



(11)

EP 4 772 601 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:

08.07.2026 Bulletin 2026/28

(21) Application number: **24859552.2**

(22) Date of filing: **20.08.2024**

(51) International Patent Classification (IPC):

C11D 1/75 ^(2006.01) **B08B 3/08** ^(2006.01)
C11D 1/68 ^(2006.01) **C11D 17/08** ^(2006.01)

(52) Cooperative Patent Classification (CPC):

B08B 3/08; C11D 1/75; C11D 3/2003; C11D 17/08

(86) International application number:

PCT/JP2024/029528

(87) International publication number:

WO 2025/047519 (06.03.2025 Gazette 2025/10)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA

Designated Validation States:

GE KH MA MD TN

(30) Priority: **31.08.2023 JP 2023140604**

(71) Applicant: **Nitto Denko Corporation**
Ibaraki-shi, Osaka 567-8680 (JP)

(72) Inventors:

- **IWAMOTO, Riki**
Ibaraki-shi, Osaka 567-8680 (JP)
- **SUZUKI, Toshihide**
Ibaraki-shi, Osaka 567-8680 (JP)

(74) Representative: **Müller-Boré & Partner**

Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)

(54) **RESIN-DEPOSIT REMOVER LIQUID AND METHOD FOR CLEANING POLYMERIZATION VESSEL**

(57) Provided is a remover that can favorably remove resin deposits derived from adhesive polymers without relying on organic solvents. Provided also is a method for cleaning a polymerization vessel with polymer scale deposits. A resin deposit remover is provided for remov-

ing resin deposits derived from adhesive polymers. The resin deposit remover comprises electrolyzed water and a surfactant having an amine structure or amide group in its molecule. The resin deposit remover has a pH of 12.5 or higher.

EP 4 772 601 A1

Description

[Technical Field]

[0001] The present invention relates to a resin deposit cleaning solution used to remove a resin deposit derived from an adhesive polymer and to a method for cleaning a polymerization vessel. This application claims priority to Japanese Patent Application No. 2023-140604 filed on August 31, 2023; and the entire content thereof is herein incorporated by reference.

[Background Art]

[0002] In general, pressure-sensitive adhesive (PSA) exists as a soft solid (a viscoelastic material) in a room temperature range and has a property to adhere easily to an adherend with some pressure applied. For the easy application to adherends, PSA is widely used in various fields as a PSA sheet with support, which has a PSA layer on a support substrate; or as a PSA sheet without support, which is free of a support substrate.

[0003] Polymerization vessels used for producing such PSA accumulate gels and resins (hereinafter collectively referred to as "resin deposits") inside, derived from the adhesive polymers. Thus, they need to be periodically cleaned and washed to remove the resin deposits from their inner walls. However, resin deposits firmly attached to the vessel walls cannot be easily removed by washing with typical organic solvents alone. This often requires manual scraping using sharp blades, which can be both tedious and dangerous. Manual cleaning can also be insufficient or time-consuming, and cleaning efficiency is not necessarily high. Therefore, various studies have been conducted on cleaning solutions for removing resin deposits from polymerization vessels. Examples of related art include Patent documents 1 and 2.

[Citation List]

[Patent Literature]

[0004]

[Patent Document 1] Japanese Patent Application Publication No. 2003-292994

[Patent Document 2] Japanese Patent Application Publication No. 2022-118434

[Summary of Invention]

[Technical Problem]

[0005] For instance, Patent Document 1 describes cleaning polymerization vessels with a mixed solution of water, an alcohol and an alkaline compound. Patent Document 2 teaches cleaning polymerization vessels with a cleaning agent comprising an aromatic alcohol, an inorganic alkaline compound and a solubilizing agent. However, because these conventional cleaning solutions all include organic solvents such as alcohols, there are limitations to reducing the flammability risk due to static electricity, the risk of adverse effects of volatile substances on worker health, and the burden on wastewater treatment facilities when disposing of the cleaning agent after use. Accordingly, it would be beneficial to develop a remover (cleaning solution) that can effectively remove resin deposits without relying on organic solvents.

[0006] If a resin deposit remover is made available to reduce the risk of adverse health effects on workers and the burden on wastewater treatment facilities, it could also be used for other purposes besides just cleaning polymerization vessels. For instance, possible advantageous uses include removal of adhesive residue left on adherends after peeling off PSA sheets as well as removal of PSA sheets firmly adhered to adherends.

[0007] The present invention has been made in view of these circumstances with an objective to provide a remover capable of favorably removing resin deposits derived from adhesive polymers without relying on organic solvents. Another objective is to provide a method for cleaning a polymerization vessel with insoluble polymer deposits (or "polymer scales" hereinafter).

[Solution to Problem]

[0008] This description provides a resin deposit remover used to remove resin deposits derived from adhesive polymers. The resin deposit remover comprises electrolyzed water and a surfactant with an amine structure or an amide group in its molecule, and has a pH of 12.5 or higher. The resin deposit remover can favorably remove resin deposits derived from adhesive polymers without relying on organic solvents which can pose problems such as the flammability risk due to static electricity, the risk of adverse effects on worker health, and the burden on wastewater treatment facilities.

[0009] In some embodiments, a surfactant selected among alkylamine oxides and polyoxyethylene alkylamides is used as the surfactant. The use of such a surfactant with electrolyzed water facilitates removal of resin deposits derived from adhesive polymers.

[0010] In some embodiments, the surfactant content is 0.05 % by weight (wt%) or greater and 5 wt% or less. When the surfactant is used in such an amount along with electrolyzed water, the effects of this invention can be favorably obtained.

[0011] This description also provides a method for removing resin deposits derived from adhesive polymers, the method using a resin deposit remover disclosed herein. According to the method, resin deposits derived from adhesive polymers can be easily removed while reducing the flammability risk due to static electricity, the risk of adverse effects on worker health, and the burden on wastewater treatment facilities when disposing of the remover after use.

[0012] This description also provides a method for cleaning a polymerization vessel with polymer scale deposits. The cleaning method comprises placing a resin deposit remover disclosed herein into the polymerization vessel with polymer scale deposits, and stirring the resin deposit remover in the polymerization vessel at 50 °C or above. According to the cleaning method, polymer scales can be easily removed from the polymerization vessel while reducing the flammability risk due to static electricity, the risk of adverse effects on worker health, and the burden on wastewater treatment facilities.

[Description of Embodiments]

[0013] Preferred embodiments of the present invention are described below. Matters necessary to practice this invention other than those specifically referred to in this description may be comprehended by a person of ordinary skill in the art based on the instruction regarding implementations of the invention according to this description and the common technical knowledge in the pertinent field. The present invention can be practiced based on the contents disclosed in this description and common technical knowledge in the subject field.

[0014] As used herein, "adhesive polymer" refers to a polymer that has adhesive properties, typically the base polymer in a PSA. "Base polymer" in a PSA here refers to the primary component of rubber-like polymers in the PSA. The rubber-like polymers are polymers that show rubber elasticity around room temperature. As used herein, "primary component" refers to a component that accounts for more than 50 wt% unless otherwise specified.

(pH)

[0015] The resin deposit remover disclosed herein is an alkaline solution (a basic solution) having a pH of 12.5 or higher. The higher the pH of the resin deposit remover is, the better it tends to remove resin deposits derived from adhesive polymers. The pH of the resin deposit remover can be 12.8 or higher, 13.0 or higher, 13.2 or higher, or 13.4 or higher. The maximum pH of the resin deposit remover is not particularly limited. It is typically 14 or lower.

[0016] The pH of various aqueous solutions in this description can be determined, for instance, using a pH meter (e.g., a glass electrode pH meter (Model F-23)) as follows: After three-point calibration is performed using standard buffer solutions (phthalate pH buffer solution at pH 4.01 (25 °C), neutral phosphate pH buffer solution at pH 6.86 (25 °C) and carbonate pH buffer solution at pH 10.01 (25 °C)), the glass electrode is placed in the aqueous solution of interest. When stabilized after at least two minutes, the value is measured.

(Electrolyzed Water)

[0017] The resin deposit remover disclosed herein includes electrolyzed water. As used herein, "electrolyzed water" refers to an aqueous solution obtained by electrolyzing water that has been chemically treated as needed. In water electrolysis, alkaline electrolyzed water (basic electrolyzed water) is produced at the negative electrode and acidic electrolyzed water is produced at the positive electrode in a water-containing electrolysis chamber. Thus, in general, electrolyzed water can be divided into two types, namely alkaline electrolyzed water and acidic electrolyzed water. The electrolyzed water in the art disclosed herein is preferably alkaline electrolyzed water. The electrolyzed water in the art disclosed herein can also be electrolyzed so-called strong alkaline electrolyzed water.

[0018] As described above, the resin deposit remover disclosed herein is an alkaline solution having a pH of 12.5 or higher. In view of obtaining such a basic resin deposit remover, the pH of the electrolyzed water included in the resin deposit remover disclosed herein is preferably 12.5 or higher. The electrolyzed water may have a pH of 12.8 or higher, 13.0 or higher, 13.2 or higher, or 13.4 or higher. The maximum pH of the electrolyzed water is not particularly limited. It is typically 14 or lower. The higher the pH of the electrolyzed water is, the better its cleaning properties are and the better it tends to remove resin deposits.

[0019] Despite of being an alkaline solution with a very high pH, electrolyzed water tends to be safer for the skin and have a smaller impact on the environment than the likes of aqueous sodium hydroxide solutions with similar pH values. Thus, electrolyzed water can be used to obtain a resin deposit remover that exhibits excellent resin deposit removability while reducing the risk of adverse effects on worker health and the burden on drainage equipment. The use of electrolyzed water

can also realize an aqueous remover, helping to obtain a resin deposit remover that does not rely on organic solvents such as alcohols.

[0020] In some embodiments, the inorganic alkaline compound content of the electrolyzed water is 1.0 wt% or lower, preferably 0.5 wt% or lower, or more preferably 0.3 wt% or lower. Here, in this description, the inorganic alkaline compound (an inorganic base) content of the electrolyzed water is the amount of inorganic alkaline (basic) ions (e.g., alkali metal ions) in the electrolyzed water, expressed in terms of its hydroxide. When the electrolyzed water includes two or more kinds of inorganic alkaline ions (e.g., potassium ions, sodium ions, etc.), the inorganic alkaline compound content refers to the total amount of the two or more kinds of inorganic alkaline ions, expressed in terms of their hydroxides.

[0021] The amount of electrolyzed water in the resin deposit remover is not particularly limited. In view of resin deposit removability, the amount of electrolyzed water is typically suitably 65 wt% or greater, preferably 70 wt% or greater, more preferably 75 wt% or greater, yet more preferably 80 wt% or greater, possibly 85 wt% or greater, 90 wt% or greater, 98 wt% or greater, 98.5 wt% or greater, or 99.0 wt% or greater. In view of including a suitable amount of the undermentioned surfactant A, the amount of electrolyzed water in the resin deposit remover can be 99.9 wt% or less, 99.8 wt% or less, 99.5 wt% or less, or 99.2 wt% or less.

(Surfactant)

[0022] The resin deposit remover disclosed herein includes a surfactant. The inclusion of surfactant tends to facilitate resin deposit removal. As the surfactant, it is preferable to use a surfactant having an amine structure or an amide group in its molecule (or "surfactant A" hereinafter). The use of surfactant A in combination with electrolyzed water helps facilitate removal of resin deposits derived from adhesive polymers.

[0023] Here, in this description, the "amine structure" refers to a structure obtained by substituting at least one (i.e., one to three) of the hydrogen atoms of ammonia with an atom or atomic group, or to a quaternary ammonium salt structure.

[0024] There are no particular limitations as to why the use of surfactant A facilitates removal of resin deposits, but it can be understood as follows: Having an amine structure or amide group in the molecule, surfactant A is highly compatible with resin deposits and tends to penetrate and swell the resin deposits. The swollen resin deposits easily peel off the adherend surface, and the presence of electrolyzed water with its high cleansing ability further facilitates removal of resin deposits.

[0025] Surfactant A is not particularly limited except that it has an amine structure or an amide group. Any of anionic, cationic, nonionic, and amphoteric surfactants can be used. Among them, nonionic, anionic and amphoteric surfactants are preferable. Nonionic and amphoteric surfactants are more preferable. Examples of surfactant A include polyoxyethylene alkylamines such as polyoxyethylene laurylamine, polyoxyethylene stearylamine and polyoxyethylene oleylamine; polyoxyethylene alkylamides such as polyoxyethylene fatty acid amides; and alkylamine oxides. In particular, alkylamine oxides and polyoxyethylene alkylamides are preferable. As surfactant A, solely one species or a combination of two or more species can be used.

[0026] The number of carbon atoms of the long chain alkyl group in the alkylamine oxides is not particularly limited. In some embodiments, in view of resin deposit removability, the number of carbon atoms of the long chain alkyl group in an alkylamine oxide is 8 or greater (e.g., 10 or greater), preferably 11 or greater, or more preferably 12 or greater. It can be 20 or less, 18 or less, 16 or less, or 14 or less. The long chain alkyl group may be substituted with a functional group. A favorable example is an alkylamine oxide that has a long chain alkyl group with 10 or more and 14 or fewer (preferably 12 or more and 14 or fewer) carbon atoms and also has one or two alkyl groups with 2 or fewer carbon atoms (e.g., one carbon atom). Examples of such alkylamine oxides include N,N-dimethylaurylamine oxide and N,N-dimethylmyristylamine oxide.

[0027] The number of carbon atoms of the long chain alkyl group in the polyoxyethylene alkylamide is not particularly limited. In some embodiments, in view of resin deposit removability, the number of carbon atoms of the long chain alkyl group in a polyoxyethylene alkylamide is 10 or greater (e.g., 12 or greater), preferably 14 or greater, more preferably 16 or greater, possibly 17 or greater, or 18 or greater. It can be 22 or less, 20 or less, or 19 or less. The long chain alkyl group may be substituted with a functional group. Favorable examples of polyoxyethylene alkylamides include polyoxyethylene oleamide.

[0028] The average number of moles of ethylene oxide added in the polyoxyethylene alkylamide is not particularly limited. For instance, it can be 3 or greater, 4 or greater, or 5 or greater. It can be 10 or less, 8 or less, or 6 or less.

[0029] The amount of surfactant A in the resin deposit remover (when two or more species of surfactant A are included, their total amount) is not particularly limited. In view of resin deposit removability, the amount of surfactant A is typically suitably 0.05 wt% or greater, preferably 0.1 wt% or greater, possibly 0.15 wt% or greater, 0.3 wt% or greater, 0.5 wt% or greater, or 0.8 wt% or greater. The amount of surfactant A is typically suitably 5 wt% or less, possibly 4.5 wt% or less, 4 wt% or less, 3 wt% or less, 2 wt% or less, 1 wt% or less, or 0.5 wt% or less.

[0030] The resin deposit remover disclosed herein may include other surfactants besides surfactant A as long as the effects of this invention are not significantly impaired. The amount of the other surfactants excluding surfactant A is not particularly limited. For instance, it can be 1 wt% or less, 0.1 wt% or less, 0.01 wt% or less, or 0.001 wt% or less. The resin deposit remover disclosed herein may be essentially free of other surfactants besides surfactant A. Here, being essentially

free of other surfactants besides surfactant A means that, for instance, the amount of other surfactants excluding surfactant A in the resin deposit remover is 1×10^{-4} wt% or less (preferably 1×10^{-5} wt% or less) and possibly 0 wt%.

[0031] The art disclosed herein uses electrolyzed water and a specific surfactant together, thereby enabling easy removal of resin deposits without relying on organic solvents (e.g., alcohols). Thus, in view of reducing the disadvantages of using organic solvents (e.g., alcohols), it is advantageous to limit the organic solvent content of the resin deposit remover disclosed herein. In some preferable embodiments, the organic solvent content of the resin deposit remover is less than 60 wt%, possibly 50 wt%, 35 wt% or less (e.g., 30 wt% or less), preferably less than 20 wt%, more preferably 10 wt% or less, yet more preferably 5 wt% or less, also possibly 1 wt% or less, 0.5 wt% or less, 0.1 wt% or less, or 0.05 wt% or less. The resin deposit remover disclosed herein may be essentially free of organic solvents (e.g., alcohols). Here, being essentially free of organic solvents (e.g., alcohols) means that the organic solvent content of the resin deposit remover is 0.01 wt% or less (preferably 0.001 wt% or less) and possibly 0 wt%. The resin deposit remover with a limited organic solvent content can reduce the flammability risk due to static electricity, the risk of adverse effects of volatile substances on worker health, the burden on wastewater treatment facilities when disposing of the cleaning agent after use, and so on.

[0032] In some embodiments, the inorganic alkaline compound (an inorganic base) content of the resin deposit remover disclosed herein is 1.0 wt% or less, preferably 0.5 wt% or less, or more preferably 0.3 wt% or less. Here, in this description, the inorganic alkaline compound content of the resin deposit remover refers to the amount of inorganic alkaline (basic) ions (e.g., alkali metal ions) in the resin deposit remover, expressed in terms of its hydroxide. When the resin deposit remover includes two or more species of inorganic alkaline ions (e.g., potassium ions, sodium ions, etc.), the inorganic alkaline compound content refers to the total amount of the two or more species of inorganic alkaline ions, expressed in terms of their hydroxides.

(Applications)

[0033] According to the resin deposit remover disclosed herein, resin deposits derived from adhesive polymers can be easily removed from the adherend. The resin deposit remover disclosed herein can remove resin deposits without relying on organic solvents such as alcohols. Thus, as compared with conventional organic solvent-containing removers, it can reduce the flammability risk due to static electricity, the risk of adverse effects on worker health, the burden on wastewater treatment facilities, and so on.

[0034] The adherend from which resin deposits are being removed is not particularly limited. For instance, the adherend may have a surface formed from a metal material such as anti-corrosive stainless steel; a glass material; or a resin material of various types such as polyester resin (PET, etc.), polyolefin resin (polyethylene (PE), polypropylene (PP), etc.), fluoropolymer, polystyrene, polyoxymethylene, and polyvinyl acetate. In particular, a preferable adherend has a surface formed from a material that is not easily swollen by the resin deposit remover. For instance, when using the resin deposit remover to remove polymer scales accumulated on polymerization vessels, the adherends may have surfaces formed from metal materials or glass materials. For instance, when using the resin deposit remover disclosed herein to remove adhesive residue left on adherends when removing PSA sheets (or PSA) from the adherends or to remove PSA sheets firmly adhered to adherends, the adherends may have surfaces formed from metal materials, glass materials, resin materials, etc.

[0035] The resin deposit remover disclosed herein is favorably used to remove polymer scales accumulated on a polymerization vessel (reaction vessel) from the polymerization vessel. The polymerization vessel is typically used for PSA production and made of metal or glass. The concept of polymerization vessel may include those called polymerization kettle, reaction kettle, polymerization tank, etc.

[0036] The resin deposit remover disclosed herein can be used to remove adhesive residue (PSA-derived residue) left on adherends when removing PSA sheets (or PSA) from the adherends. It can also be used to remove PSA sheets (or PSA) firmly adhered to adherends from the adherends.

(Resin Deposits)

[0037] In the art disclosed herein, the resin deposits derived from adhesive polymers are not particularly limited while being adhesive polymer-derived. Typical examples of adhesive polymer-derived resin deposits include insoluble polymer deposits (polymer scales) left stuck to the inner wall of a polymerization vessel used for PSA production. Other examples include PSA residue left on an adherend when the PSA is removed from the adherend as well as PSA stuck on adherends.

[0038] The type of adhesive polymer is not particularly limited. Examples of the adhesive polymer include acrylic polymers, rubber polymers, polyester polymers, urethane polymers, polyether polymers, silicone polymers, polyamide polymers, and fluoropolymers. The following description is given with acrylic polymers as examples of applicable adhesive polymers of the art disclosed herein, but this is not to limit the applications of this invention.

[0039] As the acrylic polymer, for example, a polymer of a monomeric starting material comprising an alkyl (meth)acrylate as a primary monomer and possibly comprising a secondary monomer copolymerizable with the primary

monomer is preferable. The primary monomer here refers to a component that accounts for higher than 50 wt% of the monomer composition in the monomeric starting material.

[0040] As the alkyl (meth)acrylate, for instance, a compound represented by the following formula (1) can preferably be used:



[0041] Herein, R^1 in the formula (1) is a hydrogen atom or a methyl group. R^2 is an acyclic alkyl group having 1 to 20 carbon atoms (hereinafter, such a numerical range of carbon atoms may be indicated as " C_{1-20} "). From the standpoint of the storage elastic modulus of the PSA, etc., an alkyl (meth)acrylate having a C_{1-12} (e.g. C_{2-10} , typically C_{4-8}) acyclic alkyl group for R^2 is preferable. For the alkyl (meth)acrylate having a C_{1-20} acyclic alkyl group for R^2 , solely one species or a combination of two or more species can be used. Preferable alkyl (meth)acrylates include n-butyl acrylate and 2-ethylhexyl acrylate.

[0042] The secondary monomer copolymerizable with the alkyl (meth)acrylate as the primary monomer may be useful in introducing crosslinking points into the acrylic polymer and increasing the cohesive strength of the acrylic polymer. As the secondary monomer, one, two or more species can be used among functional group-containing monomers such as carboxy group-containing monomers, hydroxy group-containing monomers, acid anhydride group-containing monomers, amide group-containing monomers, amino group-containing monomers, and monomers having nitrogen-containing rings. The secondary monomer may also be a vinyl ester-based monomer such as vinyl acetate, an aromatic vinyl compound such as styrene, a sulfonate group-containing monomer, a phosphate group-containing monomer, etc. For instance, from the standpoint of increasing the cohesive strength, an acrylic polymer in which a carboxy group-containing monomer or a hydroxy group-containing monomer is copolymerized as the secondary monomer is preferable. Preferable examples of the carboxy group-containing monomer include acrylic acid and methacrylic acid. Preferable examples of the hydroxy group-containing monomer include 2-hydroxyethyl acrylate and 4-hydroxybutyl acrylate.

[0043] The amount of the secondary monomer is suitably 0.5 wt% or more of all monomers in the acrylic polymer, or preferably 1 wt% or more. The amount of the secondary monomer is suitably 30 wt% or less of all the monomers, or preferably 10 wt% or less (e.g. 5 wt% or less). When a carboxy group-containing monomer is copolymerized in the acrylic polymer, from the standpoint of combining adhesive strength and cohesive strength, the carboxy group-containing monomer content is preferably about 0.1 wt% or greater (e.g. 0.2 wt% or greater, typically 0.5 wt% or greater); it is preferably about 10 wt% or less (e.g. 8 wt% or less, typically 5 wt% or less). When a hydroxy group-containing monomer is copolymerized in the acrylic polymer, from the standpoint of combining adhesive strength and cohesive strength, the hydroxy group-containing monomer content is preferably within a range of about 0.001 wt% or greater (e.g. 0.01 wt% or greater, typically 0.02 wt% or greater); it is preferably about 10 wt% or less (e.g. 5 wt% or less, typically 2 wt% or less). When a vinyl ester-based monomer such as vinyl acetate is copolymerized as the secondary monomer, the vinyl ester-based monomer content is preferably about 30 wt% or less (typically 10 wt% or less) of all the monomers used in the synthesis of the acrylic polymer; it can be, for instance, 0.01 wt% or greater (typically 0.1 wt% or greater).

[0044] As for the adhesive polymers (e.g., acrylic polymers) to which the art disclosed herein is applied, the synthetic method is not particularly limited. It can be applied to adhesive polymers obtained by various polymerization methods known as synthetic methods for acrylic polymers, such as solution polymerization, emulsion polymerization, bulk polymerization and suspension polymerization. It can be also applied to adhesive polymers obtained by active energy ray radiation polymerization which involves irradiation of UV, etc. Especially in solution polymerization and emulsion polymerization, insoluble polymer deposits (polymer scales) tend to adhere firmly to the inner walls of the polymerization vessel after polymerization. Thus, when applying the art disclosed herein to clean polymerization vessels, the resin deposit remover can be applied to resin deposits derived from adhesive polymers prepared by solution polymerization or emulsion polymerization.

(Method for Cleaning Polymerization Vessel)

[0045] The art disclosed herein provides a method for cleaning a polymerization vessel with polymer scales. Here, the polymer scales are insoluble polymer deposits left stuck to the inner wall of the polymerization vessel used for PSA production. The cleaning method comprises placing a resin deposit remover disclosed herein into a polymerization vessel that has accumulated polymer scales, and stirring the resin deposit remover in the polymerization vessel.

[0046] In particular, the resin deposit remover is put into a polymerization vessel with polymer scales, ensuring that the polymer scales are sufficiently immersed in the resin deposit remover. For this, in view of polymer scale removability, it is preferable to heat the resin deposit remover in the polymerization vessel to a temperature of 50°C or above, more preferably 60 °C or above, or yet more preferably 70 °C or above and 90 °C or below. Inside the polymerization vessel, the resin deposit remover is agitated by rotating propellers or other means to create a water current. The water current facilitates the removal of resin deposits. Here, the likes of resin beads may be added to further promote the removal of

polymer scale. The immersion time in the resin deposit remover is not particularly limited. In typical, it is suitably about 1 minute to 3 hours, or preferably 30 minutes to 1.5 hours. When immersed in the resin deposit remover in such a manner, polymer scales will swell and lift from the inner wall of the polymerization vessel.

[0047] The resin deposit remover and the lifted polymer scales are then washed away, using water, etc. As needed, the polymerization vessel may be washed, using a high-pressure cleaning machine. After removing polymer scales (descaling), as needed, the polymerization solution may be dried by air blow, etc.

[0048] According to the cleaning method, without relying on organic solvents, polymerization vessels with polymer scales can be easily cleaned. Thus, while reducing the flammability risk due to static electricity, the risk of adverse effects on worker health and the burden on wastewater treatment facilities, polymer scales can be easily removed to clean polymerization vessels.

[0049] As understood from the above description and the working examples below, the matters disclosed by this description include the following:

(1) A resin deposit remover used to remove resin deposits derived from adhesive polymers,

comprising electrolyzed water and a surfactant that has an amine structure or an amide group in its molecule, and having a pH of 12.5 or higher.

(2) The resin deposit remover according to (1) above, wherein the surfactant is selected among alkylamine oxides and polyoxyethylene alkylamides.

(3) The resin deposit remover according to (1) or (2) above, wherein the surfactant content is 0.05 wt% or greater and 5 wt% or less.

(4) The resin deposit remover according to any of (1) to (3) above, comprising less than 60 wt% organic solvent (e.g., alcohol).

(5) A method for removing resin deposits derived from adhesive polymers, using the resin deposit remover according to any of (1) to (4) above.

(6) A method for cleaning a polymerization vessel with polymer scale deposits, the cleaning method comprising:

placing the resin deposit remover according to any of (1) to (4) above into the polymerization vessel with polymer scale deposits, and stirring the resin deposit remover in the polymerization vessel while heating the remover to 50 °C or higher.

[Examples]

[0050] Several working examples related to the present invention are described below, but the present invention is not intended to be limited to these examples. In the description below, "parts" and "%" indicating amounts used or included are by weight unless otherwise specified.

[0051] The surfactants used in Examples are shown below.

Surfactant A1: alkylamine oxide (C14) (N,N-dimethylmyristylamine oxide)

Surfactant A2: alkylamine oxide (C12) (N,N-dimethylaurylamine oxide)

Surfactant A3: polyoxyethylene oleamide (5E. O.)

Surfactant B: sodium alkyl diphenyl ether disulfonate

Surfactant C: sodium dodecyl sulfate

Surfactant D: sodium polyoxyethylene alkyl ether sulfate

(Example 1)

[Preparation of resin deposit remover]

[0052] Were mixed electrolyzed water and surfactant A1 to prepare a solution of 0.15 % surfactant A1 and 99.85 % electrolyzed water as the resin deposit remover of this example. This resin deposit remover had a pH of 13.5.

[Production of acrylic polymer A in polymerization vessel]

[0053] To the inner wall of a polymerization vessel equipped with a thermometer, stirrer, nitrogen inlet and reflux condenser, was attached a rectangular stainless-steel plate measuring 120 mm long, 360 mm wide and 0.3 mm thick. In this polymerization vessel, was produced an aqueous polymer emulsion. In particular, to the polymerization vessel, were

added 0.10 part of a surfactant (product name LATEMULE E-118B available from Kao Corporation) and 61 parts of distilled water. While stirring, the vessel was purged with nitrogen at room temperature (25 °C) for one hour. Subsequently, to this, was added 0.10 part of a polymerization initiator (product name VA-057 available from FUJIFILM Wako Pure Chemical Corporation). The resulting mixture was heated to 60 °C. To this, at 60 °C, were added dropwise over 4 hours an emulsion (85 parts of 2-ethylhexyl acrylate (2EHA), 13 parts of methyl acrylate (MA), 1.25 parts of acrylic acid (AA), 0.75 part of methacrylic acid (MAA), 0.048 part of t-dodecanethiol (chain transfer agent), 0.02 part of 3-methacryloxypropyltrimethoxysilane (product name KBM-503 available from Shin-Etsu Chemical Co., Ltd.) and 1.8 parts of a surfactant (product name LATEMULE E-118B available from Kao Corporation) in 28 parts of distilled water) to carry out polymerization. The mixture was further allowed to cure at 60 °C for 3 hours. To this, were added 0.087 part of sodium hydrogen peroxide and 0.17 part of ascorbic acid. The mixture was allowed to cool to room temperature and adjusted to pH 6 using 10 % ammonia water as a pH-adjusting agent to prepare acrylic polymer A.

[Cleaning of polymerization vessel and inspection of state of polymer scale deposition]

[0054] The resulting acrylic polymer A was completely removed from the polymerization vessel, and the inner wall of the vessel was washed with a weak stream of water so as not to scrape off the polymer scale on the wall. Subsequently, the SUS plate attached to the inner wall of the vessel was collected and the initial polymer scale deposit area X (mm²) was measured. The SUS plate was reattached to the same position on the inner wall of the polymerization vessel, and the resin deposit remover of this example was poured into the vessel to full immersion of the entire SUS plate, and was allowed to stir at 80 °C for 1 hour to wash the vessel. The polymerization vessel was then cooled to room temperature. The resin deposit remover in the vessel was discarded and the empty vessel was lightly rinsed with water. The SUS plate was then removed from the polymerization vessel and the final polymer scale deposit area Y (mm²) after cleaning was measured. To measure the polymer scale deposit area, the SUS plate surface was photographed to obtain a surface image and the surface image was analyzed using image analysis software.

(Examples 2 to 4 and Comparative Examples 2 to 4)

[0055] The amount of electrolyzed water, the surfactant species and/or its amount were changed as shown in Table 1. Otherwise in the same manner as Example 1, was prepared the resin deposit remover of each example. Using the resulting resin deposit remover, but otherwise in the same manner as Example 1, acrylic polymer A was produced in a polymerization vessel; the polymerization vessel was cleaned; and the state of polymer scale deposition was inspected.

(Example 5)

[0056] The polymerization vessel was cleaned at 50 °C for one hour. Otherwise in the same manner as Example 4, a resin deposit remover was prepared; acrylic polymer A was produced in a polymerization vessel; the vessel was cleaned; and the state of polymer scale deposition was inspected.

(Comparative Example 1)

[0057] Using distilled water in place of electrolyzed water, but otherwise in the same manner as Example 1, was prepared a resin deposit remover of this example. The resulting resin deposit remover had a pH of 7.5. Using this resin deposit remover, but otherwise in the same manner as Example 1, acrylic polymer A was produced in a polymerization vessel; the vessel was cleaned; and the state of polymer scale deposition was inspected.

[0058] The features of Examples 1 to 5 and Comparative Examples 1 to 4 are summarized in Table 1. In Table 1, "-" indicates that the item was not used.

(Evaluation)

[0059] The polymer scale removability was evaluated based on the removal rate. The removal rate was determined according to the next formula: % Removal = $[(X-Y)/X] \times 100$; in the formula, X is the initial polymer scale deposit area (mm²), and Y is the final polymer scale deposit area (mm²) after cleaning. Based on the removal rate obtained, the removability was evaluated on the four-level grades shown below. The results are shown in Table 1.

- AA (excellent): removal rate of 98 % or higher
- A (good): removal rate of 90 % or higher and below 98 %
- B (acceptable): removal rate of 20 % or higher and below 90 %
- C (poor): removal rate below 20 %

[Table 1]

[0060]

Table 1

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
	Electrolyzed water (wt%)	99.85	99	99	96	96	-	95	95	95
	Distilled water (wt%)	-	-	-	-	-	99.85	-	-	-
	Surfactant (wt%)	A1	0.15	1	-	-	0.15	-	-	-
		A2	-	-	1	-	-	-	-	-
		A3	-	-	-	4	4	-	-	-
		B	-	-	-	-	-	5	-	-
		C	-	-	-	-	-	-	5	-
		D	-	-	-	-	-	-	-	5
	pH	13.5	13.5	13.5	13.5	13.5	7.5	13.5	13.5	13.5
	Temperature (°C)	80	80	80	80	50	80	80	80	80
	Removability	A	A	AA	AA	A	C	C	C	C

[0061] As evident in Table 1, the resin deposit removers of Examples 1 to 5 including electrolyzed water and a surfactant having an amine structure or amide group in its molecule showed superior removability to Comparative Example 1 using distilled water instead of electrolyzed water and Comparative Examples 2 to 4 using other surfactants instead of surfactants with an amine structure or amide group. A comparison of the results between Examples 4 and 5 shows that when immersing polymer scales in a resin deposit remover, greater removability is obtained when the temperature of the resin deposit remover is raised to 80 °C.

[0062] In addition, by the method shown below, acrylic polymer B was prepared instead of acrylic polymer A. Otherwise in the same manner as Examples 1 to 5 and Comparative Examples 1 to 4, polymer scale removal was carried out using the resin deposit removers. The results of polymer scale removal showed a similar tendency to the results obtained when acrylic polymer A was used.

[Preparation of acrylic polymer B]

[0063] To a reaction vessel equipped with a thermometer, stirrer, nitrogen inlet and reflux condenser, was added 40 parts of distilled water. While stirring, the vessel was purged with nitrogen at 60 °C for one hour. Subsequently, to this, was added 0.10 part of a polymerization initiator (product name VA-057 available from FUJIFILM Wako Pure Chemical Corporation). The resulting mixture was heated to 60 °C. To this, at 60 °C, were added dropwise over 4 hours an emulsion (68 parts of butyl acrylate (BA), 29 parts of 2-ethylhexyl acrylate (2EHA), 2.8 parts of acrylic acid (AA), 0.05 part of lauryl mercaptan (L-SH), 0.03 part of 3-methacryloxypropyltrimethoxysilane (product name KBM-503 available from Shin-Etsu Chemical Co., Ltd.) and 2.0 parts of a surfactant (product name LATEMULE E-118B available from Kao Corporation) in 25 parts of distilled water) to carry out polymerization. The mixture was further allowed to cure at 60 °C for 3 hours. To this, were added 0.075 part of sodium hydrogen peroxide and 0.15 part of ascorbic acid. The mixture was allowed to cool to room temperature and adjusted to pH 6 using 10 % ammonia water as a pH-adjusting agent to prepare acrylic polymer B.

[0064] Although specific embodiments of the present invention have been described in detail above, these are merely for illustrations and do not limit the scope of claims. The art according to the claims includes various modifications and changes made to the specific embodiments illustrated above.

Claims

1. A resin deposit remover used to remove resin deposits derived from adhesive polymers,

comprising electrolyzed water and a surfactant that has an amine structure or an amide group in its molecule, and having a pH of 12.5 or higher.

5 **2.** The resin deposit remover according to Claim 1, wherein the surfactant is selected among alkylamine oxides and polyoxyethylene alkylamides.

3. The resin deposit remover according to Claim 1 or 2, wherein the surfactant content is 0.05 % by weight or greater and 5 % by weight or less.

10 **4.** A method for removing resin deposits derived from adhesive polymers, using the resin deposit remover according to Claim 1 or 2.

5. A method for cleaning a polymerization vessel with polymer scale deposits, the cleaning method comprising:

15 placing the resin deposit remover according to Claim 1 or 2 into the polymerization vessel with polymer scale deposits, and
 stirring the resin deposit remover in the polymerization vessel at 50 °C or above.

20

25

30

35

40

45

50

55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/029528

A. CLASSIFICATION OF SUBJECT MATTER

C11D 1/75(2006.01)i; *B08B 3/08*(2006.01)i; *C11D 1/68*(2006.01)i; *C11D 17/08*(2006.01)i
 FI: C11D1/75; C11D1/68; C11D17/08; B08B3/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D; B08B; C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2024
 Registered utility model specifications of Japan 1996-2024
 Published registered utility model applications of Japan 1994-2024

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2012-067152 A (KAO CORPORATION) 05 April 2012 (2012-04-05) claims, paragraphs [0002], [0019]-[0022], [0053]-[0068]	1-5
Y	WO 2000/20549 A1 (MIZU KK) 13 April 2000 (2000-04-13) claims	1-5
Y	JP 2010-155435 A (ASAHI KASEI E-MATERIALS CORP.) 15 July 2010 (2010-07-15) claims	1-5
A	JP 2019-172844 A (KAO CORPORATION) 10 October 2019 (2019-10-10)	1-5
A	US 2006/0089281 A1 (GIBSON, G. L.) 27 April 2006 (2006-04-27)	1-5
A	US 6358914 B1 (GABRIEL, G. S.) 19 March 2002 (2002-03-19)	1-5

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“D” document cited by the applicant in the international application

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

30 October 2024

Date of mailing of the international search report

12 November 2024

Name and mailing address of the ISA/JP

**Japan Patent Office (ISA/JP)
 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915
 Japan**

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2024/029528

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2012-067152 A	05 April 2012	(Family: none)	
WO 2000/20549 A1	13 April 2000	US 6743351 B1 claims EP 983806 A1 KR 10-0663116 B1 CN 1289361 A	
JP 2010-155435 A	15 July 2010	(Family: none)	
JP 2019-172844 A	10 October 2019	US 2021/0115359 A1 WO 2019/188307 A1 EP 3778845 A1 CN 111788288 A	
US 2006/0089281 A1	27 April 2006	WO 2006/026784 A1	
US 6358914 B1	19 March 2002	(Family: none)	

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2023140604 A [0001]
- JP 2003292994 A [0004]
- JP 2022118434 A [0004]