

Background of the Invention

Field of the Invention

The present invention relates to a cleaning agent composition and a precision cleaning method in which a specified cleaning agent is employed. More particularly, the present invention is concerned with a cleaning agent composition for hand wiping and a hand wiping cleaning method. The terminology "hand wiping cleaning" used herein means cleaning an item surface by wiping it by hand with fibrous matter impregnated with a cleaning agent composition.

Discussion of Related Art

With respect to an optical element and a semicon-

to the workings before being formed into the product. While the material is passed through such steps, various dirt adheres thereto. Cleaning for removing such dirt must be carried out taking into account the influence of the cleaning on the material, so that cleaning quality requirements are very strict. The conventional precision cleaning method for optical elements is conducted in the sequence of organic solvent → water-base cleaning agent → water → isopropanol (IPA) → freon as described on pages 193 to 195 of "Precision Cleaning Technology Manual" published by New Technology Development Center, Japan. Various modifications have been effected which include replacing the isopropanol with a dewatering agent comprising freon and, added thereto, a surfactant and also replacing the final freon with vapor cleaning. Without exception, the conventional cleaning methods employ a cleaning line composed of a multiplicity of cleaning agents, none of which can be avoided. Further, the above published literature lists cleaning agents and cleaning methods employed in various industrial fields, from which it is apparent that wide use is made of chlorinated solvents and specified freons.

hydrocarbon solvent such as kerosene, benzene or xylene and applying thereto ultrasonic and/or barreling. On the other hand, electrical and electronic parts have been freed of dirt with the use of, mainly, a chlorinated solvent such as trichloroethane or a freon solvent such as freon 113.

However, in recent years, substitution for the above cleaning agents has increased in consideration of the global atmosphere problem and orientation toward safety. For example, Japanese Patent Application Laid-Open Specification No. 4076/1993 proposed a cleaning method for mechanical parts comprising removing dirt with the use of a cleaning agent composed mainly of a hydrocarbon having a boiling point of 100 to 350°C and finishing with the use of a completely fluorinated compound having a boiling point of 80 to 200°C, which method was described as being excellent in cleaning and finishing performance and permitting short-time drying. Japanese Patent Application Laid-Open Specification No. 43893/1993 describes cleaning with the use of a cleaning agent composition composed mainly of a hydrocarbon fraction of 150 to 240°C in boiling point which is

tion No. 2100927/1989 describes a precision cleaning drying method in which an item having passed through a cleaning step and dipping in pure water is lifted at a very low rate from the liquid level into a dry gas. Still further, Japanese Patent Application Laid-Open Specification No. 17148/1993 describes a cleaning method in which a hydrocarbon-based organic solvent is heated and sprayed at a reduced pressure. On the other hand, with respect to the hand wiping cleaning agent, Japanese Patent Application Laid-Open Specification No. 25499/1993 proposed a cleaning agent for brake device comprising 20 to 97% by weight of cyclopentane and 3 to 60% by weight of an aliphatic monohydric lower alcohol having 1 to 3 carbon atoms along with the balance of a hydrocarbon having 6 to 8 carbon atoms. Moreover, a variety of other cleaning agents such as a water-base cleaning agent, a cleaning agent composed mainly of a glycol ether and a cleaning agent composed mainly of a terpene, e.g., limonene have been proposed.

In recent years it has become apparent that a chlorinated solvent such as trichloroethane and a specified freon such as freon 113 are chemically stable and, upon evaporation, arrives at the ozonosphere where

ozonosphere surrounding the earth. The prohibition of industrial use thereof became effective in 1995 and the application thereof to industrial cleaning is no longer permitted.

Although being excellent in cleaning and drying performance and advantageous in cost, the hydrocarbon solvent such as kerosene or benzene is a substance regulated by the organic solvent control regulation, has been demonstrated to be highly carcinogenic and has problems with respect to the nonhazardousness to human and smell. Further, its purity is so poor that the problem is encountered that, for example, stain occurs in the drying to thereby disenable attaining high-quality item finishing.

The cleaning agent composed mainly of a glycol ether has drawbacks in that the smell is strong when use is made of one having excellent cleaning performance and that the dryability is generally poor. The cleaning agent composed mainly of a terpene such as limonene has problems that it emits strong smell although being excellent in safety and cleaning power and that it is derived from a natural product, so that it lacks quality stability and is highly expensive.

method using this water-base cleaning agent has a drawback in that the disposal of rinse water, drying and metal rusting must be taken into consideration, there are heavy constraints on the facilities and item to be cleaned.

The cleaning method comprising removing dirt with the use of a cleaning agent composed mainly of a hydrocarbon and finishing with the use of a completely fluorinated compound as described in Japanese Patent Application Laid-Open Specification No. 4076/1993 is excellent in cleaning and finishing performance, permits short-time drying and is advantageously free from the problems of waste water disposal and rusting because of the nonuse of water. However, the problem is encountered that the completely fluorinated compound employed in finishing is highly expensive. Further, an additional problem is encountered that special measures such as improving the hermetic sealing of the cleaning apparatus and attaching a vapor recovery device must be taken for limiting the consumption of the completely fluorinated compound to thereby complicate the apparatus and render the control thereof difficult.

The cleaning agent composition described in Japa-

environmental pollution, excellent in dirt removing capability and available at low cost. However, it is a mixture of a multiplicity of hydrocarbons, so that stain is likely to occur on the surface of the cleaned and dried item. Thus, the use of this cleaning agent composition in precision cleaning involves difficulties. Further, the 100% removal of aromatic hydrocarbons suspected of carcinogenesis is unfeasible, so that the problem is encountered that not only is nonhazardousness to human not ensured but also the smell is strong.

The cleaning method using pure water and dry gas as described in Japanese Patent Application Laid-Open Specification No. 210092/1989 needs a large amount of energy in the heating and drying because of large specific heat and large latent vaporization heat. Further, this cleaning method involves not only the problems that dewing occurs on the surface of the cleaned item at the time of drying, large surface tension prevents penetration into minute regions and the surface of the metal material is rusted but also the problem that production of pure water and dry gas causes cost increase and complicates the cleaning

hydrocarbon solvent as described in Japanese Patent Application Laid-Open Specification No. 17148/1993, the solvent in which, for example, cutting oil liberated by the cleaning has been mixed is simultaneously sprayed to thereby cause the cutting oil to remain on the surface of the cleaned item with detriment to the cleaning quality. Thus, precision cleaning cannot be attained by this method. Periodic solvent replacements would have to be conducted at short intervals for avoiding this detriment, which, however, disadvantageously increases running cost.

In the cleaning method described in Japanese Patent Application Laid-Open Specification No. 25499/1993, cyclopentane as the main component has unique benzene smell to thereby deteriorate the working atmosphere. Further, it damages a plastic such as polystyrene, so that the scope of employable items to be cleaned is limited.

Summary of The Invention

In view of the above drawbacks of the prior art, the invention advantageously provides

in which use is made of the cleaning agent composition of
5 the present invention.

The foregoing and other features and advantages of the present invention will become apparent from the following detailed description and appended claims taken in connection with the accompanying drawings.

10 Brief Description of the Drawings

In the drawings:

Fig 1 is a graph showing the relationship between lower alcohol mixture component ratio of liquid phase and lower alcohol mixture component ratio of vapor phase measured in
15 Example 1;

Fig 2 is a graph showing the relationship between lower alcohol mixture component ratio of liquid phase and lower alcohol mixture component ratio of vapour phase measured in Example 2;

20 Fig 3 is a graph showing the relationship between lower alcohol mixture component ratio of liquid phase and lower alcohol mixture component ratio of vapor phase measured in Example 6.

Detailed Description of the Invention

25 According to the present invention there is provided a cleaning agent composition for hand wiping comprising 66 to 90% by weight of at least one aliphatic hydrocarbon with 6 carbon atoms containing at least 44% by weight of 2-methylpentane and 10 to 34% by weight of at least one lower
30 alcohol with 1 to 3 carbon atoms containing at least 85% by weight of ethyl alcohol to thereby exhibit azeotropic or azeotrope-like characteristics. Moreover, there is provided

hydrocarbon with 6 carbon atoms containing at least 44% by
5 weight of 2-methylpentane and 10 to 34% by weight of at
least one lower alcohol with 1 to 3 carbon atoms containing
at least 85% by weight of ethyl alcohol so as to exhibit
azeotropic or azeotrope-like characteristics and wiping a
surface of an item to be cleaned with the impregnated
10 fibrous matter by hand.

invention contain no halogen elements destructing the ozonosphere in the molecules, so that, even if evaporated and scattered into the atmosphere by the use in cleaning operation, the composition containing them do not adversely affect the ozonosphere and are clearly nonhazardous to the global atmosphere.

The composition of the present invention comprising the aliphatic saturated hydrocarbon having 6 carbon atoms and the lower alcohol having 1 to 3 carbon atoms exhibits azeotropic or azeotrope-like characteristics. The terminology "azeotropic" used herein means the property such that a mixture of a plurality of compounds has a single stable apparent boiling point and behaves like a single compound. The boiling point of the azeotropic mixture is lower than that of each of the plurality of compounds forming the azeotropic mixture. Further, with respect to the azeotropic mixture, the component ratios are identical between the vapor phase and the liquid phase at the vapor-liquid equilibrium. The terminology "azeotrope-like" used herein means the property such that a mixture of a plurality of compounds has a boiling point range falling up to 5°C of the boiling point of the azeotropic

The composition of the invention advantageously has a boiling point ranging from 52 to 55.5°C at atmospheric pressure. This boiling point is significantly lower than those of the components (aliphatic saturated hydrocarbon having 6 carbon atoms and lower alcohol having 1 to 3 carbon atoms) as shown in Table 20.

10

Table 20

Compound	2-methyl-pentane	3-methyl-pentane	n-hexane	methanol	ethanol	n-propanol	iso-propanol
b.p. (°C)	60.3	63.3	68.7	64.6	78.3	97.2	82.4

The relative evaluation of drying rate of solvent-based cleaning agent compositions can be made by comparing boiling points. Generally, the lower the boiling point, the greater the drying rate. Therefore, the cleaning agent composition of the invention has a drying rate greater than those of the components.

15

sure is within 5°C and the composition exhibits azeotropic or azeotrope-like properties so that the composition change is scarce irrespective of the vaporization or evaporation. Therefore, the composition change attributed to uneven evaporation of cleaning agent components during the cleaning operation can be prevented and uniform cleaning capability can be retained irrespective of the use for a prolonged period of time. Further, the composition change can be avoided in the storage vessel during the storage thereof.

The cleaning agent composition preferably comprises 82 to 88% by weight of at least one aliphatic hydrocarbon with 6 carbon atoms containing at least 56% by weight of 2-methylpentane and 12 to 18% by weight of at least one lower alcohol with 1 to 3 carbon atoms containing at least 85% by weight of ethyl alcohol. This cleaning agent composition exhibits azeotropic properties to thereby not only have its boiling point lowered as compared with those of the components thereof but also exhibit a composition change upon distillation as low as less than about 5% with respect to each of the lower alcohol component and the aliphatic saturated hydrocarbon component, which attests to stabili-

...aporation or evaporation
during the cleaning operation is very slight.

The cleaning power will be described below. The cleaning power of the solvent-based cleaning agent composition can be expressed by the dirt dissolving capability. The solubility parameter (hereinafter referred to as "SP") is generally known as a scale for estimating the dissolving capability. The SP value is strongly influenced by the polarity of the compound. Chain compounds such as 2-methylpentane, 3-methylpentane and n-hexane as the aliphatic saturated hydrocarbon being a component of the cleaning agent composition of the invention have properties very similar to each other from the viewpoint of polarity because of the molecular structures. On the other hand, methanol, ethanol, isopropanol and n-propanol as the lower alcohol component have also properties very similar to each other from the viewpoint of polarity. Therefore, the cleaning power is influenced by the ratio of the component of aliphatic saturated hydrocarbon as an aggregate of 2-methylpentane, 3-methylpentane and n-hexane to the component of lower alcohol as an aggregate of methanol, ethanol, isopropanol and n-propanol.

For example, finger sebum, marking ink, waxes such

ing agent composition of the invention. When it is intended to clean these dirt components by hand wiping or dipping with the use of a cleaning agent composition whose lower alcohol component content is less than 10% by weight, the cleaning power is unsatisfactory for finger sebum, marking ink and rosin oil and removal thereof by hand wiping cleaning becomes difficult. Thus, the content of at least one lower alcohol is required to be at least 10% by weight for obtaining satisfactory cleaning power and is desired to be at least 12% by weight for facilitating the cleaning.

The damage on the item to be cleaned will be described below. The cleaning agent composition of the invention is applied to metals, glasses, ceramics, thermoplastic resins and plastic elastomers as the material of the item to be cleaned. The corrosion of these materials caused by dipping or hand wiping cleaning depends on the content of lower alcohol component. When the lower alcohol component ratio ranges from 5 to 50% by weight based on the composition, metals and glasses have no changes and are free from the influence of the cleaning agent composition. Also, thermoplastic resins whose internal stress residue is slight are free from any

ranges from 5 to 50% by weight based on the composition. However, thermoplastic resin products whose internal stress residue is extensive because of injection or other rework occasionally suffer from cracking or other corrosion effect when the lower alcohol mixture component ratio exceeds 35% by weight based on the composition. Therefore, it is requisite that the ratio of lower alcohol mixture component be not greater than 34% by weight based on the composition for ensuring wide applications to various items to be cleaned irrespective of the type of the material thereof as a cleaning agent. The ratio is preferred to be not greater than 20% by weight based on the composition taking into account safety factor set in consideration of the difference of residual stress level between various products.

The cleaning agent composition is preferably one whose total content of n-hexane, methanol, isopropanol and n-propanol is less than 10% by weight based on all of the composition. This composition ensures greater safety.

Among the components of the cleaning agent composition, n-hexane, isopropanol and methanol are categorized as the Class 2 organic solvent by the organic solvent control regulation of Japanese Industrial

concentrations of n-hexane, methanol, isopropanol and n-propanol are 50, 100, 400 and 200 ppm, respectively. These values are lower than the permissible concentrations of other components and, taking safety into account, it is preferred that the total content of n-hexane, methanol, isopropanol and n-propanol be limited.

The cleaning agent composition is preferably one whose water content is less than 2000 ppm by weight so that the composition is substantially free of water. This composition realizes the state of having no stain after drying while maintaining azeotropic or azeotrope-like characteristics, so that the cleaning quality improvement can be attained to thereby enable application to precision cleaning.

When the water content of the cleaning agent composition is high, water is not entirely evaporated even after the evaporation of the cleaning agent composition because water has a very large latent vaporization heat, so that the phenomenon appears that particulate water remains on the surface of the cleaned item. The inventors' study has showed that, when the water content is 2000 ppm or higher, particulate water remains on the

and the retarded evaporation of the water causes stain on the surface of the cleaned item. The lower the water content, the more effectively can the staining be suppressed. Therefore, it is preferred that the water content be less than 1000 ppm, especially, less than 500 ppm. The water content of the composition can be reduced by putting an adsorbent or a molecular sieve (for example, commercially available Molecular Sieve) in the composition of the present invention. This method may be applied for controlling the water content.

The cleaning agent composition is preferably one in which the total amount of components having a boiling point of 120°C or higher at 760 mmHg is less than 1% by weight and the total amount of components having a boiling point of 170°C or higher at 760 mmHg is less than 1000 ppm by weight. This composition can satisfactorily be applied to precision cleaning.

There is the possibility that high-boiling-point hydrocarbons and other impurities mix into the aliphatic saturated hydrocarbon to be used as a component of the cleaning agent composition according to the present invention during the process or intermediate step for producing the same. These occasionally remain as residue on the surface of the cleaned item, depending

occurrence of residue in the precision cleaning, for example, finish cleaning conducted prior to optical coating of lenses, defects such as peeling of the optical coating film from the lenses would result, so that the contaminated saturated hydrocarbon cannot be employed. The inclusion of high-boiling-point components may cause a drop of the drying rate. The inventors' study has showed that the inclusion of components with a boiling point of 120°C or higher in an amount of greater than 1% by weight renders the retardation of the drying rate conspicuous while the inclusion of components with a boiling point of 170°C or higher in an amount of greater than 1000 ppm would cause residue to remain on the surface of the cleaned and dried item, so that the application to precision cleaning becomes difficult.

From the viewpoint of inhibiting the inclusion of impurities, it is preferred that the aliphatic saturated hydrocarbon be synthesized directly from a gaseous hydrocarbon.

There is also provided a precision cleaning method comprising

impregnating fibrous matter with the cleaning agent composition of the present invention adapted to exhibit azeotropic or azeotrope-like characteristics

As mentioned above, the respective ratios of the aliphatic saturated hydrocarbon and lower alcohol components to the composition are highly stable irrespective of the vaporization or evaporation, so that the cleaning performance of the composition is also highly stable in the present invention. Therefore, when fibrous matter is impregnated with the cleaning agent composition of the present invention and wiping is carried out by hand with the use of impregnated fibrous matter, the cleaning agent composition remaining in the fibrous matter has little change of component ratios irrespective of the evaporation of the cleaning agent composition from the fibrous matter, so that wiping cleaning can be performed while exerting cleaning power which is stable up to the complete drying of the fibrous matter. Examples of fibrous matters to be impregnated with the cleaning agent composition include cloths such as natural fiber cloth, synthetic fiber cloth and nonwoven fabric and papers such as wiping paper.

Effect of The Invention

The cleaning agent composition comprising 66 to 90% by weight of at least one aliphatic hydrocarbon with 6 carbon atoms containing at least 44% by weight of 2-methylpentane and 10 to 34% by weight of at least one lower alcohol with 1 to 3 carbon atoms containing at least 85% by weight of ethyl alcohol to exhibit azeotropic or azeotrope-like characteristics not only exerts very excellent dryability and cleaning capability but also enables maintaining low corrosive effect on various materials and excellent composition stability during the cleaning operation and storage.

Further, the cleaning agent composition whose total content of n-hexane, methanol, isopropanol and n-propanol is less than 10% by weight based on all of the composition enables ensuring nonhazardousness to human.

Still further, the cleaning agent composition whose water content is less than 2000 ppm by weight enables suppressing staining and improving cleaning quality.

The cleaning agent composition in which the total amount of components having a boiling point of 120°C or

total amount of components having a boiling point of 170°C or higher at 760 mmHg is less than 1000 ppm by weight enables maintaining extremely low residue and excellent dryability.

In the precision cleaning method comprising impregnating fibrous matter with a cleaning agent composition for hand wiping comprising 66 to 90% by weight of at least one aliphatic hydrocarbon with 6 carbon atoms containing at least 44% by weight of 2-methylpentane and 10 to 34% by weight of at least one lower alcohol with 1 to 3 carbon atoms containing at least 85% by weight of ethyl alcohol so as to exhibit azeotropic or azeotrope-like characteristics and wiping a surface of an item to be cleaned with the impregnated fibrous matter by hand, the cleaning agent composition has little change of component ratios irrespective of the evaporation of the cleaning agent composition from the fibrous matter, so that wiping cleaning can be performed while maintaining stable cleaning power up to the complete drying of the fibrous matter.

Preferred Embodiment of The Invention

The present invention will now be described in greater detail with reference to the following Examples and Comparative Examples, which should not be construed



Example 1

A hydrocarbon mixture consisting of 60.1% by weight of 2-methylpentane, 36.2% by weight of 3-methylpentane and 3.7% by weight of n-hexane was used as the aliphatic saturated hydrocarbon with 6 carbon atoms. A lower alcohol mixture consisting of 85.5% by weight of ethanol, 4.9% by weight of isopropanol and 9.6% by weight of n-propanol was used as the lower alcohol with 1 to 3 carbon atoms. The hydrocarbon mixture and the lower alcohol mixture were mixed together in varied proportions (lower alcohol mixture component ratio: 0, 10, 15, 20, 30 and 100% by weight in Table 7) to thereby obtain mixture compositions in an amount of 200 g each. These compositions were subjected to simple distillation at atmospheric pressure, and the boiling point of initial distillate, initial distillate composition component ratio (hereinafter referred to as "component ratio of vapor phase") and

initial distillate composition (hereinafter referred to as "component ratio of liquid phase") were measured.

The results are given in Table 1. The above initial distillate composition is a distillate composition harvested when the boiling point rise has been stabilized after the start of outflow of distillate.

Table 1

b.p. (°C)	62.0	55.5	55.0	55.1	55.3	78.5
Lower alcohol mixt. component ratio (wt.%) of liq. phase	0.0	9.6	15.1	20.8	31.8	100.0
Lower alcohol mixt. component ratio (wt.%) of vapor phase	0.0	15.7	16.1	16.5	16.7	100.0

Referring to Table 1, the boiling point of the mixture composition ranged from 55.0 to 55.5°C when the lower alcohol mixture (consisting of 85.5% by weight of ethanol, 4.9% by weight of isopropanol and 9.6% by weight of n-propanol) component ratio of liquid phase ranged from 9.6 to 31.8% by weight (corresponding to ethanol: 8.5 to 27.2% by weight, isopropanol: 0.4 to 1.6% by weight and n-propanol: 0.9 to 3.1% by weight) and when the hydrocarbon mixture (consisting of 60.1%

methylpentane and 3.7% by weight of n-hexane) component ratio of liquid phase ranged from 90.4 to 68.2% by weight (corresponding to 2-methylpentane: 54.3 to 40% by weight, 3-methylpentane: 32.7 to 24.7% by weight and n-hexane: 3.3 to 2.5% by weight). The above boiling point is conspicuously lower than both of the boiling point of the hydrocarbon mixture only, 62.0°C, and the boiling point of the lower alcohol mixture only, 78.5°C, thereby exhibiting a conspicuous boiling point lowering phenomenon and demonstrating the realization of approximately azeotropic state. The realization of boiling point lowering enabled providing the cleaning agent composition with very excellent dryability.

A vapor-liquid equilibrium diagram (X-Y diagram) with respect to mixtures of the hydrocarbon mixture and the lower alcohol mixture was drawn on the basis of the results of Table 1, in which the X-axis (axis of abscissa) represented the lower alcohol mixture component ratio of liquid phase and the Y-axis (axis of ordinates) represented the lower alcohol mixture component ratio of vapor phase, and the azeotropic composition was determined. The X-Y diagram is shown in Fig. 1.

In the azeotropic state, the component ratio of liquid phase and the component ratio of vapor phase are iden-

X-Y diagram and the function $Y = X$ represents an azeotropic composition. Therefore, an azeotropic composition was determined from the X-Y diagram of Fig. 1, which was found to consist of 16.1% by weight of the lower alcohol mixture component and 83.9% by weight of the hydrocarbon mixture component. Accordingly, specifically, it was found that the azeotropic composition consisted of 50.4% by weight of 2-methylpentane, 30.4% by weight of 3-methylpentane, 3.1% by weight of n-hexane, 13.7% by weight of ethanol, 0.8% by weight of isopropanol and 1.6% by weight of n-propanol.

100 g of a cleaning agent composition of the above azeotropic composition was prepared and simple distillation thereof was carried out at atmospheric pressure. Distillate and bottoms (liquid phase) were simultaneously harvested at time intervals, and the composition change thereof was measured. The component ratios were determined by gas chromatography with the use of calibration curve. Gas chromatography was conducted with the use of gas chromatograph GC-14B manufactured by Shimadzu Corporation, column DB-1 (inner diameter: 0.53 mm and length: 30 m) manufactured by Hewlett Packard and detector FID under the conditions such that injection hole temperature: 210°C, detector temperature:

min), column temperature rise rate: 10°C/min and finally reached column temperature: 200°C. The results are given in Tables 2 and 3. Table 2 shows the relationship between distillate sampling timing and the analytical result of each component ratio along with total lower alcohol and hydrocarbon component ratios (% by weight). On the other hand, Table 3 shows the relationship between bottoms (liquid phase) sampling timing and the analytical result of each component ratio along with total lower alcohol and hydrocarbon component ratios (% by weight). The distillate composition change was in the range of 0.4% by weight only until the end of the distillation, and the composition change of bottoms harvested simultaneously with the distillate was in the range of 4.7% by weight until the end of the distillation. Thus, very excellent composition stability was confirmed.

	before distilla- tion	distilla- tion 1	distilla- tion 2	distilla- tion 3	end of distilla- tion
ethanol	13.7	14.9	14.0	13.6	13.2
isopropanol	0.8	0.5	0.7	0.8	1.0
n-propanol	1.6	0.5	1.0	1.4	1.8
2-methylpentane	50.4	52.4	50.6	49.5	48.1
3-methylpentane	30.4	29.4	30.9	31.6	32.4
n-hexane	3.1	2.2	2.8	3.1	3.5
lower alcohol mixture	16.1	15.9	15.7	15.8	16.0
hydrocarbon mixture	83.9	84.1	84.3	84.2	84.0

Table 3

	before distilla- tion	liq. phase 1	liq. phase 2	liq. phase 3	end of liq. phase
ethanol	13.7	13.7	13.4	13.1	13.4
isopropanol	0.8	0.9	1.0	1.3	1.7
n-propanol	1.6	1.7	2.3	3.5	5.7
2-methylpentane	50.4	49.5	48.1	45.9	42.3
3-methylpentane	30.4	31.2	31.8	32.4	32.6
n-hexane	3.1	3.0	3.4	3.8	4.3
lower alcohol mixture	16.1	16.3	16.7	17.9	20.8
hydrocarbon mixture	83.9	83.7	83.3	82.1	79.2

Example 2

A hydrocarbon mixture consisting of 97.3% by weight of 2-methylpentane and 2.7% by weight of n-

ing of 100% by weight of ethanol was used as the lower alcohol with 1 to 3 carbon atoms. The hydrocarbon mixture and the lower alcohol mixture were mixed together in varied proportions (lower alcohol mixture component ratio: 0, 10, 15, 20, 35 and 100% by weight in Table 4) to thereby obtain mixture compositions in an amount of 200 g each. These compositions were subjected to simple distillation at atmospheric pressure, and the boiling point of initial distillate, component ratio of vapor phase and component ratio of liquid phase were measured. The results are given in Table 4.

Table 4

b.p. (°C)	60.5	53.5	53.3	53.7	54.0	78.3
Lower alcohol mixt. component ratio (wt.%) of liq. phase	0.0	9.6	15.2	20.6	34.0	100.0
Lower alcohol mixt. component ratio (wt.%) of vapor phase	0.0	16.4	16.5	16.8	16.4	100.0

Referring to Table 4, the boiling point of the mixture composition ranged from 53.4 to 54.0°C when the lower alcohol mixture (consisting of 100% by weight of

conspicuously lower than both of the boiling point of the hydrocarbon mixture only, 60.5°C, and the boiling point of the lower alcohol mixture only, 78.3°C, thereby exhibiting a conspicuous boiling point lowering phenomenon and demonstrating the realization of approximately azeotropic state. A vapor-liquid equilibrium diagram (X-Y diagram) with respect to mixtures of the hydrocarbon mixture and the lower alcohol mixture was drawn on the basis of the results of Table 4, in which the X-axis (axis of abscissa) represented the lower alcohol mixture component ratio of liquid phase and the Y-axis (axis of ordinates) represented the lower alcohol mixture component ratio of vapor phase, and the azeotropic composition was determined. The X-Y diagram is shown in Fig. 2. An azeotropic composition was determined from the X-Y diagram of Fig. 2, which was found to consist of 16.6% by weight of the lower alcohol mixture component and 83.4% by weight of the hydrocarbon mixture component. Accordingly, specifically, it was found that the azeotropic composition consisted of 81.2% by weight of 2-methylpentane, 2.2% by weight of n-hexane and 16.6% by weight of ethanol.

Example 3

weight of n-propanol, 50.3% by weight of 2-methylpentane, 30.4% by weight of 3-methylpentane and 3.1% by weight of n-hexane was put in a distillation flask and distilled at atmospheric pressure by the use of a rectifying column having a theoretical plate number of 25 packed with coiled packing of SUS 306 (Helipack manufactured by Tokyo Special Wire Netting Co., Ltd.). Thus, a distillate of 53.0°C in boiling point was obtained. This distillate was analyzed by the same gas chromatography as in Example 1 with the use of calibration curve and was found to consist of 16.0% by weight of ethanol, 55.4% by weight of 2-methylpentane, 27.9% by weight of 3-methylpentane and 0.7% by weight of n-hexane. This composition had a boiling point lower than those of the components thereof, attesting to the formation of an azeotropic composition.

Example 4

The same hydrocarbon mixture and lower alcohol mixture as in Example 1 were mixed together in varied proportions (lower alcohol mixture component ratio: 5, 10, 15, 20, 30 and 40% by weight in Table 5) to thereby obtain mixture compositions in an amount of 200 g

to stand still at ordinary temperature and humidity for 24 hr and also by dipping slide glass pieces in an oil marking ink and a solution obtained by dissolving 40% by weight rosin oil in 1,1,1-trichloroethylene as a solvent, respectively, and evaporating the solvent from the dipped slide glass pieces. Hand wiping cleaning of the specimens was performed with the use of wiping paper (Kimwipe produced by Jujo Kimberley) impregnated with the above mixture compositions of varied component ratios. Cleaning performance was evaluated and the criterion therefor was such that:

- o: dirt was completely removed by less than 10 hand wipes,
- Δ: dirt was removed by at least 10 hand wipes, and
- x: dirt was not removed irrespective of at least 10 hand wipes.

The results are given in Table 5. When the lower alcohol mixture component ratio is decreased to 10% by weight, the removal of any of finger sebum, marking ink and rosin oil tends to be difficult. When the lower alcohol mixture component ratio is less than 10% by weight, it occurs that marking ink and rosin oil cannot be removed.

component ratio (wt.%)	5	10	15	20	30	40
finger sebum	Δ	o	o	o	o	o
marking ink	Δ - x	o - Δ	o	o	o	o
rosin oil	x	Δ	o	o	o	o

The cleaning performance of each of the compositions specified in Table 6 was evaluated with respect to various dirt components. The same evaluation was made of a mixture of diethyl ether and ethanol and ethanol as references. With respect to specimens having dirt components adhering thereto, rosin oil and marking ink specimens were prepared in the same manner as described above. Pitch specimen was prepared by dipping a slide glass in a solution obtained by dissolving 40% by weight pitch in 1,1,1-trichloroethylene as a solvent and evaporating the solvent from the dipped slide glass. With respect to epoxy resin, use was made of a specimen prepared by forming an about 0.5 mm thick layer of bisphenol epoxy resin (Epikote produced by Showa Shell Sekiyu K.K.) on a slide glass according to the metal mask printing technique. The cleaning performance was evaluated in the same manner

the present invention exhibit excellent cleaning capability for any of varied dirt components and thus have a very broad range of applicability to dirt.

Table 6

		Compsn. 1	Compsn. 2	Compsn. 3	Mixt. of diethyl ether & ethanol	Ethanol
	2-methylpentane	50.4 wt. %	81.2 wt. %	50.2 wt. %		
	3-methylpentane	30.4 wt. %		30.2 wt. %		
	n-hexane	3.1 wt. %	2.2 wt. %	3.1 wt. %		
	ethanol	13.7 wt. %	16.6 wt. %	14.1 wt. %	20 vol. %	100 wt. %
	methanol			0.2 wt. %		
	isopropanol	0.8 wt. %		2.2 wt. %		
	n-propanol	1.6 wt. %				
	diethyl ether				80 vol. %	
Dirt cleaning capability	pitch	o	o	o	o - Δ	x
	rosin oil	o	o	o	o	o
	lanolin	o	o	o	o - Δ	Δ
	marking ink	o	o	o	o	o
	epoxy resin	o - Δ	o - Δ	o - Δ	o	o

Example 5

The same hydrocarbon mixture and lower alcohol mixture as in Example 1 were mixed together in varied proportions (lower alcohol mixture component ratio: 10, 15, 20, 25, 30, 35, 40 and 50% by weight in Table 7) to thereby obtain mixture compositions. One-minute

mixture compositions. Thereafter, the materials were inspected to find any appearance change. The evaluation was made on the criterion such that:

o: no appearance change was caused by the dipping test and hand wiping,

Δ: appearance change was observed only after the dipping test, and

x: appearance change was observed after not only the dipping test but also the hand wiping.

The results are given in Table 7. Metals and glasses encountered no problems irrespective of the lower alcohol mixture component ratio ranging from 10 to 50% by weight. When the lower alcohol mixture component ratio ranged from 10 to 40% by weight, the thermoplastic resins also encountered no problems. However, PMMA having residual stress attributed to molding occasionally had cracking caused by hand wiping at a lower alcohol mixture component ratio of 35% by weight or higher. The PMMA had slight cracking made by the dipping test but had no appearance change caused by hand wiping at a lower alcohol mixture component ratio of 30% by weight. These showed that the lower alcohol mixture component ratio is required to be less than 35%

composition to a wide spectrum of materials of items to be cleaned.

Table 7

Lower alcohol mixt. component ratio (wt.%)	10	15	20	25	30	35	40	50
iron (SPCC)	o	o	o	o	o	o	o	o
copper	o	o	o	o	o	o	o	o
brass	o	o	o	o	o	o	o	o
SUS304	o	o	o	o	o	o	o	o
optical glass BK7	o	o	o	o	o	o	o	o
optical glass SF15	o	o	o	o	o	o	o	o
colorless plate glass	o	o	o	o	o	o	o	o
polyamide (nylon 6)	o	o	o	o	o	o	o	o
PMMA	o	o	o	o	o	o	o	Δ
polycarbonate	o	o	o	o	o	o	o	o
polystyrene	o	o	o	o	o	o	o	Δ
ABS	o	o	o	o	o	o	o	Δ
polyacetal	o	o	o	o	o	o	o	o
PMMA (with residual stress)	o	o	o	o	Δ	x	x	x

Example 6

A hydrocarbon mixture consisting of 60.1% by weight of 2-methylpentane, 36.2% by weight of 3-methylpentane and 3.7% by weight of n-hexane was used as the aliphatic saturated hydrocarbon with 6 carbon atoms. A lower alcohol mixture consisting of 85.5% by

hol with 1 to 3 carbon atoms. The hydrocarbon mixture and the lower alcohol mixture were mixed together in varied proportions (lower alcohol mixture component ratio: 0, 10, 15, 20, 30 and 100% by weight in Table 8) to thereby obtain mixture compositions in an amount of 200 g each. These compositions were subjected to simple distillation at atmospheric pressure, and the boiling point of initial distillate, component ratio of vapor phase and component ratio of liquid phase were measured. The results are given in Table 8.

Table 8

b.p. (°C)	62.0	54.5	54.2	54.4	54.5	78.5
Lower alcohol mixt. component ratio (wt.%) of liq. phase	0.0	9.8	15.0	20.5	31.6	100.0
Lower alcohol mixt. component ratio (wt.%) of vapor phase	0.0	16.1	16.4	16.7	17.2	100.0

Referring to Table 8, the boiling point of the mixture composition ranged from 54.2 to 54.5°C when the lower alcohol mixture (consisting of 85.5% by weight of ethanol, 13.4% by weight of isopropanol and 1.1% by weight of methanol) component ratio of liquid phase ranged from 9.8 to 31.6% by weight. The above boiling

78.5°C, thereby exhibiting a conspicuous boiling point lowering phenomenon and demonstrating the realization of approximately azeotropic state. A vapor-liquid equilibrium diagram (X-Y diagram) with respect to mixtures of the hydrocarbon mixture and the lower alcohol mixture was drawn on the basis of the results of Table 8, in which the X-axis (axis of abscissa) represented the lower alcohol mixture component ratio of liquid phase and the Y-axis (axis of ordinates) represented the lower alcohol mixture component ratio of vapor phase, and the azeotropic composition was determined. The X-Y diagram is shown in Fig. 2. In the azeotropic state, the component ratio of liquid phase and the component ratio of vapor phase are identical with each other, so that the intersection of the X-Y diagram and the function $Y = X$ represents an azeotropic composition. Therefore, an azeotropic composition was determined from the X-Y diagram of Fig. 2, which was found to consist of 16.4% by weight of the lower alcohol mixture component and 83.6% by weight of the hydrocarbon mixture component. Accordingly, specifically, it was found that the azeotropic composition

hexane, 14.0% by weight of ethanol, 2.2% by weight of isopropanol and 0.2% by weight of methanol.

100 g of a cleaning agent composition of the above azeotropic composition was prepared and simple distillation thereof was carried out at atmospheric pressure. Distillate and bottoms (liquid phase) were simultaneously harvested at time intervals, and the composition change thereof was measured. The component ratios were determined by gas chromatography with the use of calibration curve. Gas chromatography was conducted in the same manner as in Example 1. The results are given in Tables 9 and 10. Table 9 shows the relationship between distillate sampling timing and the analytical result of each component ratio along with total lower alcohol and hydrocarbon component ratios (% by weight). On the other hand, Table 10 shows the relationship between bottoms (liquid phase) sampling timing and the analytical result of each component ratio along with total lower alcohol and hydrocarbon component ratios (% by weight). With respect to the lower alcohol mixture and hydrocarbon mixture components, the distillate composition change from before the distillation to the end of the distillation was 0.6% by weight and the

stability was confirmed.

Table 9

	Feedstock liq.	Initial stage of disti- llation	Middle stage of disti- llation	Final stage of disti- llation	End of disti- llation
ethanol	14.0	14.6	14.4	14.2	14.0
isopropanol	2.2	1.4	1.8	2.2	3.0
methanol	0.2	0.3	0.2	0.1	0.0
2-methylpentane	49.5	51.4	50.2	49.0	46.7
3-methylpentane	31.2	29.9	30.7	31.5	32.7
n-hexane	2.9	2.4	2.7	3.0	3.6
lower alcohol mixt. total	16.4	16.3	16.4	16.5	17.0
hydrocarbon mixt. total	83.6	83.7	83.6	83.5	83.0

Table 10

	Feedstock liq.	Initial stage of disti- llation	Middle stage of disti- llation	Final stage of disti- llation	End of disti- llation
ethanol	14.0	14.0	14.1	13.9	14.7
isopropanol	2.2	2.3	2.6	3.1	5.5
methanol	0.2	0.1	0.1	0.1	0.0
2-methylpentane	49.5	49.1	48.2	46.9	41.7
3-methylpentane	31.2	31.5	31.8	32.5	33.6
n-hexane	2.9	3.0	3.2	3.6	4.5
lower alcohol mixt. total	16.4	16.4	16.8	17.1	20.2
hydrocarbon mixt. total	83.6	83.6	83.2	82.9	79.8

as "liquid before distillation" in each of Tables 11 to 19 was put in a distillation flask and distilled at atmospheric pressure by the use of a rectifying column having a theoretical plate number of 25 packed with coiled packing of SUS 306 (Helipack manufactured by Tokyo Special Wire Netting Co., Ltd.). Thus, distillates of component ratios specified in Tables 11 to 19 were obtained at time intervals. The Tables show the relationship between distillate sampling timings and the respective boiling point measurements and analytical results of component ratios along with total lower alcohol and hydrocarbon component ratios (% by weight). The component ratios were analyzed by the same gas chromatography as in Example 1 with the use of calibration curve. The component ratio change was slight and, especially, the changes of lower alcohol and hydrocarbon component ratios were extremely slight, attesting to the formation of azeotropic or azeotrope-like compositions.

Table 11

	measured b.p. (°C)	ethanol	methanol	iso- propanol	n- propanol	2-methyl- pentane	3-methyl- pentane	n- hexane	lower alcohol mixt. total
Liq. before disti- llation	-	14.3	0.0	0.8	1.6	80.5	0.0	2.8	16.8
Initial disti- llate	52.0	16.4	0.0	0.0	0.0	83.6	0.0	0.0	16.4
Initial stage of disti- llation	52.0	15.8	0.0	0.0	0.0	84.2	0.0	0.0	15.8
Middle stage of disti- llation	52.4	15.9	0.0	0.0	0.0	82.8	0.0	1.3	15.9
Final stage of disti- llation	52.5	15.9	0.0	0.0	0.0	83.2	0.0	0.9	15.9

Table 12

	measured b.p. (°C)	ethanol	methanol	iso- propanol	n- propanol	2-methyl- pentane	3-methyl- pentane	n- hexane	lower alcohol mixt. total	hyd car mix tot
Liq. before disti- llation	-	14.5	0.2	2.3	0.0	80.2	0.0	2.8	17.0	83
Initial disti- llate	52.0	14.3	3.3	0.0	0.0	82.4	0.0	0.0	17.6	82
Initial stage of disti- llation	52.0	15.2	0.8	0.0	0.0	83.9	0.0	0.1	16.0	84
Middle stage of disti- llation	52.4	15.5	0.3	0.2	0.0	82.5	0.0	1.5	16.0	84
Final stage of disti- llation	52.5	15.3	0.3	0.4	0.0	82.5	0.0	1.5	16.0	84

Table 13

	measured b.p. (°C)	ethanol	methanol	iso- propanol	n- propanol	2-methyl- pentane	3-methyl- pentane	n- hexane	lower alcohol mixt. total	hyd- car- mixt. total
Liq. before disti- llation	-	14.1	0.2	2.2	0.0	49.7	30.6	3.2	16.5	83
Initial disti- llate	52.5	14.2	2.2	0.0	0.0	67.2	16.3	0.1	16.4	83
Initial stage of disti- llation	52.5	15.4	0.6	0.0	0.0	62.2	21.6	0.2	16.0	84
Middle stage of disti- llation	53.0	15.9	0.3	0.1	0.0	53.4	28.4	1.9	16.3	83
Final stage of disti- llation	53.4	15.4	0.2	0.7	0.0	52.8	28.8	2.1	16.3	83

Table 14

	measured b.p. (°C)	ethanol	methanol	iso- propanol	n- propanol	2-methyl- pentane	3-methyl- pentane	n- hexane	lower alcohol mixt. total	hyd car mix tot
Liq. before disti- llation	-	14.1	0.0	0.8	1.6	51.7	31.8	0.0	16.5	83
Initial disti- llate	52.5	15.6	0.0	0.0	0.0	67.1	17.3	0.0	15.6	84
Initial stage of disti- llation	52.5	15.9	0.0	0.0	0.0	61.1	23.1	0.0	15.9	84
Middle stage of disti- llation	53.0	15.8	0.0	0.3	0.0	54.5	29.4	0.0	16.1	83.
Final stage of disti- llation	53.0	15.8	0.0	0.3	0.0	54.2	29.7	0.0	16.1	83.

Table 15

	measured b.p. (°C)	ethanol	methanol	iso- propanol	n- propanol	2-methyl- pentane	3-methyl- pentane	n- hexane	lower alcohol mixt. total	hy- dro- car- bon mi- to
Liq. before disti- llation	-	14.1	0.2	2.2	0.0	51.7	31.8	0.0	16.5	8
Initial disti- llate	52.5	14.6	1.6	0.0	0.0	67.6	16.2	0.0	16.2	8
Initial stage of disti- llation	52.5	15.5	0.6	0.0	0.0	61.2	22.8	0.0	16.1	8
Middle stage of disti- llation	53.0	15.5	0.3	0.4	0.0	54.7	29.1	0.0	16.2	8
Final stage of disti- llation	53.1	15.5	0.1	0.5	0.0	54.7	29.2	0.0	16.1	8

Table 16

	measured b.p. (°C)	ethanol	methanol	iso- propanol	n- propanol	2-methyl- pentane	3-methyl- pentane	n- hexane	lower alcohol mixt. total	hyd- car- mixt. total
Liq. before disti- llation	-	14.4	0.0	0.9	1.7	72.4	10.6	0.0	17.0	83
Initial disti- llate	52.5	16.2	0.0	0.0	0.0	78.9	4.9	0.0	16.2	83
Initial stage of disti- llation	52.5	15.7	0.0	0.0	0.0	78.6	5.7	0.0	15.7	84
Middle stage of disti- llation	52.5	16.0	0.0	0.0	0.0	75.6	8.4	0.0	16.0	84
Final stage of disti- llation	52.5	16.0	0.0	0.0	0.0	76.0	8.0	0.0	16.0	84

Table 17

	measured b.p. (°C)	ethanol	methanol	iso- propanol	n- propanol	2-methyl- pentane	3-methyl- pentane	n- hexane	lower alcohol mixt. total
Liq. before disti- llation	-	14.3	0.2	2.2	0.0	83.3	0.0	0.0	16.7
Initial disti- llate	52.0	10.2	2.7	0.0	0.0	87.1	0.0	0.0	12.9
Initial stage of disti- llation	52.0	15.5	0.9	0.0	0.0	83.6	0.0	0.0	16.4
Middle stage of disti- llation	52.0	15.5	0.0	0.1	0.0	84.4	0.0	0.0	15.6
Final stage of disti- llation	52.1	15.9	0.0	0.0	0.0	84.2	0.0	0.0	15.9

Table 18

	measured b.p. (°C)	ethanol	methanol	iso- propanol	n- propanol	2-methyl- pentane	3-methyl- pentane	n- hexane	lower alcohol mixt. total
Liq. before disti- llation	-	14.2	0.0	0.8	1.6	83.4	0.0	0.0	16.6
Initial disti- llate	52.0	16.6	0.0	0.0	0.0	83.5	0.0	0.0	16.6
Initial stage of disti- llation	52.0	15.7	0.0	0.0	0.0	84.3	0.0	0.0	15.7
Final stage of disti- llation	52.0	16.3	0.0	0.0	0.0	83.8	0.0	0.0	16.3

Table 19

	measured b.p. (°C)	ethanol	methanol	iso- propanol	n- propanol	2-methyl- pentane	3-methyl- pentane	n- hexane	lower alcohol mixt. total	hydro- carbon mixt. total
Liq. before disti- llation	-	13.1	0.0	0.8	1.5	51.8	29.6	3.2	15.4	84.6
Initial disti- llate	52.6	14.0	0.0	0.0	0.0	69.1	16.7	0.2	14.0	86.0
Initial stage of disti- llation	52.6	15.9	0.0	0.0	0.0	59.1	24.4	0.6	15.9	84.1
Middle stage of disti- llation 1	53.0	16.0	0.0	0.2	0.0	53.5	28.1	2.2	16.2	83.8
Middle stage of disti- llation 2	53.5	15.3	0.0	0.5	0.2	52.9	28.7	2.4	16.0	84.0
Middle stage of disti- llation 3	53.5	15.4	0.0	0.6	0.1	52.2	29.2	2.5	16.1	83.9
Final stage of disti- llation	53.5	15.3	0.0	0.8	0.1	50.5	30.5	2.8	16.2	83.8

CLAIMS

1. A cleaning agent composition for hand wiping comprising 66 to 90% by weight of at least one aliphatic hydrocarbon with 6 carbon atoms containing at least 44% by weight of 2-methylpentane and 10 to 34% by weight of at least one lower alcohol with 1 to 3 carbon atoms containing at least 85% by weight of ethyl alcohol to thereby exhibit azeotropic or azeotrope-like characteristics.
2. The cleaning agent composition for hand wiping according to claim 1, whose total content of n-hexane, methanol, isopropanol and n-propanol is less than 10% by weight based on all of the composition.
3. The cleaning agent composition for hand wiping according to claim 1 or 2, whose water content is less than 2000 ppm by weight.
4. The cleaning agent composition for hand

components having a boiling point of 120°C or higher at 760 mmHg is less than 1% by weight and the total amount of components having a boiling point of 170°C or higher at 760 mmHg is less than 1000 ppm by weight.

5. A precision cleaning method comprising impregnating fibrous matter with a cleaning agent composition for hand wiping comprising 66 to 90% by weight of at least one aliphatic hydrocarbon with 6 carbon atoms containing at least 44% by weight of 2-methylpentane and 10 to 34% by weight of at least one lower alcohol with 1 to 3 carbon atoms containing at least 85% by weight of ethyl alcohol so as to exhibit azeotropic or azeotrope-like characteristics and wiping a surface of an item to be cleaned with the impregnated fibrous matter by hand.