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LOWLY CORROSIVE CLEANER COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a cleaner composition for electrical components, electronic components, mechanical parts and so on, particularly one suitable for removing a flux and a flux residue from the components or parts after soldering.

2. Description of the Prior Art

In general, soldering is indispensable to the formation of an electric circuit in an electronic or electrical appliance, a mechanical part or the like, and it is a common practice in the art to apply a flux to the appliance or part prior to this soldering for the purpose of conducting the soldering completely and speedily. After the completion of the soldering, however, the resulting flux or flux residue is removed with a cleaning agent, because it is liable to deteriorate the electrical characteristics of the circuit or to cause the corrosion thereof.

Chlorinated solvents and flon type solvents which are free from flash point and little suffer from chemical change have been used as the above cleaning agent. However, these solvents are substances causative of the destruction of the ozonosphere, so that the use thereof is to be limited. Under these circumstances, many aqueous and solvent-type cleaners have been proposed as substitutes for the chlorinated or flon-type solvent. Further, cleaners comprising

terpenes (such as limonene, pinene and dipentene) have recently been proposed as ones which little pollute the environment and exhibit excellent flux removing properties in US Patent Specification 4511488, Japanese Pat. Appln. Toku-hyo 63-501908 (US Patent Specifications 4640719 and 4740247) and so on.

However, these cleaning agents and cleaners do not satisfy all of the requirements necessary for the cleaner composition, the requirements including low environmental pollutiveness, low deteriorativeness, low corrosiveness, low flammability, low toxicity and high flux removing properties. That is to say, the cleaners comprising chlorinated solvents or flon-type solvents are significantly problematic in safety, toxicity, environmental pollution and so on. Further, the aqueous cleaners cause rusting and lowering in the dryability and are problematic in the disposal of waste water and so on, though they are desirably less dangerous and less toxic than the organic solvent-type cleaners. Furthermore, the solvent-type cleaners mainly comprising non-hydrocarbon solvents are problematic in toxicity and exhibit poor endurance because of their high liability to deteriorate in service, though they are excellent in flux removing properties. Additionally, terpenes such as limonene exhibit low flash points and are poor in endurance because of their high liability to deteriorate in service, though they are excellent in flux removing properties. Further, they are compounds resulting from natural substances, so that the acquisition of them with constant quality is difficult and that they are expensive and limited in supply.

The use of a hydrocarbon cleaning agent alone is problematic in flux removing properties, though it

little causes environmental pollution. Therefore, hydrocarbon-base solvents improved in flux removing properties and cleaning properties for the components or parts by the addition of polar compounds such as alcohols, ethers or ketones have been proposed in Japanese Pat. Appln. Laid-Open No. 3-146597 and Japanese Pat. Appln. Toku-hyo 7-503032. Further, Japanese Pat. Appln. Laid-Open No. 3-146597 also discloses that benzotriazole may be added to such solvents for the purpose of protecting a metal surface from corrosion.

In the above-mentioned cleaners, it is a general practice in the art to use the cleaners repeatedly through reclamation by distillation for the purpose of decreasing the cost of the cleaners and the influence thereof on the environment. However, the above polar compound often decomposes during the distillation for reclamation and/or the cleaning of the components or parts to cause the deterioration of the cleaners themselves or the formation of an explosive peroxide. Japanese Pat. Appln. Laid-Open No. 7-268391 discloses examples wherein antioxidants are further added to inhibit the decomposition of the polar compound.

It has now been found that when a cleaner as described above comprising a mixture of a hydrocarbon solvent and a polar compound is used repeatedly through reclamation by distillation, the metal surface of the component or part cleaned with a recovered fluid undergoing the repetition of the reclamation is liable to corrode even in the case wherein benzotrizole is added to the cleaner as a rust preventive. The reason for this corrosion is thought to be that alicyclic carboxylic acids contained in a flux, carboxylic acids formed by thermal decomposition

of the oxygen-containing organic compounds contained in a flux or the polar compounds contained in the cleaner, and the inorganic halides or hydrogen halides contained in a flux accumulate in the recovered fluid, which makes it impossible for benzotriazole alone to prevent the rusting. Attempts to overcome of these problems have been made by adding a certain epoxy compound, which has been known to react with the rust preventive [Kinzokuhyomen Kogyo Zensho 13 "Kinzoku Fushoku Boshoku Gijutsu, p. 56, Revised Edition (1981)] or with hydrogen halide, thereby suppressing the accumulation of acids. More specifically, 2-ethyl hexyl glycidyl ether was added in an amount of 0.1% by mass. However, it was found that when thus obtained cleaner was repeatedly used, the cleaned metal surface underwent corrosion with the repetition of reclamation, as referred to the aforesaid cleaners.

SUMMARY OF THE INVENTION

The present invention aims at overcoming the above disadvantages of the prior art to provide a cleaner composition which is excellent in cleaning properties against fluxes and can keep its rust-preventing power for a prolonged period.

The inventors of the present invention have intensively studied for the purpose of solving the above problems to find that when an epoxy compound and a nitrogen-containing organic rust preventive such as benzotriazole are both added to an organic solvent-type cleaning agent, the resultant cleaner is little lowered in rust-preventing effect even after the repetition of reclamation by distillation. The present invention has been accomplished on the basis

of this finding.

Namely, the present invention relates to a lowly corrosive cleaner composition characterized by at least comprising an organic solvent-type cleaning agent, a nitrogen-containing organic rust preventive, and an epoxy compound as additive.

The cleaner composition of the present invention exhibits remarkably lowered corrosiveness even after the reclamation by distillation and is excellent in flux removing properties by virtue of the above specific additives, being suitable for cleaning electronic and electrical components, mechanical parts and so on.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Although the mechanism how the addition of an epoxy compound in combination with a nitrogen-containing organic rust preventive according to the present invention gives the above effects has not been elucidated as yet, it is thought that the epoxy compound acts both as a fixative for hydrogen halides and so on and as a protective agent for the metal surface and the nitrogen-containing organic rust preventive serves to protect the metal surface from the corrosion caused by carboxylic acids. At any rate, the cleaner composition of the present invention exhibits remarkably enhanced rust preventing effect by virtue of the presence of these compounds and the rust preventing effect is little lowered even after the repetition of the recovery by distillation.

The organic solvent-type cleaning agent to be used in the present invention is preferably one little causative of environmental pollution, though the

cleaning agent is not particularly limited but may be commercially available one. Such a cleaning agent includes those mainly comprising hydrocarbons having 5 to 20 carbon atoms, preferably 7 to 16 carbon atoms, still preferably 9 to 15 carbon atoms. A hydrocarbon having less than 5 carbon atoms is in great danger of causing fire or explosion in the cleaning operation. Therefore, there is problematic in respect of safety. On the other hand, a hydrocarbon having more than 20 carbon atoms not only exhibits poor flux removing properties but also is problematic owing to the higher boiling point of the hydrocarbon in that the reclamation of the resulting cleaner composition by distillation takes greater energy and that a large amount of a flux component is also recovered in reclaiming the cleaner composition by distillation to give a reclaimed cleaner composition different from the original one in properties.

When a flux cannot completely be removed by the use of a hydrocarbon solvent alone, a C_5-C_{20} organic compound having one or more polar groups other than epoxy compounds is added to the hydrocarbon solvent. Examples of such an organic compound having polar group(s) include alcohols, ketones, ethers, esters and so on. The organic compound should be one having 5 to 20 carbon atoms. When the organic compound has less than five carbon atoms, there is a great danger of causing fire or explosion in the operation, thus being problematic in safety. On the other hand, such an organic compound having more than 20 carbon atoms is poor in flux removing properties and is problematic owing to the higher boiling point of the compound in that the reclamation of the resulting cleaner composition by distillation takes greater energy and

that a large amount of a flux component is also recovered in reclaiming the cleaner composition by distillation to give a reclaimed cleaner composition different from the original one in properties. In particular, it is preferable that the organic compound have 6 to 17 carbon atoms, still preferably 7 to 15 carbon atoms.

When an alcohol is used as the above organic compound having polar group(s), the alcohol may be selected from those each having one or more hydroxyl groups. The use of an alcohol having three or more hydroxyl groups is undesirable, because the resulting cleaner composition is poor in flux removing properties and such an alcohol is poor in solubility in hydrocarbons. Specific examples of the alcohol include natural and synthetic alcohols such as 2-ethyl-1-hexanol, hexyl alcohol, 1-octanol, 2-octanol, lauryl alcohol, oleyl alcohol, C_{20} Guerbet alcohol, 2-cyclo-2-propanol, 1,2-dodecanediol and 1,2-octadecanediol.

The above ether may be one having 5 to 20 carbon atoms in the molecules and corresponding to an alcohol as described above wherein the hydrogen atom of the hydroxyl group is replaced by a C_1-C_4 hydrocarbon group such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or tert-butyl. Such an ether can be prepared by reacting the above alcohol with a corresponding halogenated hydrocarbon. Alternatively, the ether may be a cyclic ether of five-membered or more-membered ring. When the ether has hydroxyl group or groups, it is preferably selected from among ethers having two or less hydroxyl groups. These ethers exhibit excellent flux removing properties. Among such ethers, an ether having a methyl or ethyl group

at one end is preferable from the standpoint of flux removing properties. As specific examples of the ethers, there may be mentioned dibutyl ether, propylene glycol monobutyl ether, 1,2-diethoxy ethane, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, dipropylene glycol methyl ether, anisole, dihexyl ether and so on.

The above ketone may be one which has both a C_1-C_4 hydrocarbon group (such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or tert-butyl) and a C_1-C_{15} hydrocarbon group and in which the number of carbon atoms in the molecule is 5 to 20. Such a ketone can be prepared by oxidation or catalytic dehydrogenation of a corresponding secondary alcohol. The ketone as well as the ether exhibits excellent flux removing properties. Among such ketones, one having a methyl or ethyl group at one end is preferable from the standpoint of flux removing properties.

Similarly, the ester may be one which has both a hydrocarbon group having 1 to 4 carbon atoms (such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or tert-butyl) and a hydrocarbon group having 1 to 15 carbon atoms and in which the number of carbon atoms in the molecule is 5 to 20. Such an ester can be prepared by reacting an acid directly with an alcohol. The ester as well as the above ether or ketone exhibits excellent flux removing properties. Among such esters, one having a methyl or ethyl group at one end is preferable from the standpoint of flux removing properties. Specific examples of the esters include butyl acetate, isopentyl acetate, 3-methoxybutyl acetate, butyl propionate, butyl butyrate, isopentyl isovaleriate, methyl benzoate, diethyl malonate, ethylene glycol monoacetate and so on.

These organic compounds having one or more polar groups may be added either alone or as a mixture of two or more of them. The amount thereof is not limited so far as satisfactory flux removing properties are secured. The amount is generally from 3 to 50% by volume, preferably from 5 to 30% by volume, still preferably from about 10 to 25% by volume.

The nitrogen-containing organic rust preventive to be used in the present invention includes benzotriazole, tolyltriazole, benzotriazole derivatives having a C_2-C_{10} hydrocarbon group, benzimidazole, imidazole, imidazole derivatives having a C_2-C_{20} hydrocarbon group, thiazole, thiazole derivatives having a C_2-C_{20} hydrocarbon group and so on, which may be used either alone or as a mixture of two or more of them. In particular, benzotriazole, tolyltriazole and imidazole derivatives having a C_2-C_{20} hydrocarbon group are preferably used and these are widely used and exhibit excellent rust preventing effect on copper used as wiring material. The concentration of the nitrogen-containing organic rust preventive is preferably in the range of 0.01 to 2% by mass, more preferably in the range of 0.03 to 1% by mass. When the concentration is less than 0.01% by mass, the desired effect will not be obtained. Whereas a concentration exceeding 2% by mass may deteriorate the properties (e.g., insulating property) of the components to be cleaned.

The hydrocarbon groups of the imidazole derivative and thiazole derivative serve to enhance the solubility of these derivatives in the organic solvent-type cleaning agent, and therefore may suitably be selected depending upon the cleaning agent used. The number of carbon atoms of the hydrocarbon

groups is generally from 2 to 20, preferably from 5 to 18, still preferably from 10 to 17.

The hydrocarbon group of the benzotriazole derivative may suitably be selected from among those having 2 to 10 carbon atoms (incidentally, a benzotriazole derivative having a C_1 hydrocarbon group corresponds to tolyltriazole). It is preferable to use a benzotriazole derivative having a C_2-C_8 hydrocarbon group, particularly one having a C_2-C_5 hydrocarbon group.

The epoxy compound to be used in the present invention as an additive includes propylene oxide, epoxycyclooctane, 1,2-epoxybutane, 1,2-epoxyhexane, 1,2-epoxyheptane, 1,2-epoxyoctane, 1,2-epoxynonane, allyl glycidyl ether, propyl glycidyl ether, butyl glycidyl ether, pentyl glycidyl ether, hexyl glycidyl ether, 2-ethylhexyl glycidyl ether, 1,6-hexanediol diglycidyl ether, phenyl glycidyl ether, neopentyl glycol diglycidyl ether, ethylene glycol diglycidyl ether, and glycidyl ethers having 9-15 carbon atoms, cyclohexene oxide, 1-methylcyclohexene oxide, 4-methylcyclohexene oxide, 1,2-dimethylhexene oxide, 1-ethylcyclohexene oxide, styrene oxide, methylstyrene oxide and so on. These epoxy compounds may be used either alone or as a mixture of two or more of them. The number of carbon atoms of the glycidyl ethers may lie within such a range that the resulting glycidyl ethers can be dissolved in the cleaning agent. The number is generally from 3 to 20, preferably from 5 to 15, particularly preferably from 7 to 11. The concentration of the epoxy compound may be in the range of 0.01 to 5% by mass, preferably 0.02 to 2% by mass, more preferably 0.03 to 1% by mass. A concentration less than 0.01% by mass will not provide

the intended effect. On the other hand, a concentration exceeding 5% by mass may result in a strong smell or skin irritation.

When a cleaner composition prepared by adding only the nitrogen-containing organic rust preventive such as benzotriazole to the organic solvent-type cleaning agent and is used in the removal of a flux, as described above, a fluid recovered from the resulting cleaner composition by distillation causes a little corrosion when examined by the copper corrosion test, though the addition of the rust preventive is somewhat effective. When adding the epoxy compound alone as an additive, the effect is equivalent to that of the above case using the nitrogen-containing organic rust preventive.

On the other hand, the cleaner composition of the present invention containing both the nitrogen-containing organic rust preventive and the epoxy compound is remarkably enhanced in rust preventing effect. As a result of this enhancement, as will be described in Examples, the cleaner composition does not cause corrosion when examined by the copper corrosion test, even after it has been repeatedly reclaimed by distillation without the removal of distillation residue. As described above, the simultaneous use of the nitrogen-containing organic rust preventive and the epoxy compound is much more effective than the use of either of them alone.

Although the cleaner composition of the present invention, as described above, essentially comprises the organic solvent-type cleaning agent, the epoxy compound and the nitrogen-containing organic rust preventive, it may further contain other additives at need. Such additives include antioxidant, surfactants

and so on. As the antioxidant, there may be mentioned 2,6-di-tert-butylphenol, butyl hydroxyanisole, 2,6-di-tert-butyl-p-cresol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-diethyl-6-tert-butylphenol, 2,6-di-tert-butyl-4-hydroxymethylphenol, diphenol-p-phenylenediamine, 4-amino-p-diphenylamine, p,p'-dioctyl diphenylamine, phenyldiisodecyl phosphite, diphenyldiisooctyl phosphite, diphenyldiisodecyl phosphite, triphenyl phosphite, trisnonylphenyl phosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol phosphite, dilauryl-3,3'-thiodipropionate, dimyristyl-3,3'-thiodipropionate, distearyl-3,3'-thiodipropionate and so on. Although the surfactant to be used at need may be selected from among anionic surfactants, cationic surfactants, amphoteric surfactants and so on, the use of a nonionic surfactant is the best, because this surfactant has little influence on the surface to be cleaned. Preferable examples of the nonionic surfactant include polyoxyalkylene alkyl ethers, polyoxyalkylene alkylphenol ethers, polyoxyalkylene alkylfatty acid esters, polyoxyalkylene allylphenyl ethers, polyoxyalkylene-sorbitan fatty acid esters, polyoxyalkylenealkylamines, sorbitan fatty acid esters, polyoxyalkylenes and so on.

The cleaner composition of the present invention can be applied by various methods such as immersion method, ultrasonic cleaning method, oscillation method, spraying method or the like to give desirable results.

The cleaning of a printed board with a flux by the use of the cleaner composition of the present invention can be conducted effectively by, e.g., continuously conducting ultrasonic cleaning of the

printed board in a ultrasonic cleaning bath filled with the cleaner composition of the present invention and rinsing of the resulting printed board with the cleaner composition of the present invention.

The present invention will now be described in more detail by referring to the following Examples, though the present invention is not limited by them.

EXAMPLES

(Test method) 1% by mass of activated turpentine was added to a cleaning agent to prepare a pseudo used cleaning agent which had been used repeatedly for the removal of a flux. A predetermined amount of the pseudo used cleaning agent was put in a distilling reclaimer, followed by the addition of a nitrogen-containing organic rust preventive and an epoxy compound, as described in the respective examples. The mixture thus prepared was distilled at about 6700 Pa, followed by recovery. The fluid thus recovered was examined according to the following copper corrosion test. For comparison, the same cleaning agent as that used above not containing activated turpentine was subjected to the same reclamation procedure as that employed above, followed by examination of the resulting recovered fluid according to the copper corrosion test.

As a simulation of the operation of conducting the distillation and recovery repeatedly, the reclamation by distillation was repeated, while the resulting distillation residue in the distilling reclaimer was not removed and a predetermined amount of the above pseudo used cleaning agent was additionally added. In this case, a nitrogen-

containing organic rust preventive and an epoxy compound were added only in the first reclamation run.

In the copper corrosion test, 20 ml of the above cleaner composition and a surface-polished copper plate (75 mm x 12.5 mm x 3 mm, polished with silicon carbide (particle size: No. 150)) were put in a 50-ml sample vial and closed. The resulting vial was placed in a thermostat at 100°C for 24 hours and thereafter the surface of the copper plate was examined for corrosion with the naked eye.

Example 1

A mixture of 87.5% by volume of n-paraffin having a boiling point range of 150 to 215°C and 12.5% by volume of 2-ethylhexanol was used as the organic solvent-type cleaning agent, and 0.1% by mass of benzotriazole as the nitrogen-containing organic rust preventive and 0.1% by mass of 2-ethylhexyl glycidyl ether as the epoxy compound were added to the cleaning agent. According to the above specified copper corrosion test, the compositions thus obtained were examined for corrosiveness of fluid recovered by distillation. The results are given in Table 1. No difference was observed between the case containing activated turpentine and that not containing it.

Example 2

The above test was conducted in the same manner as that of Example 1 except that the benzotriazole was replaced by tolyltriazole. The results are given in Table 1. No difference was observed between the case containing activated turpentine and that not containing it.

Examples 3 to 6

The above test was conducted in the same manner

as that of Example 1 except that the 2-ethylhexyl glycidyl ether was replaced by butyl glycidyl ether, 2-methyloctyl glycidyl ether, 1,6-hexanediol glycidyl ether or 1,2-epoxyoctane. The results are given in Table 1. In all of the cases, no corrosion was observed.

Example 7

The above test was conducted in the same manner as that of Example 1 except that the benzotriazole was replaced by undecylimidazole. The results are given in Table 1. No difference was observed between the case containing activated turpentine and that not containing it.

Comparative Examples 1 and 2

A composition prepared by adding only benzotriazole to the same cleaning agent as that used in Example 1 and one prepared by adding no additive thereto were examined for corrosiveness of fluid recovered by distillation in the same manner as that of Example 1. The results are given in Table 1. In the test wherein turpentine was added, a recovered fluid from the former caused a little rusting, while one from the latter caused rusting over the whole surface.

Comparative Example 3

The above test was conducted in the same manner as that of Example 1 except that only 2-ethylhexyl glycidyl ether was added to the organic solvent-type cleaning agent. The results are given in Table 1. The results were equivalent to those attained in the case (Comparative Example 1) wherein benzotriazole was added alone.

Table 1

	N-containing organic additive (addition of 0.1%)	Epoxy compound (addition of 0.1%)	Corrosiveness of fluid recovered by distillation against copper	
			no addition of turpentine	addition of turpentine
Ex. 1	benzotriazole	2-ethylhexyl glycidyl ether	o	o
Ex. 2	tolyltriazole	2-ethylhexyl glycidyl ether	o	o
Ex. 3	benzotriazole	butyl glycidyl ether	o	o
Ex. 4	benzotriazole	2-methyloctyl glycidyl ether	o	o
Ex. 5	benzotriazole	1,6-hexanediol glycidyl ether	o	o
Ex. 6	benzotriazole	1,2-epoxyoctane	o	o
Ex. 7	undecylimidazole	2-ethylhexyl glycidyl ether	o	o
Comp. Ex. 1	benzotriazole	-	o	Δ
Comp. Ex. 2	-	-	o	x
Comp. Ex. 3	-	2-ethylhexyl glycidyl ether	o	Δ

(Evaluation of corrosiveness)

o: no corrosion Δ : a little corrosion

x: significant corrosion

Examples 8 to 10

The same test as described in Example 1 was conducted except that the organic solvent-type cleaning agent was replaced by (a) 80% by volume of a

commercially available naphthene-type solvent (boiling point range: 209-245°C) and 20% by volume of dipropylene glycol monobutyl ether, (b) 80% by volume of a commercially available isoparaffin-type solvent (boiling point range: 197-202°C) and 20% by volume of diethylene glycol monoethyl ether or (c) 80% by volume of commercially available aromatic-type solvent (boiling point range: 260-290°C) and 20% by volume of tripropylene glycol. The results were the same as those in Example 1 and no difference was observed between the case containing activated turpentine and that not containing it.

Example 11

The same test as described in Example 3 was conducted except that the benzotriazole and butyl glycidyl ether were used in amounts of 2% by mass and 0.04% by mass, respectively. The results were the same as those in Example 3 and no difference was observed between the case containing activated turpentine and that not containing it.

Example 12

The same test as described in Example 3 was conducted except that the turpentine was used in an amount of 0.2% by mass and 0.05% by mass of benzotriazole and 0.02% by mass of butyl glycidyl ether were added to the organic solvent-type cleaning agent. The results were the same as those in Example 3 and no difference was observed between the case containing activated turpentine and that not containing it.

Example 13-14

0.1% by mass of benzotriazole and 0.1% by mass of 2-ethylhexyl glycidyl ether were added to the organic solvent-type cleaning agent of Example 1 and a

simulation of the operation of conducting the distillation and recovery repeatedly was made (Example 13). Similarly, another simulation was conducted except that 0.2% by mass of benzotriazole and 0.04% by mass of butyl glycidyl ether were added to the organic solvent-type cleaning agent of Example 1 (Example 14). The test results are shown in Table 2. The fluid recovered after five repetitions of reclamation by distillation was examined for corrosiveness. No corrosion was observed.

Table 2

	N-containing organic additive	Epoxy compound	Corrosiveness of fluid after five repetitions of reclamation by distilation against copper	
			no addition of turpentine	addition of turpentine
Ex. 13	benzotriazole (addition of 0.1%)	2-ethylhexyl glycidyl ether (addition of 0.1%)	o	o
Ex. 14	benzotriazole (addition of 0.2%)	butyl glycidyl ether (addition of 0.04%)	o	o

(Evaluation of corrosiveness)
o: no corrosion

The cleaner compositions of the present invention exhibit excellent flux removing properties and do not corrode the object to be cleaned, so that the compositions can be used advantageously for

cleaning electronic components, electrical components, mechanical parts and so on.

* C L M S *

WHAT IS CLAIMED IS:

1. A lowly corrosive cleaner composition characterized by at least comprising an organic solvent-type cleaning agent, a nitrogen-containing organic rust preventive and an epoxy compound as additive.

2. A lowly corrosive cleaner composition according to claim 1, wherein the organic solvent-type cleaning agent is a composition mainly comprising a hydrocarbon which has 5 to 20 carbon atoms and an organic compound which has 5 to 20 carbon atoms and one or more polar groups.