it changes at all, changes only to a minimal or negligible extent. This is to be contrasted to non-azeotrope-like compositions in which during boiling or evaporation, the liquid composition changes to a substantial degree.

As is well known in this art, another characteristic of azeotrope-like compositions is that there is a range of compositions containing the same components in varying proportions which are azeotrope-like. All such compositions are intended to be covered by the term azeotrope-like as used herein. As an example, it is well known that at differing pressures, the composition of a given azeotrope will vary at least slightly and changes in distillation pressures also change, at least slightly, the distillation temperatures. Thus, an azeotrope of A and B represents a unique type of relationship but with a variable composition depending on temperature and/or pressure.

The 1,1,2-trichloro-1,2,2-trifluoroethane, acetone, nitromethane, and hexane components of the novel solvent azeotrope-like compositions of the invention are all commercially available. Preferably they should be used

in sufficiently high purity so as to avoid the introduction of adverse influences upon the solvency properties or constant boiling properties of the system.

A suitable grade of 1,1,2-trichloro-1,2,2-trifluoroethane, for example, is sold by Allied Corporation under the trade name "GENESOLV® D".

The term "hexane" is used herein as to mean any  $C_6$  paraffin hydrocarbon ( $C_6H_{14}$ ) (see Hackh's Chemical Dictionary, 3<sup>rd</sup> Ed., McGraw Hill Book Co. (1944) p. 408). Thus, the term "hexane" includes n-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane and any and all mixtures thereof. Specifically included is commercial "isohexane" which typically contains from about 35 to about 100 weight percent of 2-methylpentane admixed with other hexane isomers. It has been found that each hexane isomer, separately and in combination with other hexane isomers, form azeotrope-like compositions with 1,1,2-trichloro-1,2,2-trifluoroethane, acetone, and nitromethane in accordance with the invention.

It will be apparent to those skilled in the art that for specialized purposes, various additives can be incorporated with the novel azeotrope composition of the invention as, for example, lubricants, detergents and the like. These additives are chosen so as not to adversely affect the essential properties of the composition for a given application.

#### EXAMPLE 1

Approximately 5000 gms of a solvent mixture were prepared containing about 84 weight percent of 1,1,2-trichloro-1,2,2-trifluoroethane, about 12 weight percent of acetone, about 2 weight percent of n-hexane and about 1 weight percent nitromethane based on the total weight of the mixture. This mixture was distilled utilizing a five liter, three-necked distillation flask containing a four plate column, a distillation head and a ASTM calibrated thermometer. The distillation process consisted of refluxing the solvent mixture for about one

hour, and collecting eight distillation cuts. The first and last fractions of about 300 ml each were discarded and the remaining fractions were redistilled for about one hour, and six distillation cuts were collected.

5 Again, the first and last fractions were discarded. The barometric pressure was measured during the distillations at about 754.2 mm Hg. The distillation rate was about 10 ml/minute. Four fractions were collected at 44°C which had an average density of about 1.366 g/ml at  
10 (77°F) 25°C. Analysis of the five fractions by gas chromatograph is set forth in the following Table I:

TABLE I

| Fraction No. | Wgt %                    |         |        |              |
|--------------|--------------------------|---------|--------|--------------|
|              | Trichlorotrifluoroethane | Acetone | Hexane | Nitromethane |
| 15 1         | 86.0                     | 12.5    | 1.5    | 0.03         |
| 2            | 86.2                     | 12.2    | 1.6    | 0.04         |
| 3            | 86.1                     | 12.2    | 1.7    | 0.06         |
| 4            | 86.0                     | 12.2    | 1.8    | 0.07         |

EXAMPLE 2

20 The procedure of Example 1 was repeated with a solvent mixture containing about 84% weight percent 1,1,2-trichloro-1,2,2-trifluoromethane, about 12 weight percent of acetone, about 2 weight percent of n-hexane and about 1 weight percent nitromethane. All weight  
25 percents are based on the total weight of the mixture. The barometric pressure was about 744.4 mm Hg. The distillation rate was about 20 ml/minute, and the distillation temperature was about 43.8°C. The specific gravity was about 1.368 g/ml at (74°F) 23°C. The four  
30 fractions were analyzed by gas chromatograph, and the results are set forth in the following Table II.

TABLE II

| Fraction No. | Wgt %                    |         |        |              |
|--------------|--------------------------|---------|--------|--------------|
|              | Trichlorotrifluoroethane | Acetone | Hexane | Nitromethane |
| 35 1         | 85.9                     | 12.6    | 1.5    | 0.04         |
| 2            | 85.9                     | 12.4    | 1.6    | 0.06         |
| 3            | 85.9                     | 12.5    | 1.6    | 0.08         |
| 4            | 85.8                     | 12.4    | 1.8    | 0.08         |

A series of experiments were conducted to determine the flash point of the novel azeotrope composition of this invention. The analyses of the composition employed in these tests is as set forth in the following  
5 Table III.

TABLE III

|    | <u>Component</u>         | <u>Wwight Percent</u> |
|----|--------------------------|-----------------------|
|    | Trichlorotrifluoroethane | 85.5                  |
|    | Acetone                  | 12.4                  |
| 10 | Hexane                   | 1.6                   |
|    | Nitromethane             | 0.5                   |

The above-described composition was subjected to flash point determination according to ASTM Method D1310, "Flash Point of Liquids by Tag Open-Cup Apparatus." The  
15 solvent mixture was chilled so that the starting point for this test was (50°F) 10°C. This test was conducted twice, with the same results that this four component mixture has no flash point to boil, which was (114°F) 46°C.

20 EXAMPLE 4

A representative embodiment of the composition of this invention was evaluated in a stability test. The analysis of the composition employed in this test is set forth in the following Table IV.

25 TABLE IV

|    | <u>Component</u>         | <u>Weight Percent</u> |
|----|--------------------------|-----------------------|
|    | Trichlorotrifluoroethane | 85.5                  |
|    | Acetone                  | 12.4                  |
|    | Hexane                   | 1.6                   |
| 30 | Nitromethane             | 0.5                   |

Procedurally, the above-referenced composition was refluxed at autogenous pressure in the presence of zinc and aluminum metal for a period of 48 hours. The composition was then analyzed for the presence of chloride  
35 ion. The greater the amount of chloride ion, the greater the amount of solvent breakdown. For comparison purposes, a similar test and analysis were conducted

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using an azeotrope composition containing from about 83 to about 85 weight percent 1,1,2-trichloro-1,2,2-trifluoroethane, from about 12.5 to about 13.5 weight percent acetone and from about 2.5 to about 3.5 weight percent n-hexane which is manufactured and sold by Allied Corporation under the trade name "GENESOLV® 404".

The results of these tests are set forth in the following Table V.

| <u>TABLE V</u> |                   |                      |
|----------------|-------------------|----------------------|
|                | <u>Solvent</u>    | <u>Metal Present</u> |
| 10             | GENESOLV® 404     | None                 |
|                | GENESOLV® 404     | Zinc                 |
|                | GENESOLV® 404     | Aluminum             |
|                | Mixture per Above | None                 |
| 15             | Mixture per Above | Zinc                 |
|                | Mixture per Above | Aluminum             |
|                |                   | <u>Cl-, ppm</u>      |
|                |                   | 0.65                 |
|                |                   | 47                   |
|                |                   | 0.5                  |
|                |                   | <0.005               |
|                |                   | 0.1                  |
|                |                   | 0.17                 |

EXAMPLE 5

Using the procedure of Example 4, the stability of another embodiment of this invention was evaluated. The analyses of this composition is set forth in the following Table VI.

| <u>TABLE VI</u> |                          | <u>Weight Percent</u> |
|-----------------|--------------------------|-----------------------|
|                 | Trichlorotrifluoroethane | 85.8                  |
| 25              | Acetone                  | 12.5                  |
|                 | Hexane                   | 1.6                   |
|                 | Nitromethane             | 0.1                   |

The results of this test are set forth in the following Table VII.

| <u>TABLE VII</u> |                   |                      |
|------------------|-------------------|----------------------|
|                  | <u>Solvent</u>    | <u>Metal Present</u> |
| 30               | GENESOLV® 404     | None                 |
|                  | GENESOLV® 404     | Zinc                 |
|                  | GENESOLV® 404     | Aluminum             |
| 35               | Mixture per Above | None                 |
|                  | Mixture per Above | Zinc                 |
|                  | Mixture per Above | Aluminum             |
|                  |                   | <u>Cl-, ppm</u>      |
|                  |                   | 0.41                 |
|                  |                   | 130                  |
|                  |                   | 0.34                 |
|                  |                   | 0.34                 |
|                  |                   | 0.03                 |
|                  |                   | 0.04                 |

EXAMPLE 6

The azeotrope-like compositions of the invention may be determined through the use of distillation techniques designed to provide higher rectification of the distillate than found in the most demanding vapor degreaser systems. For this purpose a five theoretical plate Oldershaw distillation column was used with a cold water condensed, manual liquid dividing head. Typically, approximately 350 cc of liquid were charged to the distillation pot. The liquid was a mixture comprised of various combinations of 1,1,2-trichloro-1,2,2-trifluoroethane, acetone, nitromethane and hexane.

The mixture was heated at total reflux for about one hour to ensure equilibration. For most of the runs, the distillate was obtained using a 2:1 reflux ratio at a boil-up rate of 400-500 grams per hr. Approximately 300 cc of product were distilled and 6 approximately equivalent sized overhead cuts were collected. The vapor temperature (of the distillate), pot temperature, and barometric pressure were monitored. A constant boiling fraction was collected and analyzed by gas chromatography to determine the weight percentages of its components. A mixture was then made up according to the approximate compositions of the constant boiling fraction and was redistilled at the same conditions. Compositions of distillate and residue were compared by chromatographic analysis to verify the constant-boiling nature of the mixture. The constant boiling mixture obtained according to the present invention through the above described distillation techniques is shown in Table VIII.

TABLE VIII

| Ex. | Components                                     | Approx.<br>Composition<br>(wt%) | Baro-<br>metric<br>Pressure<br>(mm Hg) | Vapor<br>Temp<br>(°C) | Azeotrope-<br>like<br>Behavior |
|-----|------------------------------------------------|---------------------------------|----------------------------------------|-----------------------|--------------------------------|
| 5 1 | 1,1,2-trichloro-<br>1,2,2-trifluoro-<br>ethane | 81.3                            | 749                                    | 43.8                  | Yes -                          |
|     | Acetone                                        | 12.9                            |                                        |                       | Constant                       |
|     | 2-Methylpentane                                | 5.6                             |                                        |                       | Boiling                        |
|     | Nitromethane                                   | .02                             |                                        |                       |                                |

10

## EXAMPLES 7-9

To explore the constant-boiling composition range of mixtures comprised of 1,1,2-trichloro-1,2,2-trifluoroethane, acetone, nitromethane, and hexane, a distillation apparatus and procedure were utilized as previously described in Example 6. Into the distillation pot was charged a mixture of 1,1,2-trichloro-1,2,2-trifluoroethane (FC-113), acetone, nitromethane, and hexane.

These examples demonstrate that each hexane isomer exhibits its own unique compositional identity in azeotrope-like mixtures with 1,1,2-trichloro-1,2,2-trifluoroethane, acetone, and nitromethane and that each hexane isomer and mixtures thereof form azeotrope-like constant boiling mixtures at about  $44.0 \pm 0.2^\circ\text{C}$  with such components. This was particularly surprising in view of the significant variation in boiling point among the various hexane isomers. The hexane isomers and their boiling points are shown in the following Table IX.

30

TABLE IX

|    | Hexane Isomer                         | Normal Boiling Point (°C) |
|----|---------------------------------------|---------------------------|
|    | 2,2-dimethylbutane<br>(2,2-DMB)       | 49.75                     |
| 35 | 2,3-dimethylbutane<br>(2,3-DMB)       | 58.1                      |
|    | 2-methylpentane<br>(isohexane) (2-MP) | 60.13                     |
|    | 3-methylpentane (3-MP)                | 64                        |
|    | n-hexane (n-hex)                      | 68.74                     |

A number of distillations were undertaken where the composition of the starting mixture was varied considerably, resultant constant-boiling fractions were collected and analyzed by gas chromatography, and the vapor temperature and barometric pressure were recorded. To normalize observed boiling points during different days to 760 mm of mercury pressure, the approximate normal boiling points of 1,1,2-trichloro-1,2,2-trifluoroethane rich mixtures were estimated by applying a barometric correction factor of about 26 mm Hg/°C, to the observed values. However, it is to be noted that this corrected boiling point is generally accurate up to  $\pm 0.4^\circ\text{C}$  and serves only as a rough comparison of boiling points determined on different days. By the above-described method, it was discovered that a constant boiling mixture boiling at about  $44.0 \pm 0.2^\circ\text{C}$  at 760 mm Hg was formed for compositions comprising 77.9 to 81.3 weight percent 1,1,2-trichloro-1,2,2-trifluoroethane, 12.9 to 14.2 weight percent acetone, 0.05 to 0.2 weight percent nitromethane, and 5.6 to 7.9 weight percent hexane. Supporting distillation data for the mixtures studied are shown in Table X.

TABLE X

| Starting Material Compositions (wt %) |        |              |                   |      |      |             |             |       |                 |
|---------------------------------------|--------|--------------|-------------------|------|------|-------------|-------------|-------|-----------------|
| Example                               | FC-113 | Ace-<br>tone | Nitro-<br>methane | 2-MP | 3-MP | 2,3-<br>DMB | 2,2-<br>DMB | n-hex | Total<br>Hexane |
| 6                                     | 81.0   | 12.0         | 1.0               | 6.0  |      |             |             |       | 6.0             |
| 7                                     | 79.8   | 13.4         | 0.8               |      |      | 6.0         |             |       | 6.0             |
| 8                                     | 78.4   | 12.0         | 0.3               | 4.0  | 2.0  | 1.2         | 1.2         | 0.9   | 9.3             |
| 9                                     | 79.9   | 13.0         | 1.1               | 3.0  |      | 3.0         |             |       | 6.0             |

Constant Boiling Distillation Fraction (wt %)

| Example | FC-113 | Ace-<br>tone | NM   | 2-MP | 3-MP | 2,3<br>DMB | 2,2<br>DMB | n-hex | Total<br>hexane |
|---------|--------|--------------|------|------|------|------------|------------|-------|-----------------|
| 6       | 81.3   | 12.9         | 0.2  | 5.6  |      |            |            |       | 5.6             |
| 7       | 80.0   | 13.5         | 0.1  |      |      | 6.3        |            |       | 6.3             |
| 8       | 77.9   | 14.2         | 0.05 | 3.05 | 1.5  | 1.2        | 1.7        | 0.4   | 7.85            |
| 9       | 80.7   | 13.3         | 0.1  | 2.8  | 2.8  | 3.1        |            |       | 5.9             |

## Physical Properties

| Example | Vapor Temp<br>(°C) | Bar. Pressure<br>(mm Hg) | B.P. Corr to<br>760 mm (°C) |
|---------|--------------------|--------------------------|-----------------------------|
| 6       | 43.8               | 748.8                    | 44.2                        |
| 5 7     | 43.1               | 737.5                    | 44.0                        |
| 8       | 43.4               | 744.6                    | 44.0                        |
| 9       | 43.2               | 743.9                    | 43.8                        |
|         |                    |                          | mean 44.0                   |
|         |                    |                          | ± 0.2°C                     |

10 From the above, it is readily apparent that  
additional constant boiling or essentially constant  
boiling mixtures of the same components can readily be  
identified by anyone of ordinary skill in this art by  
the method described. No attempt was made to fully  
15 characterize and define the true azeotrope in the system  
comprising 1,1,2-trichloro-1,2,2-trifluoroethane,  
acetone, nitromethane and hexane, nor the outer limits  
of its compositional of ranges which are constant  
boiling or essentially constant boiling. As indicated,  
20 anyone of ordinary skill in the art can readily ascer-  
tain other constant boiling or essentially constant  
boiling mixtures, it being kept in mind that "constant  
boiling" or "essentially constant boiling" for the pur-  
poses of this invention means constant boiling or essen-  
25 tially constant boiling in the environment of a vapor  
degreaser system such as utilized in the art. All such  
mixtures in accordance with the invention which are con-  
stant boiling or essentially constant boiling are  
"azeotrope-like" within the meaning of this invention.

30 EXAMPLE 10

To illustrate the azeotrope-like nature of the  
mixtures of the invention under conditions of actual use  
in a vapor phase degreasing operation, a vapor phase  
degreasing machine was charged with a preferred  
35 azeotrope-like mixture in accordance with the invention  
comprising about 81.3 weight percent 1,1,2-trichloro-  
1,2,2-trifluoroethane (FC-113), about 13.1 weight  
percent acetone, about 5.4 weight percent of commercial

isohexane, and about 0.2 weight percent nitromethane. The mixture was evaluated for its constant boiling or non-segregating characteristics. Solvents were tested in a Baron Blakeslee refrigeration cooled 3 sump VPD (Series 5000 machine - Model No. MLR-216). The solvent charge was brought to reflux and the individual sump compositions were determined with a Hewlett Packard 5890 Gas Chromatograph. Refluxing was continued for 21 hours and sump compositions were monitored throughout this time. A mixture was considered constant boiling or non-segregating if the maximum concentration difference between sumps for any mixture component was less than 0.3%.

If the mixture were not azeotrope-like, the high boiling components would very quickly concentrate in the boil sump and be depleted in the rinse sump. As the data in Table IV show, this did not happen. These results indicate that the compositions of this invention will not segregate in a commercial vapor degreaser, thereby avoiding potential safety, performance, and handling problems. The preferred composition tested was also found to not have a flash point according to recommended procedures ASTM D-56 (Tag Closed Cup) and ASTM D-1310 (Tag open Cup).

TABLE XI  
COMPOSITION, % WEIGHT

| <u>Boil Sump</u> |                      | <u>0<sup>a)</sup> hr</u> | <u>5 hr</u> | <u>21 hr</u> |
|------------------|----------------------|--------------------------|-------------|--------------|
| 30               | Acetone              | 13.05                    | 12.86       | 12.87        |
|                  | Nitromethane         | 0.20                     | 0.55        | 0.57         |
|                  | FC-113               | 81.39                    | 81.19       | 81.11        |
|                  | Commercial Isohexane | 5.36                     | 5.40        | 5.47         |

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Work Sump

|                         | <u>0<sup>a</sup>) hr</u> | <u>5 hr</u> | <u>21 hr</u> |
|-------------------------|--------------------------|-------------|--------------|
| Acetone                 | 13.07                    | 13.15       | 13.12        |
| Nitromethane            | 0.20                     | 0.15        | 0.15         |
| 5 FC-113                | 81.28                    | 81.33       | 81.36        |
| Commercial<br>Isohexane | 5.44                     | 5.38        | 5.37         |

Rinse Sump

|                            | <u>0<sup>a</sup>) hr</u> | <u>5 hr</u> | <u>21 hr</u> |
|----------------------------|--------------------------|-------------|--------------|
| 10 Acetone                 | 13.08                    | 13.13       | 13.22        |
| Nitromethane               | 0.21                     | 0.15        | 0.12         |
| FC-113                     | 81.29                    | 81.34       | 81.28        |
| Commercial<br>15 Isohexane | 5.43                     | 5.39        | 5.38         |

a) Analytical Standard - representative of initial composition of all three sumps

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EXAMPLE 11

This example illustrates the use of the preferred azeotrope-like composition of the invention to clean metal parts.

25 Cleaning was performed in a Branson B-400 two-sump vapor degreaser. A first sump was used as the working sump and held boiling solvent comprising about 81.3 weight percent 1,1,2-trichloro-1,2,2-trifluoroethane, about 13.2 weight percent acetone, about 5.4 weight  
30 percent commercial isohexane, and about 0.1 weight percent nitromethane. A second sump was used as the rinse sump. Refrigerated cooling coils lined the upper inner wall of the apparatus to maintain a vapor blanket. Soils were coated on two kinds of (3/4" x 3")  
35 1.9 cm x 7.6 cm metal coupons. These were 316 stainless steel and 1010 cold rolled steel. Soils were selected from two classes of metal working fluids as follows:

| <u>Name</u> | <u>Manufacturer</u> | <u>Class</u>   |
|-------------|---------------------|----------------|
| Hocut 711   | E.F. Houghton & Co. | Semi-synthetic |
| Trimsol     | Master Chemical Co. | Emulsifiable   |

5 The metal coupons were sanded to give a totally clean, freshly exposed surface. Following a deionized water rinse, the coupons were rinsed in followed by methanol and air dried for 10 minutes. Four identical coupons were then dipped into each of the metal working

10 fluids. Cleaning tests were run on two of these coupons shortly after dipping into the metal working fluids. The other two coupons were tested after standing for 24 hours. For cleaning, the parts were placed on racks in a stainless steel wire mesh basket. In a first step,

15 this assembly was immersed in the work sump for two minutes, then transferred to the rinse sump for two minutes, followed by a two minute solvent distillate spray in the vapor zone. The final step was a one minute hold in the vapor zone.

20 The treated coupons were visually inspected for evidence of soil residue. A water-break test was also applied wherein the coupons were immersed in water and allowed to drain for 10 seconds. The coupon surface was examined for breaks in the water film over the 10 second

25 draining period. A coupon was considered totally clean if no soil residues or breaks in the water film during the water break test were noticeable on the surface of the coupon. In the above-described manner, "316" stainless steel coupons were soiled with Trimsol metal

30 working fluid, and "1010" cold rolled steel coupons were soiled with Hocut 711 metal working fluid. All these soiled coupons were cleaned with the preferred azeotrope-like compositions of the invention and evaluated for cleanliness as described above. All the

35 coupons were judged to be totally clean.

WE CLAIM:

1. Azeotrope-like compositions comprising trichlorotrifluoroethane, acetone, nitromethane, and a hexane.
2. Azeotrope-like compositions according to claim 1 wherein said trichlorotrifluoroethane is 1,1,2-trichloro-1,2,2-trifluoroethane.
3. Azeotrope-like compositions according to claim 2 wherein said hexane is n-hexane.
4. Azeotrope-like compositions according to claim 2 wherein said hexane is 2-methylpentane.
5. Azeotrope-like compositions according to claim 2 wherein said hexane is 3-methylpentane.
6. Azeotrope-like compositions according to claim 2 wherein said hexane is 2,2-dimethylbutane.
7. Azeotrope-like compositions according to claim 2 wherein said hexane is 2,3-dimethylbutane.
8. Azeotrope-like compositions according to claim 2 wherein said hexane is isohexane.
9. Azeotrope-like compositions according to claim 2 comprising from 72.7 to 87.8 weight percent 1,1,2-trichloro-1,2,2-trifluoroethane, from 10.0 to 16.6 weight percent acetone, from 0.005 to 1.5 weight percent nitromethane, and from 0.2 to 10.6 weight percent hexane.
10. Azeotrope-like compositions according to claim 2 comprising from 77.9 to 87.6 weight percent of 1,1,2-trichloro-1,2,2-trifluoroethane, from 10.0 to 14.2 weight percent acetone, from 0.05 to 0.9 weight percent nitromethane, and from 1.0 to 7.9 weight percent hexane.
11. Azeotrope-like compositions according to claim 2 comprising from 85.0 to 86.5 weight percent of 1,1,2-trichloro-1,2,2-trifluoroethane, from 12.0 to 13.0 weight percent of acetone, from 0.03 to 0.5 weight percent of nitromethane, and from 1.0 to 2.0 weight percent n-hexane.



European Patent  
Office

# EUROPEAN SEARCH REPORT

**0160854**  
Application number

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                               |                                                | EP 85104402.4                                               |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|------------------------------------------------|-------------------------------------------------------------|
| Category                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim                              | CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)              |
| D,Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US - A - 4 279 664 (F.J. FIGIEL et al.)<br>* Examples; claims *<br>--         | 1-3,9-11                                       | C 23 G 5/028<br>C 23 G 5/032<br>C 23 G 5/036<br>C 11 D 7/30 |
| D,Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US - A - 4 045 366 (F.J. FIGIEL)<br>* Examples; claims *<br>----              | 1-3,9-11                                       | C 11 D 7/32<br>C 11 D 7/50<br>B 08 B 3/00<br>B 08 B 7/00    |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                               |                                                | TECHNICAL FIELDS SEARCHED (Int. Cl. 4)                      |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                               |                                                | C 23 G<br>C 11 D<br>B 08 B                                  |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                               |                                                |                                                             |
| Place of search<br>VIENNA                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                               | Date of completion of the search<br>01-07-1985 | Examiner<br>SLAMA                                           |
| <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone<br/>Y : particularly relevant if combined with another document of the same category<br/>A : technological background<br/>O : non-written disclosure<br/>P : intermediate document</p> <p>T : theory or principle underlying the invention<br/>E : earlier patent document, but published on, or after the filing date<br/>D : document cited in the application<br/>L : document cited for other reasons<br/>&amp; : member of the same patent family, corresponding document</p> |                                                                               |                                                |                                                             |