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(54) Title: LOW-FOAMING COMPOSITION AND METHOD FOR DEGREASING METAL SURFACES

(57) Abstract

A liquid degreasing composition that can be satisfactorily substituted for vapor degreasing and can be sprayed onto the surfaces to be degreased without generating impractical volumes of foam contains water and: (A) alkalinizing agent; (B) alkali stable nonionic surfactant molecules that are not alkalinizing agents; and (C) hydrotropic agent molecules that are not either alkalinizing agents or nonionic surfactants. Preferably the alkalinizing agent is alkali metal silicate, and the composition also contains boric acid as a corrosion inhibitor.
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UZ Uzbekistan
VN Viet Nam
YU Yugoslavia
ZW Zimbabwe
BACKGROUND OF THE INVENTION

The invention relates to degreasing hard surfaces, particularly metal surfaces, more particularly aluminum and aluminum alloy metal surfaces. Preferred aqueous compositions and methods of the invention provide satisfactory degreasing of metal surfaces to replace vapor degreasing operations in many metal fabricating operations, including the aerospace industry, and the compositions are sufficiently low-foaming that they can be satisfactorily used by spraying, whereas prior art aqueous based compositions for replacement of vapor degreasing have generally been restricted to use by immersion because of their foaming tendency.

Many mechanical operations such as stamping, cutting, welding, grinding, drawing, machining, and polishing are used in the metal working industry to provide shaped metal articles. In metal working operations, lubricants, antibinding agents, machining coolants and the like are normally utilized to prevent binding and sticking of the tools to the metal articles in the various metal working operations. The lubricants, coolants, and antibinding agents and the additives present in these compositions usually leave an oily, greasy, and/or waxy residue on the surface of the metal which has been worked. The residue normally should be removed before the worked articles are given a protective surface finish or incorporated into a finished assembly.

Until a few years ago, it was practically necessary to clean oily, greasy, and/or waxy residues from metal articles by a vapor degreasing process. In a vapor degreasing process, the metal articles, at a temperature below the condensing temperature of a solvent for the oily, greasy and/or waxy residues, are suspended in vapors of refluxing solvent. The refluxing solvent condenses on the surface of the metal article, and the liquid solvent dissolves the oily, greasy, and/or waxy residues on the surface of the metal article. The condensing solvent with the high dissolving power for the contaminants to be removed from the surface of the metal article condenses on the surface of the article, dissolves the contaminants, and is returned to the source of the solvent vapor.

Solvents such as methyl ethyl ketone, methylene chloride, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, and the like are normally used in the vapor degreasing process. Since the oily, greasy, and/or waxy soils removed from the metal articles generally have a boiling point substantially higher than the boiling point of the refluxing solvent, the metal articles are contacted with a condensed solvent containing only relatively small quantities of the contaminants to be dissolved and removed from the metal
articles.

Vapor degreasing is technically effective but economically and environmentally disadvantageous. The solvents are expensive, can be environmental pollutants, and require costly methods for reclamation and disposal. Special apparatus and processes are required to reclaim used solvent for reuse and to prevent solvent vapors from escaping from the vapor degreasing process. The solvent vapors are often hazardous to human health and some of them are suspected of promoting degradation of the earth's ozone layer. In view of the drawbacks in the use of the vapor degreasing process, many attempts have been made to replace vapor degreasing with aqueous based cleaning compositions, and such compositions suitable for many uses have been taught in, e.g., U. S. Patent 5,634,979. However, to date the aqueous cleaning methods have not been entirely satisfactory for spray degreasing, which is more economical than immersion degreasing, because of foam build-up.

Accordingly, a major object of the invention is to provide a water-based liquid cleaner that, at least in its most preferred embodiments, is capable of degreasing normally worked metal articles effectively enough to meet the stringent standards established for aluminum and its alloys in the aerospace industry, when sprayed onto the surfaces to be degreased. Other alternative and/or concurrent objects are to provide a more economical process, a faster process and/or one requiring less expensive equipment for operation on a large scale, and to reduce hazards of fire and of damage to the environment from discharge of used cleaner.

Except in the claims and the operating examples, or where otherwise expressly indicated, all numerical quantities in this description indicating amounts of material or conditions of reaction and/or use are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the numerical limits stated is generally preferred, however. Also, throughout the description, unless expressly stated to the contrary: percent, "parts of", and ratio values are by weight or mass; the term "polymer" includes "oligomer", "copolymer", "terpolymer" and the like; the description of a group or class of materials as suitable or preferred for a given purpose in connection with the invention implies that mixtures of any two or more of the members of the group or class are equally suitable or preferred; description of constituents in chemical terms refers to the constituents at the time of addition to any combination specified in the description or of generation in situ within the composition by chemical reaction(s) noted in the specification between one or more newly added constituents and one or more constituents already present in the composition when the other constituents are added, and does not preclude unspecified chemical interactions among the constituents of a mixture.
once mixed; specification of constituents in ionic form additionally implies the presence of sufficient counterions to produce electrical neutrality for the composition as a whole and for any substance added to the composition; any counterions thus implicitly specified preferably are selected from among other constituents explicitly specified in ionic form, to the extent possible; otherwise such counterions may be freely selected, except for avoiding counterions that act adversely to an object of the invention; the word "mole" means "gram mole", and the word itself and all of its grammatical variations may be used for any chemical species defined by all of the types and numbers of atoms present in it, irrespective of whether the species is ionic, neutral, unstable, hypothetical, or in fact a stable neutral substance with well defined molecules; and the terms "solution", "soluble", "homogeneous", and the like are to be understood as including not only true equilibrium solutions or homogeneity but also dispersions that show no visually detectable tendency toward phase separation over a period of observation of at least 100, or preferably at least 1000, hours during which the material is mechanically undisturbed and the temperature of the material is maintained within the range of 18 - 25 °C.

The term "aluminum" when used hereinafter this specification, unless the context requires otherwise, is to be understood to include pure aluminum and all the alloys of aluminum that contain at least 45 % of aluminum by weight.

BRIEF SUMMARY OF THE INVENTION

The working and concentrate metal cleaning compositions of the invention comprise, preferably consist essentially of, or more preferably consist of, water and the following dissolved, stably dispersed, or both dissolved and stably dispersed components:

(A) a component of alkalinizing agent;
(B) a component of alkali stable nonionic surfactant molecules that are not alkalinizing agents; and
(C) a component of hydrotroping agent molecules that are not part of either of the previously recited components (A) and (B); and, optionally, one or more of the following components:
(D) a component of corrosion inhibitors that are not part of any of the previously recited components (A) through (C);
(E) a component of sequestering agents that are not part of any of the previously recited components (A) through (D);
(F) a component of coloring agent that is not part of any of the previously recited components (A) through (E); and
(G) a component of biocidal material that is not part of any of the previously recited components (A) through (F).
In this description, "stably dispersed" means that the component so described can be dispersed by mixing, within 1 hour of its introduction into the liquid phase in which the component in question is described as stably dispersed, to produce a liquid mixture which has only one bulk phase detectable with unaided normal human vision and does not spontaneously develop any separate bulk phase detectable with normal unaided human vision within 24 hours, or preferably, with increasing preference in the order given, within 7, 30, 60, 90, 120, 180, 240, 300, or 360 days, of storage without mechanical agitation at 25 °C after being initially mixed. (The word "bulk" in the preceding sentence means that, to be considered as a bulk phase, a phase must occupy at least one volume of space that is sufficiently large to be visible with unaided normal human vision and is separated from at least one other phase present in the dispersion by a boundary surface that can be observed with unaided normal human vision. Therefore, a change of the composition from clear to hazy or from hazy to clear does not indicate instability of a dispersion within this definition, unless a separate liquid or solid phase develops in the mixture in at least one volume large enough to see independently with unaided normal human vision.) Also in this description, "alkali stable" when referring to a surfactant means that the surfactant is capable of coexisting at its critical micelle concentration in an aqueous solution also containing at least, with increasing preference in the order given, 5, 10, 15, 20, 25, or 29 % of sodium hydroxide, without any chemical reaction (except possibly for reversible neutralization) between the surfactant and the sodium hydroxide and without the formation of any separate bulk phase detectable with normal unaided human vision within 24 hours, or preferably, with increasing preference in the order given, within 7, 30, 60, 90, 120, 180, 240, 300, or 360 days, of storage without mechanical agitation at 25 °C after being initially mixed.

Compositional embodiments of the invention include liquid compositions ready for use as such in cleaning (i.e., "working compositions") and concentrates suitable for preparing working compositions by dilution with water. Concentrates may be single package or multiple, usually dual, package in nature. A multiple package type of concentrate is preferred when not all of the ingredients desired in the working composition are sufficiently soluble or stably dispersible at the higher concentrations required for a one package concentrate composition, which is otherwise preferred. For example, at some concentrations, sometimes preferred polymeric organic sequestering agents and some preferred alkalinizing components can not be jointly solubilized. The two components are then placed in separate packages with other portions of the formulation so that stable solutions or dispersions can be formed after mixing and dilution. A two package concentrate system has some advantages in that the two components can be mixed in different
proportions to provide more effective cleaning for particular soils, soil combinations, and/or types of substrate to be cleaned. Ordinarily, however, at least for users for whom cleaning requirements do not vary greatly, single package concentrates are preferred because they are more convenient.

Process embodiments of the invention include at a minimum using a working composition according to the invention to remove soils from a metal substrate, and they may include other process steps, particularly those which are conventional in themselves preceding or following vapor degreasing in the prior art.

Compositions of the present invention are particularly useful for cleaning aluminum substrates, but are also useful for cleaning articles fabricated from metals such as steel, stainless steel, magnesium, titanium, tantalum, and other metals which are machined or worked during their fabrication into useful articles and for cleaning other hard surfaces such as ceramics and plastics.

The composition and the method of the present invention, at least in their most preferred embodiments, can provide removal of oily, greasy, and/or waxy residue from metal substrates to meet Boeing Aircraft Corporation ("BAC") 5763 PSD-6-14 criteria. Boeing Aircraft Corporation criteria requires the removal of all light oil (3-IN-1™ Oil), lipstick, axle grease, COSMOLENE™, black SHARPIE™ marker, red MAGIC MARKER™, BAYCO™ 363, CINFLO™, STAYPUT™ 350, CYTAL™ 81, MEROPA™ 460 and HD32 WAY OIL™ from the metal surface. The most preferred embodiments of the present invention can remove the above soils, meet the requirement for maximum etching weight loss on seven different substrates, meet the requirement of the sandwich corrosion versus DURCLEAN™ 281 test, meet requirements for avoiding inter-granular attack, corrosion resistance, paint adhesion, avoiding hydrogen embrittlement (steel), stress corrosion cracking, hydrogen content, and operating bath temperature. However, compositions of the present invention can be particularly useful even when requirements for cleaning are not as stringent as those in the Boeing BAC 5763 criteria.

A composition of the present invention does not generally require the presence of an additional foam suppressing agent, but use of such a material is within the broad scope of the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

For various reasons, almost always including at least the cost saving in avoiding an unnecessary component, it is preferred that compositions according to this invention should contain minimal amounts at most of certain ingredients, including some used in prior art cleaning and degreasing compositions. More particularly, independently for each substance named below, except to the extent that one of the following categories may
include a necessary or optional ingredient as described above, a composition according to this invention preferably contains not more than, with increasing preference in the order given, 5, 2.5, 1.25, 0.75, 0.50, 0.25, 0.12, 0.08, 0.04, 0.02, 0.005, 0.002, or 0.0005 parts of any of the following components per thousand parts of the total composition (a concentration unit that may be used hereinafter for any constituent of any composition and is hereinafter usually abbreviated as "ppt"): any divalent or higher valent metal cations; molecules that include a moiety corresponding to the general chemical formula:

\[
\begin{array}{c}
  R - N - C - \overset{\text{O}}{\text{C}} - \\
  \end{array}
\]

where \( R \) represents a monovalent aliphatic moiety with the chemical formula \(-C_{2n+1}H_{2(2n+1)}\), wherein \( n \) is an integer from 6 to 22, and \( y \) is an integer from 0 to \((2n+1)\); any organic material that is a liquid at 25 °C and has a boiling point at standard atmospheric pressure that is less than 100 °C; amine oxides; and block copolymers of ethylene and propylene oxides that do not include any hydrophobic group other than one or more poly(propylene oxide) blocks.

In a working composition according to the invention, the pH preferably is, with increasing preference in the order given, not less than 9.5, 10.0, 10.2, 10.4, 10.6, 10.8, 11.0, 11.2, 11.4, or 11.6 and independently preferably is, with increasing preference in the order given, not more than 13.0, 12.8, 12.6, 12.4, 12.2, 12.0, or 11.8.

Component (A) of alkalinizing agent preferably is selected from various inorganic salts and hydroxides known to be useful as "inorganic builders" in cleaning formulations generally. Inorganic builders, except for hydroxides, are generally salts of polyfunctional inorganic acids, such as alkali metal silicates, alkali metal borates, alkali metal carbonates, alkali metal sulfates, alkali metal polyphosphates, alkali metal phosphates, alkali metal orthophosphates, and alkali metal pyrophosphates. Salts such as sodium silicate, sodium metasilicate, sodium orthosilicate, sodium tetraborate, sodium borate, sodium sulfate, sodium carbonate, trisodium phosphate, disodium orthophosphate, sodium metaphosphate, sodium pyrophosphate, and the equivalent potassium salts and sodium and potassium hydroxides and the like are all suitable alkalinizing agents for compositions according to the present invention. Lithium, rubidium, and cesium salts and hydroxides are also suitable, although usually less preferred because of their higher cost, and ammonium salts are technically suitable but are generally avoided because of the chance of loss by volatilization and the accompanying odor nuisance of ammonia fumes. Silicates are especially preferred, and may advantageously constitute the entire alkalinizing component. Sodium metasilicate in particular is most preferred.

At least when silicates are the only alkalinizing agent, the concentration of silicon
atoms from silicates in a concentrate composition according to the invention preferably is at least, with increasing preference in the order given, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.32, 0.34, 0.36, or 0.37 moles of silicon atoms per kilogram of total composition (a concentration unit that may be applied hereinafter to any other constituent in addition to silicon atoms and will usually be abbreviated "M/kg") and independently preferably is not more than, with increasing preference in the order given, 1.0, 0.9, 0.8, 0.7, 0.6, 0.55, 0.50, 0.47, 0.44, 0.42, 0.40, or 0.38 M/kg.

The nonionic surfactants required for component (B) preferably are selected from the group consisting of: ethoxylated or ethoxylated and propoxylated (non-phenolic) alcohols; ethoxylated and propoxylated carboxylic acids; and ethoxylated or ethoxylated and propoxylated alkyl phenols; all of which can be modified by substituting for the terminal hydrogen atom in the terminal ethoxy or propoxy group a capping moiety that is an alkyl moiety with from 1 to 4 carbon atoms or is a single halo atom, most preferably chloro or fluoro. More preferably, each molecule of component (B) contains at least one, most preferably exactly one, alkyl or alkyl aryl moiety that has at least, with increasing preference in the order given, 5, 6, 7, 8, or 9 carbon atoms and independently preferably has not more than, with increasing preference in the order given, 22, 20, 18, 16, 14, 13, or 12 carbon atoms.

The concentration of component (B) in a concentrate composition according to the invention preferably is at least, with increasing preference in the order given, 5, 10, 20, 30, 35, 40, 45, 50, 55, or 59 ppt and independently preferably is not more than, with increasing preference in the order given, 300, 200, 150, 130, 110, 100, 90, 85, 80, 75, 70, 65, or 61 ppt.

Most preferably, component (B) includes two distinct subcomponents. Subcomponent (B.1) consists of molecules, of one of the three types generally preferred for component (B) as described above, that include some propoxy groups along with ethoxy groups and that most preferably are ethoxylated and propoxylated (non-phenolic) alcohols, while subcomponent (B.2) consists of molecules, of one of the three types generally preferred for component (B) as described above, that do not include any propoxy groups. More preferably, in subcomponent (B.1), all of the alkyl moieties are straight chain ones, while, independently, in subcomponent (B.2), the alkyl groups include branching and most preferably include at least one tertiary carbon atom. Additionally and independently, subcomponent (B.2) is preferably selected from ethoxylated alcohols only. Independently of other preferences, subcomponent (B.2) when used preferably is selected from surfactants with a hydrophilic-lipophilic balance (hereinafter usually abbreviated as "HLB") value that is not less than, with increasing preference in the order given, 4.5, 5.0,
5.5, 6.0, 6.4, 6.8, 7.2, 7.6, 7.8, or 8.0 and independently preferably is not more than, with increasing preference in the order given, 13, 11.0, 10.4, 10.0, 9.6, 9.2, 8.8, 8.4, or 8.2.

When both subcomponents (B.1) and (B.2) are present in a composition according to the invention, the ratio of the amounts of (B.1) to (B.2) present in the composition preferably is at least, with increasing preference in the order given, 0.020:1.0, 0.04:1.0, 0.06:1.0, 0.08:1.0, 0.10:1.0, 0.12:1.0, 0.14:1.0, 0.16:1.0, 0.18:1.0, 0.190:1.0, or 0.198:1.0 and independently preferably is not more than, with increasing preference in the order given, 1.0:1.0, 0.80:1.0, 0.70:1.0, 0.60:1.0, 0.50:1.0, 0.45:1.0, 0.40:1.0, 0.35:1.0, 0.30:1.0, 0.25:1.0, or 0.21:1.0.

In the absence of any other constituents, preferred amounts and types of components (A) and (B) of a composition according to this invention as described above are not soluble in water at the same time, although either of them is readily soluble in the absence of the other. A single phase solution of both components (A) and (B) is made possible by the presence of hydrotropeing component (C), which preferably is selected from molecules that are capable of ionizing in aqueous solution to produce a dissolved electrically charged organic moiety. The most widely used hydrotropeing agents are probably alkali metal salts of benzene- and alkyl substituted benzene-sulfonic acids, but these are not preferred for compositions according to this invention. Instead, component (C) is preferably selected from the group consisting of amine salts of fatty acids, amphoteric surfactants¹, and partial esters of phosphoric acids and their salts. All of these types of hydrotropeing agents have surfactant properties of their own and therefore contribute to the cleaning effectiveness of a composition according to this invention.

The amount of hydrotropeing agent in a composition according to this invention preferably has a ratio to the amount of component (B) in the same composition that is at least, with increasing preference in the order given, 0.04:1.0, 0.06:1.0, 0.08:1.0, 0.10:1.0, 0.12:1.0, 0.14:1.0, 0.16:1.0, 0.18:1.0, 0.20:1.0, 0.22:1.0, 0.24:1.0, or 0.26:1.0 and independently preferably is not more than, with increasing preference in the order given, 1.5:1.0, 1.3:1.0, 1.1:1.0, 0.90:1.0, 0.80:1.0, 0.70:1.0, 0.60:1.0, 0.55:1.0, 0.50:1.0, 0.47:1.0, 0.45:1.0, or 0.43:1.0. Higher ratios within this range minimize foaming tendencies, but lower ratios promote more effective cleaning.

¹Alkali Surfactant JEN 2700™, commercially available from Tomah Chemical Products, Milton, Wisconsin and reported by its supplier to be an amphoteric surfactant that is a substituted β-alanine amine derivative with Chemical Abstracts Services Registry # 64972-19-6, and Surmax™ CS-504, -515, -521, -522, -555, -586, -634, -684, -727, -772, and -786, all commercially available from Chemax, Inc., Greenville, South Carolina and reported by their supplier to be amphoteric-anionic alkali stable surfactants, with other compositional information being proprietary, are examples of suitable amphoteric surfactants.
Among the optional components, at least component (D) of corrosion inhibitor is normally preferably present; without it, there is a fair likelihood of at least forming discol-oring stains on the surface being degreased and some danger of even more objection-able corrosion. Essentially any material with a corrosion inhibiting effect on aluminum may be utilized in optional component (D) according to the invention as described above. The organic corrosion inhibitors most useful in the practice of the present invention are generally nitrogen or oxygen containing organic compounds, such as amines, nitro compounds, imidazoles, diazoles, triazoles, carboxylic acids, and the like. Particularly preferred organic inhibitors are (i) aromatic triazoles and their salts and (ii) complex carboxylic acids and their salts, preferably in a ratio of type (i) to type (ii) that is, with increasing preference in the order given, from 1:1 - 20:1, 3:1 - 10:1, or 4.5:1.0 - 5.5:1.0. However, at least in part for reasons of economy, boric acid is the most preferred material for corrosion inhibition in a composition according to the invention and may effectively serve as the entire component (D), particularly when present in a concentrate composition according to the invention in a concentration that is at least, with increasing preference in the order given, 0.4, 0.8, 1.2, 1.5, 1.8, 2.1, 2.4, 2.7, or 3.0 ppt. The presence of considerably more boric acid is not harmful but is economically unjustified because of lack of substantial further improvement in corrosion inhibiting effect. Thus, primarily for reasons of economy, the concentration of boric acid in a concentrate composition according to this invention preferably is not more than, with increasing preference in the order given, 20, 15, 10, 8.0, 7.0, 6.0, 5.5, 5.0, 4.5, 4.0, or 3.5 ppt.

Optional component (E) is not needed or preferable in most compositions according to the invention, but may be useful in certain cases, particularly if the water that forms the bulk of a composition according to the invention is extraordinarily hard. Any material recognized in the art as a sequestering agent for aluminum, calcium, and/or magnesium cations in aqueous solution may be used. A particularly preferred type of sequestering agent that may be denoted "(E.1)" below is a polycarboxylate copolymer of the type generally available commercially and often known as an "organic builder". Materials such as Polymer QR1362-PMN and ACUSOL™ 102, both from Rohm and Haas, have been found to be useful in the practice of the present invention. Other preferred sequestering agents that may be denoted (E.2) below include all sufficiently water-soluble organic acids, and salts of acids, that contain at least two -OH moieties (which may or may not be part of carboxyl moieties) positioned within the acid molecule in such a way as to be capable of forming a five-membered or larger ring structure in a coordination compound with a metal ion. Common examples of such acids include nitrilotriacetic acid ("NTA"), ethylene diamine tetraacetic acid ("EDTA"), and, particularly preferred, citric
acid. In a working composition according to this invention, the concentration of polycarboxylate copolymer, if needed, preferably is, with increasing preference in the order given, at least 0.1, 0.2, 0.4, 0.8, 1.5, 2.0, 2.5, 2.8, 3.1, 3.4, 3.6, 3.7, 3.8, 3.9, 4.0, or 4.1 grams of polycarbonate polymer per liter of total working composition (a concentration unit that may be used hereinafter for any other constituent of any total composition and is hereinafter usually abbreviated as "g/L") and independently preferably is, with increasing preference in the order given, not more than 100, 50, 38, 28, 24, 20, 16, 14, 13, 12, or 11 g/L. Independently, the total concentration of all sequestering agents, if needed, preferably is, with increasing preference in the order given, not more than 100, 50, 38, 28, 24, 20, 16, 14, 13, or 12 g/L.

Colorants serve no technical purpose that is known in a composition according to the invention, but may be desirable for marketing reasons. Biocides are not generally needed, but the necessary components of the invention are believed to be capable of nourishing at least some micro-organisms, and if growth of micro-organisms on a composition according to the invention causes problems, known biocides may be added to eliminate the problems if desired.

In a working degreasing composition according to the invention, the concentrations of each constituent except water preferably are 5.0 % of the values stated above for the same constituent in a concentrate according to the invention.

Metal articles to be degreased should be contacted with the aqueous degreasing composition of the present invention at a sufficient temperature for a sufficient time to be effective for degreasing. For removing average type soils, the temperature during contact preferably is, with increasing preference in the order given, not less than 30, 34, 37, 40, 43, 46, or 48 °C and independently, primarily for reasons of economy, preferably is, with increasing preference in the order given, not more than 90, 85, 80, 75, 70, 65, or 60 °C. Higher temperatures generally provide a more rapid degreasing and can be necessary when the soil comprises high melting point waxy type materials. Under normal conditions, the time of contact between the metal to be degreased and a working composition according to this invention preferably is, with increasing preference in the order given, not less than 0.5, 1.0, 1.5, 2.0, 2.5, or 3.0 minutes and independently, primarily for reasons of economy, preferably is, with increasing preference in the order given, not more than 10.0, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, or 3.5 minutes.

The compositions and processes of the present invention are particularly useful to replace vapor degreasing of aluminum articles for use in the aerospace industry. However, the compositions and processes of the present invention are not limited to degreasing of aluminum articles but can be applied to steel, stainless steel, magnesium
and magnesium alloys, titanium, tantalum, and the numerous alloys which are utilized in rail cars, aircraft, missiles, space vehicles and the like. The compositions of the present invention can be utilized to degrease and clean extruded aluminum and magnesium articles, forged steel, stainless steel, machined articles such as engine blocks, auto transmission parts, rocket fuel tanks, aircraft panels, and other metal articles which have been machined and require degreasing before they can be assembled or a protective coating applied.

As is well understood in the art, after a vapor degreasing operation or contact with a composition of the present invention to degrease the article, the article can be processed in other usual steps such as alkaline or acid cleaning, deoxidizing, conversion coating, a conversion-coating-improving wash coat or "sealer", such as a chromium wash step, and, if required, the article can be coated with an organic or inorganic protective coating. All of the additional steps are well known in the art and may be required by a particular utility for the article which has been degreased. However, some metals will not require additional protective treatment and can be utilized after rinsing and, if required, an additional treatment with a caustic or acid cleaner to remove any residue which remains from degreasing according to this invention.

The following examples, at least some of which are according to the invention, illustrate the compositions and methods of the present invention. The examples are for illustrative purposes only and are not intended to limit the invention.

Concentrate Composition Examples 1 - 9

The ingredients and amounts of each ingredient used in these concentrate compositions are shown in Table 1.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Grams of Ingredient per Kilogram of Concentrate Number:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Sodium metasilicate pentahydrate</td>
<td>80</td>
</tr>
<tr>
<td>ANTAROX™ BL-240 surfactant</td>
<td>50</td>
</tr>
<tr>
<td>TEGITOL™ TMN-3 surfactant</td>
<td>10</td>
</tr>
<tr>
<td>AQUALOX™ 242HT surfactant</td>
<td>34</td>
</tr>
<tr>
<td>Alkali Surfactant JEN 2700™</td>
<td>0</td>
</tr>
</tbody>
</table>
The known chemical characteristics of the ingredients not identified in Table 1 itself or elsewhere herein were as follows:

ANTAROX™ BL-240 surfactant was commercially supplied by Rhône-Poulenc and was reported by its supplier to be ethoxylated and propoxylated linear alcohol with a cloud point of 40 °C.

TERGITOL™ TMN-3 surfactant was commercially supplied by Union Carbide Corp. and is reported by its supplier to be ethoxylated trimethyl nonanol with an HLB value of 8.2.

AQUALOX™ 242HT surfactant was supplied commercially by Alox Corp. (Niagara Falls, New York) and is reported by its supplier to be amine salts of acids produced by oxygenating hydrocarbon molecules.

MONAFAX™ 1293 and MONAFAX™ 831 surfactants were supplied commercially by Mona Industries and are reported by their supplier to be partial esters of phosphoric acid.

TRITON™ H-66 surfactant was supplied commercially by Union Carbide Corp. and was reported by its supplier to be an organic phosphate ester salt.

HYDROMAX™ 200 surfactant was supplied commercially by Chemax Corp. and was reported by its supplier to be an organic phosphate ester surfactant.

**Working Composition and Use Examples**

Aqueous working compositions containing 50 grams of each concentrate shown in Table 1 per liter of working composition are prepared and tested at 49 and 60 °C for cleaning aluminum panels soiled with standardized amounts of ink, lipstick, COSMO-LENE™ petroleum jelly, and/or axle grease by spraying for 1, 2, or 3 minutes on each panel. The panels are then removed from contact with the working degreasing composition according to the invention, rinsed with tap water, and examined. Highly effective removal of the soil is achieved. No etching of the aluminum panels is observed by visual inspection or by the etch rate test according to Boeing Standard Specification 7348.
The invention claimed is:

1. A liquid composition of matter, suitable directly, after dilution with water, or both directly and after dilution with water, for removing oily, waxy, and greasy type soils from soiled metal surfaces, said liquid composition of matter comprising water and the following components:
   (A) a component of alkanizing agent;
   (B) a component of alkali stable nonionic surfactant molecules that are not alkanizing agents; and
   (C) a component of hydrotroping agent molecules that are not part of either of the previously recited components (A) and (B).

2. A liquid composition according to claim 1, wherein:
   - component (A) consists of alkali metal silicates and is present in the composition in a concentration for which the stoichiometric equivalent as silicon atoms constitutes from about 0.10 to about 1.0 M/kg of silicon atoms;
   - component (B) is selected from the group consisting of: ethoxylated or ethoxyated and propoxylated non-phenolic alcohols; ethoxylated and propoxylated carboxylic acids; and ethoxylated or ethoxyated and propoxylated alkyl phenols, all of which optionally have, on their terminal ethoxy or propoxy group, a capping moiety that has from 1 to 4 carbon atoms or is a single halo atom;
   - the concentration of component (B) in the liquid composition is from about 20 to about 200 ppt;
   - there is also present in the liquid composition a component (C) of hydrotroping agent that is not part of either of components (A) and (B) and is selected from molecules that ionize in aqueous solution to produce a dissolved electrically charged organic moiety; and
   - component (C) is present in the liquid composition in an amount that has a ratio to the amount of component (B) in the same liquid composition that is from about 0.10:1.0 to about 0.90:1.0.

3. A liquid composition according to claim 2, wherein:
   - component (A) is present in the composition in a concentration for which the stoichiometric equivalent as silicon atoms constitutes from about 0.20 to about 0.7 M/kg of silicon atoms;
   - component (B) comprises two distinct subcomponents (B.1) and (B.2), wherein:
     -- (B.1) is selected from the group consisting of both ethoxylated and propoxylated non-phenolic alcohols;
-- (B.2) is selected from the group consisting of ethoxylated and not propoxylated alcohols; and
-- the ratio of the amount of subcomponent (B.1) to the amount of subcomponent (B.2) is from about 0.08:1.0 to about 0.60:1.0;

- the concentration of component (B) in the liquid composition is from about 30 to about 100 ppt;
- component (C) is selected from the group consisting of amine salts of fatty acids, amphoteric surfactants, and partial esters of phosphoric acids and their salts; and
- component (C) is present in the liquid composition in an amount that has a ratio to the amount of component (B) in the same liquid composition that is from about 0.16:1.0 to about 0.70:1.0.

4. A liquid composition according to claim 3, wherein:
- component (A) is present in the composition in a concentration for which the stoichiometric equivalent as silicon atoms constitutes from about 0.32 to about 0.44 M/kg of silicon atoms;
- (B.1) is selected from the group consisting of both ethoxylated and propoxylated non-phenolic alcohols in which all alkyl moieties are straight chain moieties;
- (B.2) is selected from the group consisting of ethoxylated and not propoxylated alcohols, each molecule of which includes at least one tertiary carbon atom;
- the ratio of the amount of subcomponent (B.1) to the amount of subcomponent (B.2) is from about 0.16:1.0 to about 0.30:1.0;
- the concentration of component (B) in the liquid composition is from about 45 to about 80 ppt;
- component (C) is present in the liquid composition in an amount that has a ratio to the amount of component (B) in the same liquid composition that is from about 0.22:1.0 to about 0.45:1.0; and
- there is also present in the liquid composition a component (D) of corrosion inhibitor that is not part of any of components (A) through (C).

5. A liquid composition according to claim 4, wherein:
- component (A) is sodium metasilicate; and
- the composition contains at least about 2.4 ppt of boric acid.

6. A process for removing oily, waxy, and greasy type soils from a metal surface, said process comprising a step of spraying onto said surface a liquid composition according to claim 1 that has a pH value from about 9.5 to about 13.0 and allowing the sprayed on composition to drain therefrom.
7. A process according to claim 6, wherein, in said liquid composition:
   - component (A) consists of alkali metal silicates and is present in the composition in a concentration for which the stoichiometric equivalent as silicon atoms constitutes from about 0.005 to about 0.05 M/kg of silicon atoms;
   - component (B) is selected from the group consisting of: ethoxylated or ethoxylated and propoxylated non-phenolic alcohols; ethoxylated and propoxylated carboxylic acids; and ethoxylated or ethoxylated and propoxylated alkyl phenols, all of which optionally have, on their terminal ethoxy or propoxy group, a capping moiety that is an alkyl moiety with from 1 to 4 carbon atoms or is a single halo atom;
   - the concentration of component (B) in the liquid composition is from about 1.0 to about 10.0 ppt;
   - there is also present in the liquid composition a component (C) of hydrotroping agent that is not part of either of components (A) and (B) and is selected from molecules that ionize in aqueous solution to produce a dissolved electrically charged organic moiety;
   - component (C) is present in the liquid composition in an amount that has a ratio to the amount of component (B) in the same liquid composition that is from about 0.10:1.0 to about 0.90:1.0;
   - the pH value is from about 10.2 to about 12.8; and
   - the temperature during the time of contact with the surface from which the soil is being removed is from about 30 to about 90 °C.

8. A process according to claim 7, wherein, in said liquid composition:
   - component (A) is present in the composition in a concentration for which the stoichiometric equivalent as silicon atoms constitutes from about 0.010 to about 0.035 M/kg of silicon atoms;
   - component (B) comprises two distinct subcomponents (B.1) and (B.2), wherein:
     -- (B.1) is selected from the group consisting of both ethoxylated and propoxylated non-phenolic alcohols;
     -- (B.2) is selected from the group consisting of ethoxylated and not propoxylated alcohols; and
     -- the ratio of the amount of subcomponent (B.1) to the amount of subcomponent (B.2) is from about 0.08:1.0 to about 0.60:1.0;
   - the concentration of component (B) in the liquid composition is from about 1.5 to about 5.0 ppt;
   - component (C) is selected from the group consisting of amine salts of fatty acids,
amphoteric surfactants, and partial esters of phosphoric acids and their salts;
- component (C) is present in the liquid composition in an amount that has a ratio to
  the amount of component (B) in the same liquid composition that is from about
  0.16:1.0 to about 0.70:1.0;
- the pH value is from about 10.6 to about 12.4; and
- the temperature during the time of contact with the surface from which the soil is
  being removed is from about 37 to about 80 °C.

9. A process according to claim 8, wherein, in said liquid composition:
- component (A) is present in the composition in a concentration for which the
  stoichiometric equivalent as silicon atoms constitutes from about 0.016 to about
  0.022 M/kg of silicon atoms;
- (B.1) is selected from the group consisting of both ethoxylated and propoxylated
  non-phenolic alcohols in which all alkyl moieties are straight chain moieties;
- (B.2) is selected from the group consisting of ethoxylated and not propoxylated
  alcohols, each molecule of which includes at least one tertiary carbon atom;
- the ratio of the amount of subcomponent (B.1) to the amount of subcomponent
  (B.2) is from about 0.16:1.0 to about 0.30:1.0;
- the concentration of component (B) in the liquid composition is from about 2.2 to
  about 4.0 ppt;
- component (C) is present in the liquid composition in an amount that has a ratio to
  the amount of component (B) in the same liquid composition that is from about
  0.22:1.0 to about 0.45:1.0;
- there is also present in the liquid composition a component (D) of corrosion inhibitor
  that is not part of any of components (A) through (C);
- the pH value is from about 11.0 to about 12.0; and
- the temperature during the time of contact with the surface from which the soil is
  being removed is from about 48 to about 60 °C.

10. A process according to claim 9, wherein, in said liquid composition:
- component (A) is sodium metasilicate; and
- there is at least about 0.12 ppt of boric acid.

11. A process according to any one of claims 6 through 10, wherein the metal surface
  from which soil is removed during the process is an aluminum surface.
### Classification of Subject Matter

- IPC: C11D 1/72, 1/722, 1/94, 3/08; B01B 3/04

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

### Fields Searched

Minimum documentation searched (classification system followed by classification symbols)

- U.S.: 510/253, 255, 258, 264, 269, 421, 423, 433, 434, 499; 134/40, 41

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

- none

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

- APS
  - search terms: metasilicate, nonionic, boric acid, amphoteric surfactant, amine, corrosion inhibitor

### Documents Considered to Be Relevant

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 5,634,979 A (CARLSON et al) 03 June 1997 (03-06-97), See Abstract; See column 1, lines 5-15, column 2, lines 50-69; column 5, lines 4-20, column 8, lines 20-45; column 9, lines 50-69; column 15, lines 1-69.</td>
<td>1-4, 6-9, 11</td>
</tr>
<tr>
<td>Y</td>
<td>US 4,788,005 A (CASTRO) 29 November 1988 (29-11-88), See Abstract; column 3, line 62 to column 4, line 35; column 5, lines 4-10; column 6, lines 10-35; column 7, lines 10-25.</td>
<td>1-11</td>
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<td>X</td>
<td>US 5,591,703 A (SADLOWSKI) 07 January 1997 (07-01-97), See Abstract; column 5, line 15 to column 6, line 35; column 7, lines 10-45; column 8, lines 1-40; column 10, lines 30-40; column 14, lines 10-60; column 15, lines 15-45.</td>
<td>1-11</td>
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</table>

* Further documents are listed in the continuation of Box C. ** See patent family annex.

### Date of the actual completion of the international search

11 JUNE 1999

### Date of mailing of the international search report

01 JUL 1999

Name and mailing address of the ISA/US

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