such as succinic acid, oxydisuccinic acid, carboxymethyloxysuccinic acid, polymaleic acid, mellitic acid and benzene 1,3,5-tricarboxylic acid, phosphates such as sodium hydrogen phosphate, sodium dihydrogen phosphate and zinc hydrogen phosphate, sulphate and sulphite containing compounds such as sodium bisulphate, sodium bisulphite, iron (II) sulphate and iron (III) sulphate, sulphonic acids such as methane sulphonic acid, phenol sulphonic acid, toluene sulphonic acid, acrylamido-2-methylpropanesulphonic acid and polyvinylsulphonic acid, polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, weak acids such as phosphoric acid, carbonic acid and hydrogen peroxide, and others including ascorbic acid and acidic ion exchange resins based on sulphonic acids such as acrylamido-2-methylpropanesulphonic acid and chelating resins based on dicarboxylic acids such as iminodiacetic acid.

[0110] In some embodiments of the invention the cleaning formulation can comprise at least one base. In some embodiments, the cleaning formulation can include bases selected from, but not limited to, one or more alkali metal containing compounds and/or salts thereof such as sodium polyacrylate, sodium acrylamido-2-methylpropanesulphonate, sodium polyvinylsulphonate, sodium carbonate, sodium hydrogen carbonate, sodium citrate, trisodium citrate, sodium oxalate, sodium phosphate, sodium phenol sulphonate, sodium toluene sulphonate, sodium methane sulphonate, sodium lactate, sodium gluconate, sodium glycolate and sodium formate and others including zinc phosphate, poly (acrylamido-N-propyltrimethylammonium chloride), polyethylene amine, zinc dithiophosphate, benzalkonium chloride, alkylaminophosphates plus the alkali metal salts of polyphosphates, ammonium salts of polyphosphates and alkanolammonium salts of polyphosphates, alkali metal silicates, alkaline earth and alkali metal carbonates, aluminosilicates, polycarboxylate compounds, ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1,3,5-trihydroxybenzene-2,4,6-trisulphonic acid, and carboxymethyl-oxysuccinic acid, alkali metal salts of polyacetic acids, ammonium salts of polyacetic acids and substituted ammonium salts of polyacetic acids such as ethylendiamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid and soluble salts thereof and basic ion exchange resins including those based on quaternary amino groups such as trimethylammonium groups, for example, poly (acrylamido-N-propyltrimethylammonium chloride).

[0111] Thus in some embodiments of the invention the cleaning of the metal substrate can be performed using bases as opposed to the acidic reagents typically employed in methods of the prior art.

[0112] In some embodiments of the invention the acids and/or bases when present in the cleaning formulation can have dissociation or ionization constants within a specified range. Thus the acids can have particular pKa values in a dilute aqueous solution, wherein pKa is defined as the negative of the logarithm of the equilibrium constant Ka for the reaction:

$$HA \rightleftharpoons H^+ + A^-$$

i.e., $Ka=[H^+][A^-]/[HA]$

where $[H^+]$, etc. represent the concentrations of the respective species in mol/L. It follows that $pKa=pH+\log[HA]-\log[A^-]$, so a solution with 50% dissociation has pH equal to the pKa of the acid.

[0113] In some embodiments of the invention the acids can have pKa values greater than about −1.7. In further embodiments, the acids can have a pKa between about −1.7 and about 15.7 (the pKa of water). In still further embodiments, the acids can have pKa values greater than about 1. In certain embodiments, the acids can have pKa values between about 1 and about 15.7. In still further embodiments, the acids can have pKa values between about 1 and about 12. In embodiments of the invention containing polyprotic acids, each pKa value may be in accordance with the ranges specified above (for example, the acidic compound can contain more than one pKa value each which is greater than about −1.7). Thus in some embodiments of the invention, the acids of the cleaning formulation are weaker than strong acids with pKa values of less than −1.7 (e.g. sulphuric acid or hydrochloric acid) that are commonly employed in methods of the prior art.

[0114] In some embodiments it is preferred that no acid present in the cleaning formulation has a pKa of less than or equal to about −1.7, more preferably no acids presents in the cleaning formulation have a pKa outside about −1.7 to about 15.7, even more preferably no acids presents in the cleaning formulation have a pKa outside about 1 to about 12. In some embodiments the cleaning formulation does not comprise a mineral acid (examples of which include sulphuric acid, hydrochloric acid, hydrofluoric acid, hydriodic acid, nitric acid and phosphonic acid)

[0115] As noted above, bases included in some embodiments of the invention can have ionization constants within a specified range. Thus the bases can have particular pKb values in a dilute aqueous solution, wherein the logarithm of the ionisation constant, pKb, is derived from the reaction: $B+H_2O \rightleftharpoons BH^+ + OH^-$. This is related to Ka by:

$$pKa+pKb=pK_{water}=14.00 \text{ (at 25° C.).}$$

[0116] In some embodiments of the invention bases included in the cleaning formulation can have pKb values greater than about −1.7. In further embodiments, the bases can have pKb between about −1.7 and about 15.7 (the pKb of water). In still further embodiments, the bases can have pKb values greater than about 1. In certain embodiments, the bases can have pKb values between about 1 and about 15.7. In still further embodiments, the bases can have pKb values between about 1 and about 12.

[0117] In some embodiments it is preferred that no base present in the cleaning formulation has a pKb of less than or equal to about −1.7, more preferably no bases presents in the cleaning formulation have a pKb outside about −1.7 to about 15.7, even more preferably no bases presents in the cleaning formulation have a pKa outside about 1 to about 12.

[0118] The solid particulate material for use in embodiments of the method of the invention can comprise a multiplicity of polymeric particles or a multiplicity of non-polymeric particles. In some embodiments, the solid particulate material can comprise a multiplicity of polymeric particles. Alternatively, the solid particulate material can comprise a mixture of polymeric particles and non-polymeric particles. In such embodiments, the mixture can contain predominantly polymeric particles. In other embodiments, the solid particulate material can comprise a multiplicity of non-polymeric particles. Thus the solid particulate material in embodiments