

[54] **METHOD OF WASHING SOILED CULINARY ARTICLES**

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[63] Continuation-in-part of Ser. No. 317,097, Dec. 20, 1972, , which is a continuation of Ser. No. 108,198, Jan. 20, 1971, abandoned.

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[57]

ABSTRACT

Soiled culinary articles are washed with an aqueous composition containing water and a catalytically effective amount of a novel catalyst. The invention is especially effective in washing soiled culinary articles which have food deposits and other foreign materials adhering tightly to the surface thereof. When desirable, the aqueous composition may also contain a surface active agent or a combination of a surface active agent and a water softening agent. The novel catalyst which is used in preparing the aqueous composition is prepared by steps including admixing a water soluble alkali metal silicate with an aqueous medium containing carefully controlled amounts of dissolved water soluble substances which are sources of calcium ion and magnesium ion, reacting the same to produce an aqueous finely divided or colloidal suspension of the reaction product, admixing a micelle-forming surfactant with the aqueous medium, and agitating the aqueous medium containing the finely divided or colloidal particles and surfactant to form catalyst-containing micelles.

37 Claims, No Drawings

METHOD OF WASHING SOILED CULINARY ARTICLES

RELATED APPLICATIONS

This application is a continuation-in-part of copending application Ser. No. 317,097, filed Dec. 20, 1972, on behalf of John W. Willard, Sr., for Novel Catalyst and Process For Preparing The Same. Application Ser. No. 317,097, in turn, is a continuation of application Ser. No. 108,198 filed Jan. 20, 1971, now abandoned. The disclosures of applications Ser. Nos. 108,198 and 317,097 are incorporated herein by reference.

BACKGROUND OF THE INVENTION

This invention relates to a novel method of washing soiled culinary articles. The invention is especially useful in removing tightly adhering food deposits and foreign materials in general from the surface of soiled culinary articles.

A large number of surface active agents have been used heretofore in formulating dishwashing detergents. Examples include the alkali metal soaps of long chain fatty acids, the alkali metal soaps of rosin acids and the derivatives of rosin acids, synthetic detergents of the anionic, cationic or nonionic types and mixtures of one or more of these substances. It has been common practice to use inert diluents such as sodium sulfate, or builders such as polyphosphates, polysilicates or sodium carboxymethylcellulose in combination with one or more surface active agents. A number of nitrogen-containing sequestering agents, anti-bacterial agents, bleaching agents and water softening agents also have been added to dishwashing detergents heretofore.

The commercially available prior art detergent compositions recommended for washing dishes and other culinary articles are not entirely satisfactory for a number of reasons. For instance, dishwashing detergents widely used at the present time often include a phosphorous or nitrogen-containing compound which either directly or indirectly results in a pollution problem. The phosphorous and nitrogen-containing compounds promote the growth of microorganisms and alga in streams and other bodies of water into which sewage is introduced and this results in an adverse change in the ecology. The presence of a high concentration of sodium sulfate and other soluble fillers is undesirable when the water is to be reused down stream for purposes which require a low sodium or solubles content. In instances where the prior art dishwashing detergents contain synthetic surfactants which are not destroyed by microorganisms at a sufficiently rapid rate, the surfactant concentration in streams also tends to increase to an objectionable level.

Many of the prior art dishwashing detergents are not sufficiently fast acting to remove tightly adhering food deposits and/or food stains within the period of time available when washing dishes in modern automatic dishwasher. As a result, dried food deposits and thermally decomposed food deposits on burned or scorched culinary articles are not removed effectively. Also, food stains resulting from tea, coffee, fruits and the like are not removed effectively even in the presence of strong bleaching agents which often tend to destroy colored designs on dishes and chemically attack metallic culinary articles.

The prior art dishwashing detergents often have still other disadvantages such as requiring hot water for ef-

fective cleaning action and tending to produce excessive suds and especially if too much is added inadvertently to an automatic dishwasher. Many dishwashing detergents also leave unsightly films or residua on the surface of the washed and dried culinary articles.

In view of the foregoing, the prior art has long sought an entirely satisfactory method of washing culinary articles which overcomes the above mentioned and other well known deficiencies of presently used dishwashing detergents. However, an entirely satisfactory method of washing soiled culinary articles was not available prior to the present invention in spite of the long standing need.

It is an object of the present invention to provide a novel method of washing soiled culinary articles having food deposits adhering to the surface thereof comprising intimately contacting the same with water containing a catalytically effective amount of a unique catalyst to be described more fully hereinafter.

It is a further object to provide a novel method of washing soiled culinary articles wherein the culinary articles are intimately contacted with an aqueous composition containing water, a surface active agent and/or a water softening agent in the presence of a catalytically effective amount of the catalyst of the invention.

Still other objects and advantages will be apparent to those skilled in the art upon reference to the following detailed description and the specific examples illustrating the present invention.

DETAILED DESCRIPTION OF THE INVENTION INCLUDING PREFERRED VARIANTS THEREOF

In accordance with the present invention, soiled culinary articles are washed in an aqueous composition containing water and a catalytically effective amount of a novel catalyst to be described more fully hereinafter. The aqueous composition may contain a surface active agent, or a combination of a surface active agent and a water softening agent when desired. Other prior art additives for dishwashing detergents also may be present but usually they are not necessary and in some instances undesirable.

In instances where the aqueous composition also contains a surface active agent, it may be selected from the surface active agents used in washing culinary articles in accordance with prior art practice. Examples of surface active agents include the alkali metal soaps of long chain fatty acids and especially the sodium and potassium soaps of fatty acids containing 14-25 carbon atoms and preferably about 16-18 carbon atoms. Other surface active agents include detergents which are not derived directly from fatty acids such as synthetic anionic, cationic and nonionic detergents. Specific examples of synthetic anionic detergents include the alkali metal salts of organic sulfonates or organic sulfates, and especially the alkali metal salts of high molecular weight alkyl or alkylaryl sulfonates such as sodium or potassium dodecyl benzene sulfonate, and the sodium and potassium sulfates of fatty alcohols or products of the "Oxo" process. Specific examples of cationic detergents include the quaternary ammonium halides such as benzethonium chloride, and often members of this group have outstanding germicidal activity as well as surface active properties. Specific examples of non-ionic detergents include compounds having a polyoxyethylene or other oxygenated side chain and the re-

mainder of the molecule may be derived from fatty acids, alcohols, phenols, amides or amines.

Further examples of surface active agents are disclosed in the section on detergency appearing in the Kirk-Othmer Encyclopedia of Chemical Technology (2nd Edition), Volume 6, pages 853-895, the disclosure of which is incorporated herein by reference. Still additional specific examples of detergent compositions are found in numerous U.S. patents, including the following which are incorporated herein by reference:

| | | | |
|-----------|-----------|-----------|-----------|
| 3,031,510 | 3,118,000 | 3,222,287 | 3,382,177 |
| 3,043,780 | 3,119,848 | 3,223,647 | 3,382,285 |
| 3,048,548 | 3,140,261 | 3,282,852 | 3,422,021 |
| 3,053,771 | 3,144,412 | 3,314,891 | 3,424,689 |
| 3,061,551 | 3,156,655 | 3,320,172 | 3,429,822 |
| 3,067,143 | 3,173,877 | 3,326,807 | 3,437,697 |
| 3,082,172 | 3,203,955 | 3,337,463 | 3,444,242 |
| 3,095,381 | 3,208,949 | 3,349,038 | 3,499,841 |
| 3,101,297 | 3,213,028 | 3,359,205 | 3,507,798 |
| 3,101,374 | 3,215,633 | 3,382,176 | |

It is understood that the above surface active agents are given by way of example only, and that other suitable surface active agents may be used. A mixture of one or more of the above surface active agents may be used when desired.

In instances where the aqueous composition also contains a water softening agent, it likewise may be selected from the water softening agents used in washing culinary articles in accordance with prior art practice. Examples of water softening agents include washing soda, trisodium phosphate, sodium metaphosphate, sodium tetrphosphate and other substances effective to remove calcium and/or magnesium ions from water. Mixtures of water softening agents may be used. The water softening agent may be employed in the usual amount necessary to soften the water content of the aqueous composition.

The water used in preparing the aqueous composition for use in washing the soiled culinary articles may be untreated or softened tap water derived from municipal water sources, wells or springs. A soft water usually gives better results and is preferred. The additives described above, when used, may be admixed with the water in the quantity recommended in accordance with prior art practices, such as $\frac{1}{4}$ -2 cups of surface active agent for each 5-20 gallons of water. However, the catalyst of the invention increases the effectiveness of a given quantity of surface active agent or other additive and the amount required to produce equally satisfactory results is usually about one-eighth to one-half of that normally required, and often about one-fourth as much, as is used in prior art dish washing compositions.

The catalyst is present in the aqueous composition in a catalytic quantity which results in the desired improvement. Usually the catalyst is present in an amount of about 0.00001-0.1 weight percent, and preferably about 0.0004-0.001 weight percent of the aqueous composition, but larger or smaller amounts may be present as it is only necessary to provide the catalyst in catalytic amount. The aqueous composition may be prepared by diluting the aqueous suspension of the catalyst as produced by the process described herein. In such instances, the aqueous suspension of catalyst as produced may be diluted with about 100-10,000 volumes of water and then used. For better results, the aqueous suspension of catalyst as produced may be diluted with about 250-2000 parts of water before use,

and for still better results it may be diluted with about 500-1000 parts by weight of water before use. A surface active agent and/or a water softening agent may be added thereto in the above described quantities when desired.

Alternatively, when the aqueous composition contains a surface active agent, the catalyst may be added to commercially available solid or liquid surface active compositions such as Cascade, Ivory Snow, Tide and Thrill, or to the surface active compositions disclosed in the patents listed herein. The catalyst is present in a quantity to provide a catalytic amount when the commercial surface active composition is admixed with water in the recommended ratio to wash dishes. Usually the catalyst is present in an amount to provide about 0.00001-0.1 weight percent, and preferably about 0.0004-0.001 weight percent in the water that is added thereto at the time of use. Often the catalyst is present in an amount of about 0.01-1 weight percent based upon the weight of the concentrated surface active composition. Larger or smaller amounts may be present as it is only necessary to provide the catalyst in catalytic amounts in the aqueous composition prepared by diluting the surface active composition with water.

It is not necessary to use special dish washing procedures or equipment and prior art hand washing and machine washing techniques are equally effective in the presence of the catalyst. Ordinary small household automatic dish washing machines are preferred for household use, and large industrial dish washing machines for larger scale use such as in restaurants, hospitals and other institutions. It also is not necessary to change the surface active agent, the amount or ratio of water and surface active agent, the dish washing cycle, or other operating procedure with the exception of adding the catalyst. However, often it is preferred to use much less surface active agent to obtain equally satisfactory results and/or to allow the culinary articles to soak in water containing the catalyst and/or surface active agent prior to commencing the washing cycle. The soaking action is especially effective as it allows the catalyst to break the bond between the tightly adhering food particles and the surface of the culinary articles before the washing cycle begins and often a surface active agent is not needed. The culinary articles may be soaked, for example, for about five minutes to several hours and preferably for about 15 minutes to 1 hour. The dish washing cycle for an automatic dish washer may be, for example, a period of about 5-30 minutes and preferably about 10-20 minutes.

The catalyst markedly speeds up the cleaning action and allows the food particles, stains and other foreign substances to be removed from the surface of the culinary articles in a minimum period of time and with minimum effort. Cold water is satisfactory and it is not necessary to use warm or hot water. The catalyst is especially effective in the removal of tightly adhering dried initially liquid or semi-liquid films and particles of food and burned or thermally decomposed food. In such instances, the catalyst seems to loosen the bond between the surface of the culinary articles and the foreign substances, thereby allowing the foreign substances to be easily removed. The catalyst does not contain nitrogen or phosphorous compounds and it is non-polluting. The catalyst also aids in the uniform and complete removal of food stains, films, streaks and residues in general and the washed and dried culinary articles are very pleasing

in appearance. Colored designs on dishes and other culinary articles are not harmed and the catalyst does not chemically attack metallic culinary articles such as pots, pans, knives, forks, spoons and the like.

The catalyst used in practicing the present invention is unique and has many unusual and unexpected properties. It is presently thought that these unusual and unexpected properties result from the way the catalyst is prepared, and thus it should be prepared following the process described hereinafter.

PREPARATION OF THE CATALYST

The catalyst used in practicing the present invention may be prepared as described below. In the presently preferred process for preparing an aqueous suspension of the catalyst, a water soluble alkali metal silicate is admixed and reacted with an aqueous solution of a water soluble dissolved substance which is a source of calcium ion and a water soluble dissolved substance which is a source of magnesium ion to produce a finely divided or colloidal suspension of the reaction product. The aqueous solution contains the dissolved substances initially in amounts to provide between about 1×10^{-4} and 1×10^{-1} mole per liter each of calcium ion and magnesium ion, preferably between about 1×10^{-3} and 1×10^{-2} mole per liter, and for still better results between 1×10^{-3} and 6×10^{-3} mole per liter. The dissolved substances should also be present in amounts to provide a molar ratio of calcium ion to magnesium ion between about 2.0:1.0 and 1.0:2.0, and preferably about 1.5:1.0 and 1.0:1.5. For best results, the aqueous medium should contain the dissolved substances in amounts to provide between about 2.5×10^{-3} and 3.0×10^{-3} mole per liter each of calcium ion and magnesium ion, and the molar ratio of calcium ion to magnesium ion should be about 1.0:1.0, e.g., 2.9×10^{-3} mole per liter of calcium ion and 2.7×10^{-3} mole per liter of magnesium ion. The alkali metal silicate should have an alkali metal oxide to silicon dioxide ratio between about 0.9:1.0 and less than 2.0:1.0, and preferably between about 0.9:1.0 and 1.2:1.0. The alkali metal silicate should be admixed with the aqueous medium in an amount of about 0.05–2 moles per liter, preferably about 0.1–1 mole per liter, and for still better results about 0.2–0.5 mole per liter. For best results, the alkali metal silicate should be an alkali metal meta-silicate having an alkali metal oxide to silicon dioxide ratio of about 1:1, and it should be admixed with the aqueous medium in an amount to provide about 0.2–0.3 mole per liter, e.g., about 0.25 mole per liter.

Examples of sources of calcium ion and magnesium ion for use in preparing the aqueous solution include mineral acid salts such as the halides, sulfates, bisulfates, nitrites, and nitrates of calcium and magnesium. The chlorides are usually the preferred halides, and both calcium and magnesium chloride are soluble and may be used. Magnesium sulfate and bisulfate are soluble and often are the preferred sources of magnesium ion. Calcium sulfate is only slightly soluble in water and usually is not a preferred source of calcium ion, but calcium bisulfate is somewhat more soluble. While calcium and magnesium nitrite or nitrate are soluble in water and may be used, these substances are not preferred in most instances. The sources of calcium ion and magnesium ion are dissolved in the aqueous medium in amounts to provide calcium ion and magnesium ion within the above ranges. Complete ionization

is assumed when calculating the quantities to be dissolved and any desired order of addition is satisfactory. For example, the source of calcium ion may be added to the aqueous medium before, during or after the source of magnesium ion.

The alkali metal silicate to be admixed with the aqueous medium is preferably a water soluble sodium or potassium silicate having an alkali metal oxide (M_2O) to silicon dioxide (SiO_2) mole ratio between about 0.9:1.0 and less than 2.0:1.0, and preferably between about 0.9:1.0 and 1.2:1.0. The best results are usually obtained with an alkali metal metasilicate having an alkali metal oxide to silicon dioxide ratio of about 1:1. Hydrated alkali metal silicates dissolve faster and should be used for best results when the alkali metal silicate is added in solid form. In instances where an anhydrous alkali metal silicate is used, it may be desirable to dissolve it in water and then add the solution to the aqueous medium. Sodium metasilicate is preferred and usually a hydrated sodium metasilicate such as the pentahydrate gives the best results.

Carbonate ion and/or bicarbonate ion should not be present in the aqueous medium in substantial concentrations as the calcium ion and magnesium ion are precipitated in the form of their respective carbonates. The free carbonate ion and/or bicarbonate ion concentrations in the aqueous medium should not exceed about 10 parts per million by weight based upon the combined weight of the water and the ingredients added thereto and for this reason, the alkali metal silicates should be substantially free of carbonate ion and bicarbonate ion. A small amount of precipitated calcium carbonate and/or magnesium carbonate may be present in the aqueous medium provided additional calcium ion and magnesium ion are available to meet the above defined concentrations.

Distilled water and/or deionized water are usually preferred over a natural or untreated water when preparing the aqueous medium. In instances where water is used which contains substantial initial concentrations of alkaline earth metal ions, then this should be taken into consideration in calculating the amounts of the sources of calcium ion and magnesium ion which are necessary to arrive at the final concentrations previously discussed.

An electrolyte which aids in the preparation of colloidal suspensions may be present in the aqueous medium at the time of admixing the alkali metal silicate therewith. Examples of electrolytes include those used in preparing prior art colloidal suspensions such as the alkali metal halides, sulfates and bisulfates. Sodium chloride, sodium sulfate and sodium bisulfate are usually preferred. The electrolyte should be added in small amounts such as, for example, about 0.00001–0.1 mole per liter, but often larger or smaller amounts may be present.

The conditions under which the alkali metal silicate is admixed with the aqueous medium and reacted with the sources of calcium ion and magnesium ion are not critical provided the reaction mixture is maintained in the liquid phase. The reaction temperature may be, for example, between the freezing point and boiling point of water under the existing pressure conditions. At atmospheric pressure, the temperature is usually about 10° – 90° C and often a more convenient temperature is about 20° – 50° C. In many instances, ambient or normal room temperature is satisfactory.

The degree of agitation is not critical, and mild to vigorous agitation may be employed during addition of the alkali metal silicate. For the best results, the aqueous medium should be agitated sufficiently to assure rapid and uniform admixing of the alkali metal silicate. After completing the addition of the alkali metal silicate, when desired the agitation may be continued for a sufficient period of time to assure complete reaction and aging of the resulting colloidal suspension, such as for approximately 1-5 minutes to 1 hour or longer.

Upon admixing the alkali metal silicate with the aqueous medium, it takes on a turbid appearance but in most instances no significant amount of visible precipitate is formed. The colloidal suspension of the reaction product thus produced should be strongly basic and may have a pH value of, for example, approximately 10-14 and preferably about 11-13, and for best results about 12. In view of this, the initial pH value of the aqueous medium containing the dissolved sources of calcium ion and magnesium ion is of importance and should be about 6-9 and preferably about 7-8. When necessary, it is possible to adjust the pH value of the aqueous medium to the foregoing levels either before during or after addition of the alkali metal silicate by adding bases such as sodium or potassium hydroxide, or mineral acids such as sulfuric or hydrochloric acid.

The colloidal suspension may be stored for several weeks or longer while awaiting the further treatment described hereinafter. In instances where the colloidal suspension is to be stored over a substantial period of time, the pH value should be maintained at the above described level and the storage vessel is preferably a tightly capped polyethylene bottle or other inert plastic container which prevents the contents from absorbing carbon dioxide from the atmosphere.

The colloidal suspension of the reaction product is not suitable for use as a catalyst as prepared and it should be agitated sufficiently in the presence of a micelle-forming surfactant to form catalyst-containing micelles. The degree of agitation, the length of the agitation period, and the amount of the micelle-forming surfactant that is present in the colloidal suspension are controlled at levels favorable to the formation of micelles. For example, the surfactant may be present in an amount of about 0.001-0.1 mole per liter and preferably about 0.03-0.07 mole per liter for most surfactants. Smaller or larger amounts may be effective with some surfactants such as 0.0001 mole per liter or less, or 0.2 mole per liter or more. About 0.05 mole per liter gives the best results with many surfactants.

The minimum period of agitation and the minimum degree of agitation that are required for micelle formation varies somewhat with temperature and the type and amount of surfactant. As is well understood in this art, gradually increasing these variants in the presence of an effective amount of the micelle-forming surfactant will result in micelle formation when the proper levels are reached. As a general rule, longer periods of agitation and/or more vigorous agitation are required to form micelles at lower temperatures approaching the freezing point of the colloidal suspension than at higher temperatures approaching the boiling point. In instances where the aqueous suspension has a temperature of approximately 50°-90°C., then mild agitation over a period of about 10-60 minutes is satisfactory. Often longer or shorter periods of mild to vigorous agitation may be employed such as from about 1-5 min-

utes to several hours at temperatures varying, respectively, between the boiling point and the freezing point. When desired, the agitation may be continued long after the catalyst-containing micelles are formed as continued agitation does not seem to have an adverse affect.

As a general rule, the micelle-forming surfactants known in the prior art may be used in practicing the present invention. Micelle-forming surfactants used in the emulsion polymerization of monomeric organic compounds are disclosed in the text *Synthetic Rubber*, by G. S. Whitby, et al., John Wiley & Sons Incorporated, New York (1954), and surface active agents in general are disclosed on pages 418-424 of the text *Organic Chemistry*, Fieser and Fieser, 2nd Edition, Reinhold Publishing Corporation, New York, New York (1950), the disclosures of which are incorporated herein by reference. Examples of surfactants disclosed in the above texts include the alkali metal soaps of long chain fatty acids, and especially the sodium and potassium soaps of fatty acids containing about 14-25 carbon atoms and preferably about 16-18 carbon atoms, and the sodium and potassium soaps of the rosin acids, abietic acid and the derivatives thereof. Other micelle forming surfactants include fats and oils such as corn oil, cotton seed oil, castor oil, soy bean oil and safflower oil which have been fully or partially saponified with alkali metal bases to produce mixtures including saponified long chain fatty acids, the mono- or diglycerides thereof, and glycerin.

Examples of synthetic micelle-forming surfactants include the sulfonates of long chain alcohols prepared by hydrogenation of naturally occurring fats and oils of the above types and especially sulfonated long chain alcohols containing about 10-20 and preferably about 12-14 carbon atoms, the alkali metal salts of the monosulfonates of monoglycerides such as sodium glyceryl monolaurate sulfonate, the sulfonates of succinic acid esters such as dioctyl sodium sulfosuccinate and the alkylaryl alkali metal sulfonates. Specific examples of presently preferred micelle-forming surfactants include sodium and potassium sulforicinoleate, tetrahydronaphthalene sulfonate, octahydroanthracene sulfonic acid, butyl naphthalene sulfonic acid, sodium xylene sulfonate, alkyl benzene sulfonic acid and potassium benzene sulfonate.

Sulfated long chain hydroxycarboxylic acids containing about 14-25 carbon atoms and preferably about 16-18 carbon atoms, and sulfated fats and oils containing hydroxycarboxylic acids of this type produce exceptionally good micelle-forming surfactants. At least 25% of the hydroxyl groups and preferably at least 50% should be sulfated, and up to 95-100% may be sulfated. It is usually preferred that the sulfated oils and/or long chain hydroxycarboxylic acids be neutralized with an alkali metal base, and that the corresponding alkali metal salts be added to the colloidal suspension in the form of an aqueous solution. The aqueous solution may contain at least 25% of water and preferably at least 35-40% by weight. Much larger percentages of water may be present when desired such as 75-80% or more by weight.

A very active catalyst is produced when using sulfated castor oil as the micelle-forming surfactant (Turkey Red oil.) Sulfated castor oil which has been purified sufficiently to be of U.S.P. or medicinal grade produces an exceptionally active catalyst. For the best re-

sults, the castor oil is reacted with about an equal weight of concentrated sulfuric acid (e.g., 20% by weight) at a temperature of approximately 25°–30°C. The mixture may be reacted for about two hours with stirring and is then neutralized with sodium hydroxide solution. The reaction mixture separates into three layers, i.e., an upper layer which is a water solution, an intermediate or oily layer, and a white curdy precipitate. The intermediate oily layer is separated from the upper and lower layers, and may be added to the colloidal suspension as the micelle-forming surfactant in an amount, for example of 0.001–0.1 mole per liter, and preferably about 0.005 mole per liter.

The activity of the catalyst may be increased very markedly by cooling the aqueous catalyst suspension to a temperature approaching the freezing point such as about 0°–10°C., and then warming over one or more cycles. For best results, the aqueous catalyst suspension should be frozen and thawed over one or more cycles. The reason for the increased catalytic activity is not fully understood at the present time but cooling and then warming the aqueous catalyst suspension seems to increase the concentration of the catalyst-containing micelles and/or increases the catalytic activity thereof.

The aqueous suspension of the catalyst contains a relatively small percentage by weight of the active catalyst as produced. When desired, it may be concentrated by evaporating a portion of the water to produce a concentrated liquid catalyst suspension which may be stored and used more conveniently. It is also possible to prepare a dry catalyst concentrate by evaporating substantially all of the water. The preferred method of producing the dry catalyst concentrate is by flash evaporation using a technique analogous to that employed in preparing powdered milk. The catalyst concentrates produced upon partial or complete evaporation of the water content of the initially prepared aqueous suspension may be reconstituted by addition of water with little or no loss of catalytic activity. Preferably, the water is added to the dry catalyst concentrate under sufficiently vigorous conditions of agitation to assure that the catalyst micelles are resuspended and uniformly distributed.

The aqueous catalyst suspension may be used as produced in practicing the invention, but preferably it is diluted with approximately 100–10,000 parts by weight of water and then used. For better results, the catalyst suspension should be diluted with about 250–2,000

concentration in the quantities previously discussed. The weight of the catalyst is calculated on a dry solids basis, i.e., the weight of the catalyst ingredients in the aqueous suspension as produced after removal of the water.

The invention is further illustrated by the following specific examples.

EXAMPLE I

This example illustrates one presently preferred process for preparing the novel catalyst used in practicing the invention.

Anhydrous calcium chloride in an amount of 0.66 gram and magnesium sulfate heptahydrate in an amount of 1.32 grams were dissolved in two liters of deionized water with stirring and warming until solution was complete. Then 95 grams of sodium silicate pentahydrate having a molecular ratio of sodium oxide to silicon dioxide of 1:1 were added to the solution with stirring and continued warming to produce a white colloidal suspension of the reaction product.

After setting for 10 minutes, the colloidal suspension was heated to 80°C. and sulfated castor oil in an amount of 201 grams was added with stirring. The average molecular weight of the sulfated castor oil was 940 and it contained 50% of water. The turbidity lessened somewhat as the colloidal suspension was heated at 80°–90°C. for 1 hour with vigorous stirring to produce catalyst micelles. The aqueous suspension of catalyst micelles thus prepared had a viscosity similar to that of water and it was used as the catalyst in certain Examples as noted hereinafter.

A dry or solid catalyst concentrate was prepared in a further run by evaporating water from the initially prepared aqueous catalyst suspension. The resulting dry catalyst concentrate was resuspended in water and there was no substantial loss of catalytic activity. In still other runs, the catalytic activity of the aqueous suspension of catalyst as initially prepared, the diluted aqueous suspension of catalyst, and the reconstituted aqueous catalyst suspension was enhanced by freezing and thawing.

EXAMPLE II

This example illustrates the preparation of additional catalyst suspensions.

Five suspensions of the catalyst were prepared from the same ingredients as used in Example I and following the general procedure of Example I. The ratios of ingredients were varied as follows:

| Ingredient | Amount of Ingredient | | | | |
|--|----------------------|--------|--------|--------|--------|
| | Run 1 | Run 2 | Run 3 | Run 4 | Run 5 |
| Deionized water | 2 l | 1.5 l | 1.5 l | 1.5 l | 0.25 l |
| CaCl ₂ | 0.66 g | 0.5 g | 0.5 g | 1.0 g | 0.5 g |
| MgSO ₄ ·7H ₂ O | 1.32 g | 1.0 g | 1.0 g | 2.0 g | 1.0 g |
| Na ₂ SiO ₄ ·5H ₂ O | 165 g | 132 g | 71 g | 185 g | 71 g |
| Sulfated Castor oil (approximately 50% by weight H ₂ O) | 100 ml | 150 ml | 150 ml | 200 ml | 150 ml |

parts by weight of water before use, and for best results it should be diluted with about 500–1,000 parts by weight of water before use. The surface active agent may be added thereto when desired as previously discussed. Alternatively the dry catalyst or liquid catalyst concentrate may be admixed with water and/or the surface active agent to provide an effective catalyst con-

The catalyst suspensions prepared by the above five runs were used in certain examples as noted hereinafter.

EXAMPLE III

This example illustrates the use of a catalyst prepared in accordance with Example I in washing dishes. A

standard household automatic dishwasher was used in this Example.

In the first run, an attempt was made to remove food particles from soiled dishes using a commercially available dish washing detergent. The recommended amount of detergent and the recommended washing cycle was used. In a second run, the same procedure was used as in the first run with the exception of also adding approximately six fluid ounces of the catalyst suspension. Otherwise, the second run was identical with the first run.

The dishes washed in the first run in the absence of the catalyst had some food particles adhering to the surface and also had a noticeable film thereon. The dishes washed in the second run using the catalyst were much cleaner and free of food particles, and dried without leaving a noticeable soap film.

EXAMPLE IV

The general procedure of Example III was repeated in a series of runs with the exception of reducing the amount of dishwashing detergent to between one-half and one-eighth of the recommended amount employed in Example III. It was found that about $1\frac{1}{4}$ as much dish washing detergent is required to obtain equally satisfactory results when washing dishes in the presence of a catalytic amount of the catalyst.

EXAMPLE V

The general procedures of Examples III and IV are repeated in a further series of runs with the exception of using the catalysts prepared in accordance with Example II. The Example II catalysts are active and produce comparable results.

EXAMPLE VI

The general procedure of Example III was repeated with the exception of washing the dishes by hand. The results obtained in this Example are substantially the same as those of Example III. The dishes washed in the run using the catalyst are cleaner, brighter and are free of food particles. When the dishes were washed in the absence of the catalyst, much more effort was required to remove dried food particles and also the dishes did not appear to be as clean and bright due to a residual surface film.

EXAMPLE VII

This Example illustrates the use of only a diluted catalyst suspension in washing dishes.

A catalyst suspension was prepared in accordance with Example I and diluted with 1,000 volumes of water. The resulting diluted catalyst suspension was used in washing soiled culinary articles including dishes, knives, forks, spoons, pots and pans. The culinary articles were soaked in the diluted catalyst suspension for approximately 10 minutes to loosen the bond between the food particles and the surface of the culinary articles, and were then washed by hand. Very little effort was required to remove the food particles and the culinary articles dried bright and free of a residual film.

In a further run, pots having a tightly adherent layer of scorched food therein were soaked for 15 minutes in the diluted catalyst suspension and then scrubbed. The catalyst suspension was effective to break the bond between the scorched food layer and the surface of the pot, thereby allowing the pots to be washed with very

little effort. Only a light scrubbing action was necessary to remove the scorched food layer. In a similar run in the absence of the catalyst, several minutes of hard work was required with a conventional dish washing detergent.

EXAMPLE VIII

A catalyst suspension was prepared in accordance with Example I and the water content was evaporated to produce a dried catalyst concentrate.

The dried catalyst concentrate is admixed with a commercially available dish washing detergent (Cascade) in an amount of 1% by weight. The resulting admixture of catalyst and detergent is used in one series of runs to wash soiled dishes with dried food particles thereon in a standard household automatic dishwasher. In a second series of runs which are otherwise identical, the catalyst is omitted and only the initial commercial detergent formulation is used. The recommended amount of detergent and the recommended washing cycle is used in each series of runs.

The dishes washed in the series of runs using the catalyst are much cleaner and are free of food particles. The dishes from these runs also dry without leaving a noticeable soap film. The dishes washed in the absence of the catalyst have some food particles adhering to the surfaces. The dry dishes also have a noticeable film thereon.

I claim:

1. A method of washing soiled culinary articles having food deposits adhering to the surface thereof comprising

intimately contacting the soiled culinary articles with water containing an effective amount of a catalyst until at least a portion of the said food deposits are removed from the surface thereof,

the catalyst being prepared by a process comprising admixing a water soluble alkali metal silicate with an aqueous medium containing a dissolved substance which provides calcium ions in the aqueous medium and a dissolved substance which provides magnesium ions in the aqueous medium,

the aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of between about 1×10^{-4} and 1×10^{-1} mole per liter each of calcium ions and magnesium ions,

the aqueous medium containing said dissolved substances in amounts to provide a molar ratio of calcium ions to magnesium ions between about 2.0:1.0 and 1.0:2.0,

the alkali metal silicate having an alkali metal oxide to silicon dioxide ratio between about 0.9:1.0 and less than 2.0:1.0 and being admixed with the aqueous medium in an amount of about 0.05-2 moles per liter,

reacting the alkali metal silicate with said dissolved substances providing calcium ions and magnesium ions to produce an aqueous suspension of finely divided particles of the reaction product,

admixing a micelle-forming surfactant with the aqueous medium in an amount to form catalyst micelles including said finely divided particles of the reaction product upon agitating the aqueous medium, and

agitating the aqueous medium containing said finely divided particles of the reaction product and surfactant to form said catalyst micelles, the said resulting aqueous medium being diluted with at least 100 volumes of water prior to washing the soiled culinary articles therein and the said catalyst micelles being present therein in a concentration effective to promote the removal of the said food deposits.

2. The method of claim 1 wherein in the process for preparing the catalyst, said ratio of calcium ions to magnesium ions is between about 1.5:1.0 and 1.0:1.5.

3. The method of claim 1 wherein in the process for preparing the catalyst, said ratio of calcium ions to magnesium ions is about 1.0:1.0.

4. The method of claim 1 wherein in the process for preparing the catalyst, the alkali metal silicate is admixed with an aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of between about 1×10^{-3} and 6×10^{-3} mole per liter each of calcium ions and magnesium ions.

5. The method of claim 1 wherein in the process for preparing the catalyst, the alkali metal silicate is admixed with an aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of between about 2.5×10^{-3} and 3.0×10^{-3} mole per liter each of calcium ions and magnesium ions.

6. The method of claim 1 wherein in the process for preparing the catalyst, about 0.2–0.5 mole per liter of the alkali metal silicate is admixed with the aqueous medium.

7. The method of claim 1 wherein in the process for preparing the catalyst, the alkali metal silicate has an alkali metal oxide to silicon dioxide ratio between about 0.9:1.0 and 1.2:1.0.

8. The method of claim 1 wherein in the process for preparing the catalyst, the alkali metal silicate is alkali metal metasilicate having an alkali metal oxide to silicon dioxide ratio of about 1.0:1.0.

9. The method of claim 1 wherein in the process for preparing the catalyst, about 0.01–0.1 mole per liter of the surfactant is admixed with the aqueous medium.

10. The method of claim 1 wherein in the process for preparing the catalyst, the surfactant comprises sulfated castor oil.

11. The method of claim 1 wherein in the process for preparing the catalyst, the alkali metal silicate is admixed with an aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of between about 1×10^{-3} and 6×10^{-3} mole per liter each of calcium ions and magnesium ions, the ratio of calcium ions to magnesium ions is between about 1.5:1.0 and 1.0:1.5, about 0.2–0.5 mole per liter of the alkali metal silicate is admixed with the aqueous medium, and the alkali metal silicate has an alkali metal oxide to silicon dioxide ratio between about 0.9:1.0 and 1.2:1.0.

12. The method of claim 1 wherein in the process for preparing the catalyst, the alkali metal silicate is admixed with an aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of between about 2.5×10^{-3} and 3.0×10^{-3} mole per liter each of calcium ions and magnesium ions, the aqueous medium contains about equimolar amounts of calcium ions and magne-

sium ions, about 0.2–0.3 mole per liter of the alkali metal silicate is admixed with the aqueous medium, and the alkali metal silicate has an alkali metal oxide to silicon dioxide ratio of about 1.0:1.0.

13. The method of claim 12 wherein in the process for preparing the catalyst, the alkali metal metasilicate is sodium metasilicate having an alkali metal oxide to silicon dioxide ratio of about 1.0:1.0.

14. The method of claim 12 wherein in the process for preparing the catalyst, about 0.01–0.1 mole per liter of the surfactant is admixed with the aqueous medium.

15. The method of claim 14 wherein in the process for preparing the catalyst, the surfactant comprises sulfated castor oil.

16. The method of claim 15 wherein in the process for preparing the catalyst, the alkali metal metasilicate is sodium metasilicate having a sodium oxide to silicon dioxide ratio of about 1.0:1.0.

17. The method of claim 16 wherein in the process for preparing the catalyst, at least 25% of the hydroxy groups of the castor oil are sulfated, and about 0.03–0.07 mole per liter of the sulfated castor oil is admixed with the aqueous medium.

18. The method of claim 12 wherein in the process for preparing the catalyst, the alkali metal silicate is admixed with an aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of about 2.9×10^{-3} mole per liter of calcium ions and about 2.7×10^{-3} mole per liter of magnesium ions, about 0.25 mole per liter of sodium metasilicate having a sodium oxide to silicon dioxide ratio of about 1.0:1.0 is admixed with the aqueous medium, the aqueous medium contains not more than 10 parts per million by weight of carbonate ions and bicarbonate ions, the surfactant comprises sulfated castor oil and at least 50% of the hydroxy groups of the castor oil are sulfated, and about 0.05 mole per liter of the sulfated castor oil is admixed with the aqueous medium.

19. In a method of washing soiled culinary articles wherein the culinary articles are intimately contacted with an aqueous composition containing water and an active ingredient comprising at least one material selected from the group consisting of (1) a surface active agent and (2) a combination of a surface active agent and a water softening agent, the culinary articles having food deposits thereon and being intimately contacted with the aqueous composition under conditions whereby at least a portion of the said food deposits are removed,

the improvement in combination therewith comprising intimately contacting the soiled culinary articles with the said aqueous composition in the presence of an effective amount of a catalyst,

the catalyst being prepared by a process comprising admixing a water soluble alkali metal silicate with an aqueous medium containing a dissolved substance which provides calcium ions in the aqueous medium and a dissolved substance which provides magnesium ions in the aqueous medium,

the aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of between about 1×10^{-4} and 1×10^{-1} mole per liter each of calcium ions and magnesium ions,

the aqueous medium containing said dissolved substances in amounts to provide a molar ratio of cal-

cium ions to magnesium ions between about 2.0:1.0 and 1.0:2.0,

the alkali metal silicate having an alkali metal oxide to silicon dioxide ratio between about 0.9:1.0 and less than 2.0:1.0 and being admixed with the aqueous medium in an amount of about 0.05–2 moles per liter,

reacting the alkali metal silicate with said dissolved substances providing calcium ions and magnesium ions to produce an aqueous suspension of finely divided particles of the reaction product,

admixing a micelle-forming surfactant with the aqueous medium in an amount to form catalyst micelles including said finely divided particles upon agitating the aqueous medium, and

agitating the aqueous medium containing the said finely divided particles and surfactant to form said catalyst micelles,

the said resulting aqueous medium being diluted with at least 100 volumes of water prior to washing the soiled culinary articles therein and the said catalyst micelles being present therein in a concentration effective to promote the removal of the said food deposits.

20. The method of claim 19 wherein the said active ingredient of the aqueous composition comprises a major proportion of a mixture of (a) at least one surface active agent, and (b) at least one water softening agent.

21. The method of claim 19 wherein in the process for preparing the catalyst, said ratio of calcium ions to magnesium ions is between about 1.5:1.0 and 1.0:1.5.

22. The method of claim 19 wherein in the process for preparing the catalyst, said ratio of calcium ions to magnesium ions is about 1.0:1.0.

23. The method of claim 19 wherein in the process for preparing the catalyst, the alkali metal silicate is admixed with an aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of between about 1×10^{-3} and 6×10^{-3} mole per liter each of calcium ions and magnesium ions.

24. The method of claim 19 wherein in the process for preparing the catalyst, the alkali metal silicate is admixed with an aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of between about 2.5×10^{-3} and 3.0×10^{-3} mole per liter each of calcium ions and magnesium ions.

25. The method of claim 19 wherein in the process for preparing the catalyst, about 0.2–0.5 mole per liter of the alkali metal silicate is admixed with the aqueous medium.

26. The method of claim 19 wherein in the process for preparing the catalyst, the alkali metal silicate has an alkali metal oxide to silicon dioxide ratio between about 0.9:1.0 and 1.2:1.0.

27. The method of claim 19 wherein in the process for preparing the catalyst, the alkali metal silicate is alkali metal metasilicate having an alkali metal oxide to silicon dioxide ratio of about 1.0:1.0.

28. The method of claim 19 wherein in the process for preparing the catalyst, about 0.01–0.1 mole per liter of the surfactant is admixed with the aqueous medium.

29. The method of claim 19 wherein in the process for preparing the catalyst, the surfactant comprises sulfated castor oil.

30. The method of claim 19 wherein in the process for preparing the catalyst, the alkali metal silicate is admixed with an aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of between about 1×10^{-3} and 6×10^{-3} mole per liter each of calcium ions and magnesium ions, the ratio of calcium ions to magnesium ions is between about 1.5:1.0 and 1.0:1.5, about 0.2–0.5 mole per liter of the alkali metal silicate is admixed with the aqueous medium, and the alkali metal silicate has an alkali metal oxide to silicon dioxide ratio between about 0.9:1.0 and 1.2:1.0.

31. The method of claim 19 wherein in the process for preparing the catalyst, the alkali metal silicate is admixed with an aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of between about 2.5×10^{-3} and 3.0×10^{-3} mole per liter each of calcium ions and magnesium ions, the aqueous medium contains about equimolar amounts of calcium ions and magnesium ions, about 0.2–0.3 mole per liter of the alkali metal silicate is admixed with the aqueous medium, and the alkali metal silicate has an alkali metal oxide to silicon dioxide ratio of about 1.0:1.0.

32. The method of claim 31 wherein in the process for preparing the catalyst, the alkali metal metasilicate is sodium metasilicate having an alkali metal oxide to silicon dioxide ratio of about 1.0:1.0.

33. The method of claim 31 wherein in the process for preparing the catalyst, about 0.01–0.1 mole per liter of the surfactant is admixed with the aqueous medium.

34. The method of claim 33 wherein in the process for preparing the catalyst, the surfactant comprises sulfated castor oil.

35. The method of claim 34 wherein in the process for preparing the catalyst, the alkali metal metasilicate is sodium metasilicate having a sodium oxide to silicon dioxide ratio of about 1.0:1.0.

36. The method of claim 35 wherein in the process for preparing the catalyst, at least 25% of the hydroxy groups of the castor oil are sulfated, and about 0.03–0.07 mole per liter of the sulfated castor oil is admixed with the aqueous medium.

37. The method of claim 36 wherein in the process for preparing the catalyst, the alkali metal silicate is admixed with an aqueous medium containing said dissolved substances in amounts to provide a total concentration in the aqueous medium of about 2.9×10^{-3} mole per liter of calcium ions and about 2.7×10^{-3} mole per liter of magnesium ions, about 0.25 mole per liter of sodium metasilicate having a sodium oxide to silicon dioxide ratio of about 1.0:1.0 is admixed with the aqueous medium, the aqueous medium contains not more than 10 parts per million by weight of carbonate ion and bicarbonate ion, the surfactant comprises sulfated castor oil and at least 50% of the hydroxy groups of the castor oil are sulfated, and about 0.05 mole per liter of the sulfated castor oil is admixed with the aqueous medium.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. 3,874,927

DATED April 1, 1975

INVENTOR(S) John W. Willard, Sr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, Line 35, read the last word as "atmosphere";
Line 36, read the words between "of" and
"product" as -- the reaction --;
Line 41, read the last word as "micelle-forming";
Line 42, read all after "colloidal" as --
suspension are --;
Line 43, read all after "the" as -- formation
of mi- --;
Line 44, read the word after "be" as -- present --;
Line 48, read all after "per" as -- liter or less,
or 0.2 -- ;
Line 49, read all after "0.05" as -- mole per
liter often --;
Line 50, read the last word as "surfactants";
Line 59, read the word after "more" as -- vigorous --;
Line 60, read the words between "at" and "approaching"
as -- lower temperatures --; and
Line 61, read the word before "suspension" as
-- colloidal --;

Column 8, Line 5, read the last word as "adverse";
Line 9, read the word after "surfactants" as -- used --;
Line 10, read the last word as "organic";
Line 23, read the last word as "acids";
Line 29, read all after "mono" as -- or di- --;
Line 31, read the last word as "surfactants";
Line 32, read the last word as "prepared";
Line 33 read all after "and" as -- oils of --;
Line 34, read the last word as "chain";

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Page 2

PATENT NO. : 3,874,927
DATED : April 1, 1975
INVENTOR(S) : John W. Willard, Sr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Line 35, read the last word as "about";
Line 36, read the last word as "mono"; and
Line 37, read the last word as "glyceryl";

Column 11, Line 24, change "1 1/4" to -- one 1/4 --.

Signed and sealed this 24th day of June 1975.

(SEAL)

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks