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CLEANER FOR FOOD RESIDUES

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This application is a continuation-in-part of my co-pending application Serial Number 115,326, filed June 7, 1961.

The present invention is concerned with cleaning compositions and is particularly directed to a composition adapted to be employed to remove heat-degraded food residues from inorganic surfaces, and the like.

In domestic and many industrial applications, the only practicable method of employing a cleaning material intended to clean or assist in cleaning a surface bearing a deposit of degraded foodstuff components is the method of applying to its deposit-bearing surface or to the surface of the deposit itself some agent which acts upon or through that deposit to cleanse or facilitate cleaning the surface. Such agents as are voluminously fluid may soften and, by flotation, remove the deposit of dirt. Other agents may act in some way to soften or release attachment of the deposit of dirt from the underlying permanent surface with the result that the deposit of dirt is readily removed in simple further operations such as flushing with water, mopping, wiping with a wet or damp cloth or the like.

The present invention, then, is concerned with an agent to be applied to a surface of a deposit of degraded foodstuff components or food residues, to modify such deposits so as to permit of almost effortless removal.

According to the present invention, I have discovered that a certain combination of agents well-known to be employed in the cleaning art, when combined in at least mutually potentiating amounts, and used together as a single composition, constitute a cleansing agent which, as an entity, manifests cleansing power several orders of magnitude greater than the additive sum of the cleansing powers of the identical components employed separately, as, for example, immediately successively.

The power, or cleaning power, of a composition including a composition of the present invention, is measured herein as the contact time a standardized amount of such composition requires to remove, or loosen so as to permit essentially effortless removal by low-pressure rinsing only, of a standardized deposit of residue of representative food degradation products. In order to have comparable results, standardized food degradation product deposits are used, as is more fully hereinafter explained. In general, a good, or preferred, cleaning composition is one which essentially completely removes, or frees for easy removal, a standardized deposit of food degradation products relatively more quickly; in general, a poor, or not preferred, such composition is one which removes, or frees, such deposit more slowly, or does so incompletely. In some applications other factors such as toxicity, skin irritation, and the like become critical, and cleansing time is not, alone, a measure of suitability.

More particularly, I have discovered that a combination comprising an alkali metal alkaline compound, ammonia, an aliphatic halohydrocarbon solvent of molecular weight below about 150, and water, each substance present in an amount at least sufficient to participate in the potentiation of the entire resulting mixture, has as a combination, cleansing power toward heat-degraded food residues very much greater than the additive sum of any lesser combination of some of the said substances, or any or all of the ingredients used separately. When a mixture of only these four components is present, the benefits of the present in-

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vention are available; however, the availability of those benefits can be much enhanced by the routine use therewith of various adjuvants of types and functions that are well known in the cleaning art: and so long as the indicated substances are present in mutually potentiating amounts, other substances present are without adverse effects and may have beneficial effects.

In the preparation, and more particularly in the selection of relative amounts of components to be used in preparation, of a composition of the present invention, typically the first step has been to determine the approximate total desired volume. On an experimental basis this may be a volume convenient to fill a container for storage or experimental use; on an industrial scale it may be the working volume of a mixer within which the composition is to be prepared.

A second step, then, has typically been a step of determining what proportion of this total volume is to be represented by aqueous and what proportion by organic fluids. Representative proportions and identities employed are more fully discussed hereinafter.

A third step has been the determination of what weight percent and what identity of alkali metal alkaline compound is to be employed, based upon weight, or approximate weight as estimated from volume, of the aqueous proportion. Amounts are hereinafter discussed. The desired amount of alkali metal alkaline compound is typically then introduced into the mixing vessel, and dissolved in water which can be the whole amount of water to be employed, or any lesser amount.

A fourth step has typically been the determination of whether to employ a bodying or thickening agent or other phase-binding agent; it may be desirable, but is critical in only some kinds of use. If employed, its identity is decided upon and it is usually best added at this step, the amount of bodying agent being determined by the desired resulting properties, and identity of material. Materials and amounts are discussed hereinafter.

A fifth step has been the addition of ammonia, usually in an amount determined as a certain weight percent of total aqueous material employed. By its addition after the addition of a thickening agent, if employed, its retention is improved. Water, if present with the ammonia, is reckoned as part of the whole amount of water discussed above.

As subsequent steps, other substances if any, soluble in or especially compatible with the aqueous portion are added. Thus, in the stated procedure, an aqueous product results to this point. Upon the completion of the addition of the aqueous portion and all substances for which it is a particularly suitable excipient, the organic portion, typically a lower aliphatic halohydrocarbon, is added. When thickener or emulsifier or the like is not employed, the organic portion is simply added and permitted to form a separate phase which is combined intimately with the aqueous phase by such means as agitation immediately prior to use. When there is used some material to delay or prevent separation of the aqueous and organic phases, techniques appropriate to the employed material, as hereinafter discussed, are applied at this juncture, to effect a uniform mixture, which is then, typically, the finished product. Odorant and coloring agents and the like can now be added, if desired. Also, the product can be placed in a container which may be a valve and orifice equipped pressure container from which it can easily be dispensed.

As alkali metal alkaline compounds, there may be employed any of numerous substances well known in the cleansing art which, upon dispersion in water, dissociates relatively freely and yields an aqueous dispersion of pH above 7. Representative such substances include the alkali metal hydroxides, of which sodium hydroxide is

the best known and least expensive, and also potassium hydroxide and lithium hydroxide. By reason of the smaller physical dimensions of the lithium ion, possibly a factor in some cleansing operations, lithium hydroxide is, in some situations, preferred, despite its higher cost. Sodium hydroxide is satisfactory. The potentiation of the whole composition of the present invention is sufficiently efficacious that relatively very small amounts of this kind of substance are needed, and, per use or in terms of results obtained, the additional cost of a lithium compound over other alkali metal compounds may be negligible.

Also, useful as alkali metal alkaline compounds are those alkali metal salts which, upon addition to water, yield an abundant supply of alkali metal ions and a resulting solution of pH substantially above 7, in which the anion can be chosen for its buffering action: although such action should not be so pronounced as to suppress alkalinity completely. Such salts include certain, but not all, of the soluble alkali metal silicates including notably the silicates representing the combination of the equivalent of from a substantial fraction of a mole such as one fifth of a mole of alkali metal oxide to two moles said oxide per mole of silicon dioxide. Typically this includes disilicates such as sodium disilicates, potassium disilicate, and lithium disilicate and the corresponding orthosilicates, sesquisilicates and metasilicates. Also useful are the numerous alkali metal phosphates known in the cleaning art; among these being substances of relatively wide variety in view of the apparent polymerization or other multiple association characteristics of the phosphate compounds: trisodium phosphate, tripotassium phosphate, trilithium phosphate, sodium metaphosphate, potassium metaphosphate, lithium metaphosphate, as well as the phosphates and silicates wherein, per molecule, more kinds of alkali metal ion than one are involved. Thus, a mixed lithium-sodium metaphosphate or other mixed salts of which this is representative can be employed. Moreover, the water soluble alkali metal phosphate "glasses" can be employed. The similar alkali metal borates are also useful. Also, alkali metal lower alkoxides can be employed as well as alkali metal oxides, although by reason of expense and, under some circumstances, instability, these are not preferred substances.

The exact weight of alkali metal alkaline compound as per unit of total composition to be employed of the pH of the resulting preparation does not appear to be critical so long as it is an amount sufficient to potentiate the four-component mixture that must be present to give the benefits of the present invention. Typically, the employed amount of alkali metal alkaline compound will be expressed as a weight percent of the whole composition, or of the aqueous component of the whole mixture. Amounts of alkali metal alkaline compound larger than about 15 weight percent of total aqueous component are seldom desirable, as giving results no better than are had by using amounts from 15 weight percent down. Amounts on the order of about 5 weight percent give good results as do also amounts down to about a half percent. Amounts smaller than about a half percent by weight of total aqueous component are also effective, the potentiation characteristic of the four-component mixture of the present invention being evidenced in compositions of which the aqueous component has as little as one tenth of one percent by weight of alkali metal alkaline compound. Below this amount, the potentiating effect appears to diminish to levels that are inefficient, but not completely to disappear until the alkali metal alkaline compound is present in only trace amounts.

The pH of the compositions of the present invention is always of a value greater than 7, corresponding to an alkaline condition. The exact pH value is apparently not critical, although typical pH values seldom are lower than about 9. Compositions of pH values above 12 are effective. However, in some applications considerations pertinent to employed amounts of alkaline compound other

than that of efficacy in cleansing become important or even critical. Such considerations include irritation to or attack upon the skin of a user whose hands might come in contact with the substance. Also, when the substance is to be employed in a gas-propelled fine-particle spray, the possibility of irritation to eyes, respiratory tract and the like becomes material and may be critical.

Ammonia is to be employed in the form of the compound itself. The compound can be supplied to the total four-component mixture in the form of gaseous ammonia, or as ammonia water, or in the form of a neutral salt or other compound of ammonia which, by room temperature reaction with part of the alkali metal alkaline compound under the conditions thereto ambient, obtains free ammonia.

Suitable salts to be employed include ammonium acetate, ammonium chloride, ammonium sulfate, ammonium bromide, ammonium carbonate, ammonium formate, ammonium iodide, ammonium oxalate, and various of the complex ammonium salts wherein a metal or metals or other element appears jointly with the ammonium as a component of the salt. Such substances include ammonium aluminum chloride, ammonium aluminum sulfate, ammonium cadmium chloride, ammonium calcium phosphate, ammonium chromium sulfate, ammonium magnesium carbonate and the like. Typically, by reason of the fact that under some conditions it can be highly flammable, ammonium nitrate will not be preferred; although where flammability is not a problem the substance can be employed. Similarly, ammonium nitrite will seldom be preferred. Although useful as to potentiating the cleansing action of the present invention, ammonium cyanide will seldom be employed for reason of its toxicity. Also, ammonium chlorate will seldom be preferred by reason of its active contribution to oxidizing reaction, and the same considerations pertain to the employment of ammonium chlorate and ammonium perchlorate.

Thus, it will be evident to skilled chemists that the ammonium salt, if employed, can be chosen for its ammonium content, reactivity with alkali metal alkaline compound under the employed conditions to liberate free ammonia, and with regard to its other known properties as they pertain to the intended application.

Because water is a necessary component of the present mixture, the ammonia exists in substantially ionized form, whatever the nature of its source. When it is to be produced in situ by reaction with part of the alkali metal alkaline compound, supplied amounts of substances can be adjusted accordingly.

The amount of ammonia is necessarily an amount that participates in the mutual potentiation of the four-component mixture, but the exact weight percent that is thus represented may vary. Expressing the content of ammonia as a percentage of the weight of the aqueous portion of the entire composition, amounts greater than about 10 percent are likely to lose ammonia content rapidly by vaporization. However, such amounts are effective. Amounts from about 1 to about 5 percent give good results, the larger amounts within such range performing little or no better than the smaller amounts. Amounts from about 0.2 to about 1 percent distinctively participate in the potentiation of the whole composition. Amounts below about 0.1 percent by weight of aqueous component of the composition show decreasing efficacy and are not preferred. However, if it is desired to employ the present composition with the minimum amount of ammonia that will give the benefits of the invention, amounts of ammonia as small as 0.05 percent by weight of aqueous portion can be used, with somewhat less than maximum potentiation.

The halogenated aliphatic hydrocarbon solvents are those of which halogen is chlorine or bromine, and those generally regarded as having the greatest solvent activity are preferred. Solvent activity tends in a general way to

vary inversely as molecular weight. Provided that the said halogenated hydrocarbon is a liquid under conditions usually contemplated for its employment, even though a volatile liquid, the lower its molecular weight, in general, the better. As tested, those substances of molecular weight above about 150, while not completely useless, are of such low efficacy as not to be favored. Considering cost, commercial availability, solvent action, volatility, potentiation of the present four-component mixture, and other factors, the halogenated hydrocarbon now most highly regarded and most preferred is dichloromethane which is known commercially as methylene chloride. Second to it in efficacy and other factors, as far as is now known, is 1,1,1-trichloroethane, which is sometimes called "methyl chloroform." Good results are obtained when employing chloroform or carbon tetrachloride. Of these two, the former will seldom be well adapted by reason of its known anesthetic properties, and the latter will sometimes be avoided by reason of its toxicity. Also suitable to be employed are 1,2-dichloroethylene, 1,2-dibromoethane, and similar low molecular weight halogenated hydrocarbon solvents. For reasons that are not understood, the unhalogenated organic solvents such as the alcohols, ketones, dioxane, and the like, do not potentiate the present mixed system and thus are not the equivalent of and not interchangeable with the halogenated hydrocarbons in the present invention. When desired, a mixture of halogenated hydrocarbons can be employed as, for instance, to gain the prompt solvent action of a more volatile solvent and, combined with it, the greater persistence of a less volatile solvent.

The aliphatic halohydrocarbon solvent does not appear to act alone, but in combination. Thus the amount to be employed is an amount which potentiates the entire four-component mixture, and, within that limitation, can vary considerably. An amount which is regarded as typical is an amount from about one fourth, to about equal, by volume as measured at room temperature, with the volume of the aqueous portion of the entire composition. However, smaller and larger amounts are effective. An amount equal to about one twentieth by volume of the aqueous portion gives good results, and can be employed. An amount equal to about nine times the volume of the aqueous portion can also be used. The resulting smaller proportion of the aqueous portion does not deny the potentiating effect of the present invention, provided allowance is made for necessary quantities of other substances. Between these relative amounts, good and mutually potentiated compositions are achieved. However, amounts relatively larger or relatively smaller can be used, although as amounts vary much beyond the indicated upper and lower amounts, the potentiation of the whole composition tends to diminish quite rapidly. Thus when the employed amount of aliphatic halohydrocarbon solvent is less than about two percent by volume of aqueous portion, durations of time required to remove food degradation products in standardized tests are substantially longer than when the employed amount of halohydrocarbon is about five volume percent. At the other extreme, when employing 95 volume percent of aliphatic halogenated hydrocarbon solvent, cleaning times tend to be much longer than when employing 90 volume percent, probably because the relative amount, and thus the potentiating effect, of the aqueous portion of the mixture is reduced.

The last component required at all times to be present in the mutually potentiating composition of the present invention is water. This is water in the ordinary sense, and it need not be distilled, deionized, or otherwise especially processed for purity although such waters are satisfactory and may be preferred. Of course, corrosive impurities, or impurities reactive with any of the present necessary components should be avoided.

The amount of water necessarily present to effect po-

tentiation of the four-component mixture of the present invention is also an amount within a considerable range. It should be at least an amount sufficient to permit the ready evolution of alkali metal ions in solution from the alkali metal alkaline compound; it should be enough also to hold in solution, for at least a useful interval of time, in open air, the employed ammonia. When present in these amounts, it will be present also in an amount sufficient to potentiate the whole four-component mixture; however, as far as can be determined, employing solvents other than water whereby to exhibit alkali metal ions and dissolve ammonia does not achieve the same result as water. The water itself appears in some way, beyond its function as solvent for other components present, to contribute necessarily to the potentiation of the entire mixture; moreover, employing only the aqueous composition alone, namely, the water solution of ammonia and alkali metal alkaline compound; and at another time (such as immediately before or immediately after) employing also the halohydrocarbon solvent, fails to achieve the potentiated results of the simultaneously used 4-component present mixture. No chemical reaction is known to occur, as a result of which the potentiation can be explained.

When water is present in an amount less than about 3 percent by volume of the entire mixture, or amounts smaller, efficacy of the resulting mixture tends to diminish rapidly as water amounts decrease; when employing amounts of water larger than about 90 percent of the entire mixture, results tend also to diminish rapidly as water amounts are increased. Between these limits as extremes, good potentiation occurs. While no particular component amount of water within this range is known to be critically superior, an amount approximately equal in volume to the volume of aliphatic halohydrocarbon solvent has given excellent results. Amounts moderately greater, as when carrying a thickening agent, or moderately less, have also been very satisfactory.

In order to standardize all procedures and avoid unexpected side-effects, deionized water has usually been employed and is fully satisfactory.

Whereas a mixture of these substances, each present in at least an amount mutually potentiating to the entire mixture, is extremely active as a cleaning composition for the removal of heat-degraded food residues, any combination of three of them or two of them or each of them alone, has an effect which, arithmetically added to the separate effect of any thus-omitted component or group of components is far smaller than the effect of the mixture of all, simultaneously.

With the four-component composition of the present invention, improved results are sometimes obtained by the employment of a surfactant, which may also be called a wetting agent, an amphipathic agent, or a detergent. Such surfactant will typically be incorporated into the four-component mixture and will become distributed therein according to its properties, typically in the aqueous component of the mixture. Its use is not usually necessitated, nor rendered undesirable, by the presence of other substances such as viscosity-modifying agents and the like.

A surfactant can be chosen for its power to produce a stable foam, such as "soap suds," as a means of maintaining a deposit of the present composition upon a site sought to be cleansed, for a period of time.

The use of a surfactant is at times helpful in the subsequent removal of deposits of food residues that have been freed or rendered easy to remove by the four-component mixture of the present invention.

The identity of the surface active agent to be employed is, within wide limits, not critical. Most such substances are relatively stable in the presence of alkali such as characterizes the mixtures of the present invention, or are possibly potentiated and their activity improved by such alkali. So long as the wetting agent employed is relatively stable in the presence of the other components of the

present mixture, as herein identified, it can be used satisfactorily. It can remain wholly in the aqueous phase, wholly in the non-aqueous phase, can form an emulsion of which either aqueous or organic phase is the disperse phase; or can produce a solubilized system in which the phases are indistinguishable. Representative suitable surface active agents include non-ionic or anionic surface active agent and, not as a limitation but by way of general guidance, those which are set forth in U.S. Patent 2,547,724, columns 3 and 4, and also U.S. Patent 2,702,747, columns 2 and 3.

When it is desired to effect the combining of the aqueous and non-aqueous phases of the present four-component composition to obtain a homogeneous solvent system, the amphipathic agent or mixture of such agents is so to be chosen that there are present both highly hydrophilic and highly hydrophobic moieties, whether in the same or different molecules. Suitable highly hydrophilic moieties include the sulfate, sulfonate, carboxylate, phosphate, phosphonate, and oxyethylene groups. Suitable highly hydrophobic moieties include aliphatic chains, halogen substituents, typically chlorine, upon aromatic or aliphatic groups, and oxybutylene and oxypropylene groups.

Suitable amphipathic agents of which the structure embodies such groups include the sodium salt of a chlorinated, dodecylated sulfonated diphenyl oxide, commercially available as Benax 6A1, in which the chlorination renders the hydrophobic group more strongly hydrophobic with the result that the molecule possesses satisfactory properties. Also, a mixture of such substance with its unchlorinated precursor, namely, as sodium salt of a dodecylated sulfonated diphenyl oxide, is even more effective.

With the description foregoing, it will be possible to choose satisfactory amphipathic agents as needed.

One surface active agent having highly desirable properties and having given good results when tested in conjunction with the necessary components of the present invention is tall oil, a by-product from sulfate wood pulp digestion, consisting mainly of resin acids and fatty acids. When added as surface active agent to the four-component mixture of the present invention, this substance tends to bind the components together, and, as well, tends to form a heavy, clinging film on soil-coated areas to which it is applied, whereby the action of the active cleansing components takes place more intimately in contact with the surface of deposits to be removed than in the absence of such substance.

The substances may be employed according to the present invention by simply mixing them together intimately and employing them in the intimately mixed form. However, chemists will immediately recognize that the aliphatic halohydrocarbon solvent is, in the absence of some phase-binding substance, essentially immiscible in water whereas the other substances exist together as a readily separated aqueous phase.

In order to avoid phase-separation whereby the present components fail to act intimately and conjointly together, it is possible to provide continuous and violent agitation up to the instant at which application is made. This procedure gives results which manifest the benefits of the present invention. However, this is usually very inconvenient. Alternatively, some kind of phase-binding, co-solvent, or viscosity increasing agent can be employed, whereby all substances tend to be held together at a molecular or near molecular level. One such substance is starch, gelatinized in at least part of the water which must be present; and the resulting gelatinized paste mixed with the other components including the organic solvent, which tends to be entrapped in a disperse phase therein. Also, a surface active dispersant-wetting agent can be added to either aqueous or organic phase to prepare an emulsion and thus delay or prevent phase separation.

Also, by the judicious choice of surfactants, all necessary components of the mixture can be brought together

in a transparent, apparently single-phase liquid system. One such agent can be employed also, alone or conjointly with other materials, to obtain a product of increased viscosity. Better results are obtained under practical working conditions with than without a binding agent: in some situations, as where last-minute violent agitation is not available, it is critically necessary.

When a binding agent is employed to prevent or delay phase separation, it should, very preferably, be an agent that increases product viscosity but which is not itself likely upon drying, to produce residues that are difficult to remove.

Starch has been mentioned. When a starch paste comprising the present active components is employed as the present cleansing agent, and is permitted to dry to air-dryness upon a surface to be cleansed, the resulting deposit tends to adhere to the surface intended to be cleaned and may contribute to the dirt rather than to its removal. A preferred thickening agent is a polyelectrolyte polymeric substance that is water soluble and alone or with other substances, acts as a thickening phase-binder. It can also be lightly cross-linked and, instead of being soluble, can be swellable to an extreme degree in at least one liquid present in the cleansing preparation, which may be a liquid added expressly to swell the said polymeric substance.

Because the function of the thickening, or viscosity-increasing agent is purely mechanical, its identity is not critical so long as it performs its necessary mechanical function. Moreover, it need not be soluble nor swellable in an employed liquid but can be simply mechanically disposed therein.

Thus a finely divided solid such as a clay, wood flour, diatomaceous earth, or the like, can be used. A modified clay, as described in U.S. Patent 2,702,747, columns 2 and 3, and commonly known as a bentone, or analogous material can be used. It is immaterial whether the primary association of such substance be with the aqueous or organic phase of the mixed preparation. The various commercial methyl ethers of cellulose, and the carboxymethylcelluloses and their salts can be used. Also, the hydroxymethylhydroxyethyl celluloses can be used, as can also the alkali metal or ammonium salts of sulfonated polystyrene. Also, mixtures of aqueous solutions of sulfonated polystyrene or a carboxyl-bearing vinyl polymer with a polymeric N-vinyl cyclic lactam or cyclic carbamate, which produce thickened aqueous preparations, can be employed. Also, polymeric vinyl oxazolidinones, unsubstituted or, for example, substituted with methyl or phenyl groups, such as polymeric 5-methyl-3-vinyl-oxazolidin-2-one, and polymeric 5-phenyl-3-vinyl-oxazolidin-2-one. Similarly, polymeric N-vinylpyrrolidinone and polymeric N-vinylmorpholinone can be used. The salts and esters of polyacrylic acid also have desirable and useful thickening actions and are available, as are the polyglycols.

Also, for use in the aqueous phase, there are available numerous natural gums, such as gum acacia, gum guar, and others that will be known to those skilled in the art. Likewise, the pectic substances, and glucosylated cellulose can be used.

Various substances are known that will function well to thicken preparations such as the present preparation, by dissolving or dispersing in the organic phase and, typically, tending to bind it with the aqueous phase. Among such substances are the ethyl ethers of cellulose, polystyrene, various other vinyl polymers of hydrocarbon or substituted hydrocarbon nature, such as polyvinyl chloride, and the like.

Some of these substances dissolve in the organic phase and, as this phase evaporates, form a skin or film that confines further portions of the organic phase against the soiled surface to be cleaned, thereby enhancing the cleaning action. Further, as the thus-confined portions of the organic phase slowly evaporate away, the remain-

ing polymeric film tends to form a continuous skin that can be lifted at an edge and removed, more or less easily, in large areas, often removing substantial amounts of formerly adherent degraded food residue "dirt" with it. The same can be done with some of the thickening agents that are usually dispersed in the aqueous phase.

Thus while the identity and exact function of the thickening agent may be a matter of distinctive preference, and in some applications critical, it will be evident that some aspects of this invention can be practiced satisfactorily with little or no thickening agent.

A desirable aspect of the present invention involves the dispersion of the composition in an infinitely swellable resin, to such extent that the resulting preparation is of desirable viscosity or body. Such infinitely swellable resins are typically the resins that are, as to polymeric structure, lightly cross-linked; that is, cross-linked at a few sites in comparison with the number of sites at which they are linearly linked; and which contain hydrophobic or hydrophilic moieties whereby their response to a solvent-type substance is determined, except that the action of such substance is not truly solvent, but causes instead swelling and softening of the polymer. Examples of such resins include polystyrene lightly cross-linked with a polyvinyl benzene comonomer, such as a divinylbenzene; a similar material but sulfonated to the extent of sulfonate groups upon from perhaps 5 to 90 percent of the aromatic nuclei of the styrene or divinylbenzene groups. In such substance, typically, from a half percent to 8 percent of the monomer can be the polyvinylbenzene.

Not only is it not objectionable, but may in some instances be much preferred that the polymeric thickening substance contain at one and the same time sites that are hydrophobic and hydrophilic. The hydrophilic sites tend to associate with the aqueous component of the present mixture, and the hydrophobic sites tend to associate with the organic component of the present mixture. As a result there are sometimes formed mixtures of improved single-phase stability.

When desired, thickening, that is raising of the viscosity, of the composition of the present invention to permit the application of deposits of substantial thickness on vertical surfaces or upon the lower aspect of a horizontal surface, may be carried out employing multi-component thickening agents. Numerous such substances are known, whereof one component is sometimes regarded as the fundamental thickener and one or more other components is regarded as a thickening promoter. The identity of such thickener does not appear to be critical, although, in terms of optimum performance, some are preferred over others.

A preferred and highly desirable thickener of which the properties are critical in some uses is a mixture of a water dispersible salt of a polymer sulfonate resin having a molecular weight above 1,000 in which from about 50 to about 90 percent of the monomer units carry neutralized sulfonate groups, cooperating with about equal to moderately larger amounts of a water-soluble thickening promoter which can be a water-soluble alkylene glycol, a polyoxylalkylene glycol, in either of which the alkylene moiety contains from 2 to 4, inclusive, carbon atoms; the thickening promoter can also be an alkyl monoether of such glycol, an aryl monoether of such glycol, wherein any said alkyl etherifying group contains from 1 to 4, inclusive, carbon atoms and any such said aryl esterifying group contains from 6 to 10, inclusive, carbon atoms; other thickening promoters are lower alkanols containing from 2 to 4, inclusive, carbon atoms; dimethylformamide, dimethylacetamide, dioxane, tetrahydrofuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, monoalkanolamines, dialkanolamines and trialkanol amines in any of which each alkylene moiety contains from 2 to 3, inclusive, carbon atoms; or mixtures of the foregoing thickening promoters whereof the total amount,

as mixed, is sufficient cooperatively to effect the desired degree of thickening of a water dispersion of the said water-dispersible polymer sulfonate resin salt. Thickeners as described here act also as phase binders to prevent separation of the organic and aqueous liquid phases. They are critically preferred for aerosol applications because they break readily into a fine cone of spray but regain their viscosity at once, as deposited.

It is well known that many aliphatic halohydrocarbon solvents are of such volatility as quickly to escape from a site to which they are applied, whereby, through lowered concentration, such solvent becomes less effective. Various means are known to those skilled in the art whereby to retain or confine such solvent substances within a mixture of which they are a part and upon a site whereupon they are to act as solvents. One such means is the incorporation, into a mixture such as the present mixture comprising such solvents, of a paraffin or similar wax or wax-like material. A satisfactory and preferred such paraffin wax is one melting at a temperature in the range of from 100-150° F. Apparently it dissolves in the organic phase and as first portions of the organic solvent evaporate, leaves a surface "skin" which tends to confine remaining portions of the solvent.

Typically, compositions of the present invention are, or by judicious selection of component materials can be prepared to be, of a low level of unobjectionable odor. However, when it is desired to mask an odor of one or more components, or gratuitously to confer odor upon the product substance or upon an area or within a volume wherein the said substance is used, it is possible and often-times convenient to add an odorant agent. The identity of the odorant agent is not critical. Small amounts are conventional and usually satisfactory.

If desired, a composition of the present invention can contain an effective amount of any one or several of known inhibitors for corrosion of metal. Precise selection of a corrosion inhibitor, if desired, will depend somewhat upon the identity and proportion of each of the components in the present mixture, the kind of metal to be protected, and the expected temperature and duration of contact. The art of corrosion inhibition is well known and is available in support of the present invention. The presence of one or more corrosion inhibitors in effective amounts has no significant effect upon the cleansing power of the present composition.

The following examples represent the best method now known to practice the present invention, and will enable those skilled in formulation of cleansing agents to practice the present invention.

EXAMPLE 1

While the 4-component mixture hereinbefore set forth as the critically essential aspect of the present invention, without more, can be employed to obtain the advantages and benefits of the present invention, very much more convenient, and therefore much preferred compositions can be prepared employing various of the additive substances hereinbefore discussed. In a representative such preparation, an aqueous 5 weight percent sodium hydroxide solution was mixed together at room temperature with a small amount of dry starch. The resulting suspension was thereupon heated for a few minutes to a temperature near to the boiling temperature of the mixture, sufficient to bring about the swelling and coalescence, "gelatinization," of the starch preparation, to obtain a paste-like material of viscosity sufficient to maintain given general outlines. To the resulting thick starch paste, when cool, was added an equal volume of 5 weight percent aqueous ammonia. To the resulting mixture was added its own volume of dichloromethane. All components were thereupon thoroughly mixed and stirred together to obtain an intimate, slowly syneresing admixture of the organic liquid solvent in the starch-thickened aqueous preparation of alkali metal alkaline compound

and ammonia. As a result of these procedures there was obtained a paste-like substance of opalescent, translucent appearance, strongly alkaline in reaction when tested with indicator substances, and highly effective for use in cleansing of surfaces by freeing or removing heat-degraded food residues.

EXAMPLE 2

A preparation essentially the same as the foregoing is prepared except that the alkali metal alkaline compound is lithium hydroxide and it is employed in an amount representing one-half weight percent of the aqueous solution thereof which, by addition to the other ingredients, as in the foregoing example, is employed in preparing the present preparation. It is tested and found highly effective in softening of food degradation residues and freeing them from attachment to substrate surfaces.

EXAMPLE 3

20 parts by weight of dichloromethane are placed in a chilled container. Thereto, with mixing and stirring, are added 5 parts by weight of the diethyl ether of diethylene glycol, 5 parts by weight of triethanolamine, 0.2 part of paraffin wax melting at a temperature in the range of from about 100° to 150° F., and 0.05 parts by weight of distilled oil of pine needles as odorant. Thereto, is added, with further mixing and stirring, 2.3 parts by weight of an industrial product represented as the ammonium salt of a sulfonated polyvinyl toluene which salt is found, upon analysis, to be approximately 75 percent by weight of ammonium sulfate, and approximately 25 percent by weight of the ammonium salt of polyvinyl toluene sulfonated to the extent that ammonium-neutralized sulfonate groups appear on approximately 70 to 90 percent of the recurring monomeric units thereof. To the resulting mixture is added, with mixing and stirring, 5.05 parts by weight of sodium disilicate representing 33.4 percent sodium oxide and 66.6 percent silicon dioxide, all anhydrous basis; and 0.5 part by weight of sodium nitrite, dissolved in water in an amount sufficient to obtain a total of 100 parts by weight. The resulting preparation is thoroughly mixed and stirred to obtain an intimate admixture together of all the parts. As a result of these procedures, the diethylene glycol ethyl ether and triethanolamine act cooperatively with the ammonium salt of the sulfonated polyvinyl toluene to effect a thickening of the entire aqueous preparation, whereby all other components, including, in particular, the dichloromethane solution of organic substances, are intimately bound therein in an essentially homogeneous mixture. By reaction with the disilicate the sodium sulfate releases ammonia. This substance is a very effective agent for the removal of heat-degraded food residues from mineral surfaces.

EXAMPLE 4

13 parts by weight propylene dichloride (1,2-dichloropropane), 3 parts by weight dichloromethane, 0.2 part by weight paraffin wax, 10 parts by weight ethylene glycol ethyl ether, and 4.5 parts by weight of industrial product grade ammonium salt of polyvinyl toluene sulfonated to approximately the extent of 70 percent of the recurring monomeric moieties and containing about 60 percent of ammonium sulfate by weight of industrial product are mixed and stirred together. To the resulting mixture is added 7 parts by weight industrial sodium hydroxide of approximately 50 percent purity, and 14 parts by weight of an industrial sodium disilicate of analysis equivalent to approximately 1 part sodium oxide for each 3 parts sodium disilicate both by weight, pure basis. Also, 51.8 parts by weight of water are added. The resulting mixture is intimately mixed and stirred to obtain a highly viscous, essentially self-supporting paste-like homogeneous product which is highly effective in the softening and removal from mineral surfaces of heat-degraded

food substances to a major surface of which it is applied as a coating.

EXAMPLE 5

Partially resinified lard was painted as a thin, uniform coating over the surface of a vitreous enamel coating upon a metal base, commonly known in kitchen use as "enamel ware." The resulting coating was then heated for approximately 64 hours at a temperature of approximately 300° F. to obtain a uniform resinified lard film representative of a food degradation substance film encountered in a soiled oven, upon a vitreous enamel sub-surface. Various cleansing materials were tested upon this coating film for efficacy in removing the same, as indicated by exposure time necessary to bring about either removal or such attack of unidentified nature as would permit effortless removal by water rinsing.

In representative operations, it was ascertained that dichloromethane alone, the supply of which was renewed as it was lost through evaporation, required more than 500 hours contact time to effect freeing or removal.

It was further ascertained that a 5 percent aqueous sodium hydroxide solution required in excess of 300 but not so long as 1,000 minutes to effect softening which would permit effortless removal by water rinsing.

In a further representative operation, it was ascertained that one-half percent aqueous ammonia, the supply of which was renewed as it was lost through evaporation, required more than 300 but not so many as 1,000 minutes to effect freeing of the film for effortless removal by water rinsing.

In a further representative test, it was ascertained that a mixture of 5 percent sodium hydroxide and one-half percent ammonia in water required approximately 2 hours contact time to effect freeing or removal.

In a further representative operation it was ascertained that a mixture of 5 percent aqueous sodium hydroxide with an equal volume of dichloromethane required 45 minutes to effect freeing or removal.

In contrast, a mixture containing as sole active cleansing agent water, 5 percent sodium hydroxide, one-half percent ammonium hydroxide, both by weight in water, and a volume of dichloromethane equal to the volume of the aqueous sodium hydroxide-ammonia mixture, required a contact time of 1.5 minutes to effect a freeing of the said film for effortless removal by water rinsing.

EXAMPLE 6

In the present example, the film of resinified lard was prepared in essentially the manner described foregoing, except that in the last heating, the partially resinified lard was baked in open air in a hot oven for 16 hours at 450° F. As a result of this baking operation there is obtained a coating of undetermined chemical identity characterized by an almost complete absence of oily characteristics, and the presence of numerous reactive sites of generally acidic nature.

The cleansing tests described in Example 5 are repeated on the coating prepared as described in this example, and with closely similar results.

EXAMPLE 7

A cleansing composition according to the present invention is prepared as follows:

Into a container are placed 57.95 grams water previously deionized by passing it successively through beds of basic and acidic ion exchange resin beads. Into this water is added with gentle stirring 0.5 gram sodium nitrite. Thereafter, to the resulting nitrite solution is added 5 grams of the ethyl ether of diethylene glycol (Dowanol DE) and then 5 grams triethanolamine.

To the resulting solution is added 2.3 grams of an industrial grade ammonium salt of sulfonated polyvinyl-toluene. This substance contains approximately 75 percent ammonium sulfate and 25 percent of the said sulfonated polymer. The polymer is of a molecular

weight which, as a 10 percent toluene solution gives an Ostwald viscosity of approximately 2,000 centipoises per second, and the polymer is sulfonated to the extent of sulfonate groups, presently neutralized with ammonium, on 70 to 90 percent of the recurring monomeric moieties. This industrial grade polymer is mixed and stirred well into the resulting solution.

In a separate container are mixed and stirred intimately together 20 grams dichloromethane (methylene chloride) and 0.2 gram paraffin wax melting in the temperature range of 115–120° F., and 0.05 percent of a commercial odorant (sometimes called also a reodorant). The paraffin is added in a molten condition to the dichloromethane with strong agitation to effect its prompt dispersion therein without its first separating as solidified particles.

This resulting methylene chloride solution is then added with gentle mixing and stirring to the aqueous preparation hitherto described and to the resulting mixture is added, lastly, 9 grams "Sodium Silicate D." This is a commercial substance and the said 9 grams represent, by analysis 1.3 grams sodium oxide, 2.64 grams silicon dioxide, and 5.03 grams water.

Various chemical reactions, incompletely known, take place within the resulting mixture. A bonding of some kind seems to occur between the ammonium salt of the sulfonated polyvinyltoluene, the glycol ether, and the triethanol amine, the two latter being thickening adjuvants for the former whereby a thickened viscous aqueous preparation is obtained. However, the ammonium sulfate by reaction with the sodium silicate yields also a thickened preparation and the two thickening actions appear to reinforce one another.

Also, reaction occurs between the sodium disilicate and the ammonium sulfate present with the sulfonated polyvinyltoluene whereby ammonium ion is released, probably in association with hydroxyl ion from the water.

The resulting substance is a stable paste-like material having excellent properties for the softening or removal of thermally degraded food residues, adapted to be applied as a paste with a brush or adapted to be applied as an aerosol spray from a can containing also propellant gas which gas is not a part of the cleaning composition itself, but only means for its mechanical delivery to a desired site.

EXAMPLE 8

An oven cleaning formulation was prepared by mixing together 2.5 parts of anhydrous sodium metasilicate, 5 parts of triethanolamine, 5 parts of diethylene glycol monoethyl ether, 20 parts of methylene chloride, 0.2 part of a paraffin wax having a melting temperature range from 115° to 120° C., 63.3 parts water, and 4 parts a water-soluble sulfonated polyvinyltoluene composition in the ammonium salt form, containing about 25 percent active polymer, and having a molecular weight of at least about 3 million, and a degree of sulfonic substitution within the range from about 80 to 90 percent. (A 0.5 percent neutral, aqueous solution of the purified polymer in the sodium salt form, which solution had been demineralized by passing it through an ion exchange resin in the acid form, exhibiting a viscosity above 30,000 centipoises at 25° C. as measured with a Brookfield viscosimeter employing a T-bar spindle rotated at 6 r.p.m.).

Methylene chloride (dichloromethane) was incorporated into the above formulation in order to improve its ability to clean highly carbonaceous deposits. In this instance, the triethanolamine was added as an emulsion stabilizer and the small quantity of paraffin added as an evaporation retardant for the methylene chloride. In other runs, water-soluble methyl cellulose ethers were employed successfully in the place of triethanolamines as emulsion stabilizers.

When mixed with about 10 percent by weight of monofluorotrichloromethane as propellant, the above formulation was conveniently utilized in the form of an aerosol

spray, the spraying being accomplished through an internal orifice 0.018 inch in diameter of an aerosol dispenser. The aerosol formulation was applied to a carbonaceous deposit obtained by baking a vegetable shortening on a porcelainized enameled surface. The above formulation loosened about one-half of the carbonaceous deposits in few minutes and accomplished complete loosening or removal thereof soon after.

Other organic solvents that can be employed in the place of methylene chloride in this example to enhance and potentiate the activity of the aforementioned oven cleaner formulation include carbon tetrachloride, ethyl chloride, 1,1,1-trichloroethane and the like halogenated organic solvents. The amount employed in combination with the thickened compositions of the invention can vary from as little as about 1 percent up to amounts in excess of 50 percent of the total composition. Generally, from about 20 to 35 percent is preferred.

EXAMPLE 9

The 4-component system of the present invention is readily formulated as a clear, transparent single-phase solubilized system which, under ordinary circumstances does not separate into aqueous and organic phases, by the use of suitable surfactant substances. One of the surfactant substances useful in the preparation of such solubilized systems is the sodium salt of a sulfated reaction product of tridecyl alcohol with three moles ethylene oxide. The product is commercially sold as "Solterge." Another such surfactant is the alkali metal salt of a sulfonated dodecylated diphenyl oxide, offered commercially under the trademark Benax 2A1. In a representative preparation, 2.5 grams sodium hydroxide dissolved as 5 grams aqueous solution thereof was placed in a mixing vessel. To this was added 4.8 grams of the sodium salt of sulfated reaction product of tridecyl alcohol with 3 moles of ethylene oxide, as aqueous solution containing 6 parts by weight of the said salt and 4 parts by weight of water. The resulting mixture was shaken to effect mixing of the two substances. To the resulting mixture was added 5 parts by weight aqueous solution of ammonia containing 28 percent ammonia by weight, (approximately one gram NH_3). The resulting mixture was again shaken until it became clear and thereto was then added 20 grams dichloromethane and subsequently an aqueous solution of the sodium salt of sulfonated dodecylated diphenyl oxide representing 13.5 grams of the said salt, and water sufficient to make 30 grams. The resulting mixture was again shaken, whereupon it became a clear 1-phase system.

The resulting preparation was applied at room temperature as a thin coating to the surface of a cast film of heat-degraded animal fat tenaciously adherent to a vitreous enamel subsurface, and of a dark brown color. The said solubilized system promptly and effectively acted upon the contacted parts of the animal fat film so to loosen it that it floated free immediately upon being lightly rinsed with water. It was also easily removed with a damp sponge.

By the judicious use of the indicated surfactant substances, solubilized 4-component cleansing compositions of the present invention are prepared as single-phase liquid systems.

Throughout the present specification and claims the expression "q.s. ad 100" is used to indicate the addition and employment of the designated component, typically water, in quantity sufficient that, added to the designated quantities of the other indicated components, the total is 100. This total is by weight except where expressly otherwise stated.

In succeeding examples herein, Surfactant I is Benax 2A1 and Surfactant II is Solterge, both as defined in the foregoing example.

[Components, as percent by weight of ultimate composition]

Example number	Dichloro-methane	Ammonia	Sodium Hydroxide	Surfactant I	Surfactant II	Water
10-----	50	2	2	7.6	6.6	Q.S. ad 100.
11-----	50	0.5	2	5.5	6.6	Q.S. ad 100.
12-----	20	1	5	12.2	4.8	Q.S. ad 100.
13-----	20	0.5	5	13	6	Q.S. ad 100.
14-----	20	2	2	8.1	6	Q.S. ad 100.
15-----	20	1	2	5.85	6	Q.S. ad 100.
16-----	20	0.5	2	5.85	6	Q.S. ad 100.
17-----	10	2	10	15.7	3	Q.S. ad 100.
18-----	10	1	10	13.5	3	Q.S. ad 100.
19-----	10	0.5	10	16.2	3	Q.S. ad 100.
20-----	10	2	5	15.2	6	Q.S. ad 100.
21-----	10	1	5	16.7	6	Q.S. ad 100.
22-----	10	0.5	2	5.4	9	Q.S. ad 100.
23-----	10	2	2	9	6	Q.S. ad 100.
24-----	10	1	2	11.5	6	Q.S. ad 100.
25-----	10	0.5	2	8.1	12	Q.S. ad 100.
26-----	5	2	10	11.2	3	Q.S. ad 100.
27-----	5	0.5	10	11.2	3	Q.S. ad 100.
28-----	5	2	2	9	6	Q.S. ad 100.
29-----	5	0.5	2	8.6	6	Q.S. ad 100.
30-----	40	2	5	21.2	4.8	Q.S. ad 100.
31-----	40	0.5	5	13.5	6	Q.S. ad 100.
32-----	40	2	2	6.8	6.6	Q.S. ad 100.
33-----	30	2	5	13.5	4.8	Q.S. ad 100.
34-----	30	0.5	5	13.5	6	Q.S. ad 100.
35-----	30	2	2	7.2	6.6	Q.S. ad 100.

Similar preparations were formulated employing, as alkali metal alkaline compound, a sodium metasilicate nonahydrate. The compound was of the formula $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, was water-soluble, and, in water solution was strongly alkaline. In all other respects, these preparations were identical with the foregoing, including the identities of surfactant substances employed. The resulting preparations were clear aqueous dispersions, soluble in all proportions in further water. The preparations were as follows:

[Components, as percent by weight of ultimate composition]

Example Number	Dichloro-methane	Ammonia	Sodium Meta-silicate Non-ahydrate	Surfactant I	Surfactant II	Water
36-----	50	2	7.2	5.4	6.6	Q.S. ad 100.
37-----	20	2	18.0	8.1	4.8	Q.S. ad 100.
38-----	20	0.5	18.0	8.1	6	Q.S. ad 100.

It is pointed out that 7.2 parts of the employed metasilicate is the equivalent, in the present examples, on a sodium oxide basis, of 2 parts sodium hydroxide; and that 18 percent of the employed metasilicate is the equivalent, sodium oxide basis, of 5 percent sodium hydroxide.

All the foregoing compositions were tested for their efficacy in freeing for effortless removal or actual removal of heat-degraded food residue substances on refractory surfaces, and all were found to be effective, although individual differences existed among them with respect to speed of action, and type of food residue upon which the greatest efficacy was apparent. The efficacy of any of them exceeded, by a substantial order of magnitude, the efficacy of any combination of less than the 4 critical ingredients. All were regarded as "solubilized systems" which were transparent liquids as prepared and could be diluted in any portion with water, without the separation out of any component.

All the foregoing compositions are readily thickened by the addition thereto of known thickening agents such as the sulfonate polymer-thickening adjuvant systems described in the examples foregoing or by the employment of starch, vegetable gums, and the like.

I claim:

1. A composition consisting essentially of, in intimate admixture, water, ammonia in an amount, expressed as

NH_3 , of from 0.05 to 10 percent by weight of water, an alkali metal alkaline compound in an amount from 0.1 to 15 percent by weight of water, and an aliphatic halo-hydrocarbon solvent of molecular weight up to about 150 whereof the halogen is selected from the group consisting of chlorine and bromine said solvent being present in an amount from 2 percent to 95 percent by volume of water, whereby the ammonia, alkaline compound, solvent, and water all contribute to the cleaning potentiation of the entire resulting mixture.

2. Composition of claim 1 wherein the alkali metal alkaline compound is sodium hydroxide and it is present in the amount of from 0.1 to 15 percent by weight of water and the aliphatic halo-hydrocarbon solvent is dichloromethane and it is present in the amount of from 2 percent to 95 percent by volume of water, and ammonia is present in the amount, expressed as NH_3 , of from 0.05 to 10 percent by weight of water.

3. Composition of claim 1 wherein the alkali metal alkaline compound is a sodium silicate and it is present in the amount of from 0.1 to 15 percent by weight of water and the aliphatic halo-hydrocarbon is dichloromethane and it is present in the amount of from 2 percent to 95 percent by volume of water, and ammonia is present in the amount, expressed as NH_3 , of from 0.05 to 10 percent by weight of water.

4. Composition of claim 1 comprising also a member of the group consisting of a nonionic and an anionic surfactant.

5. Composition of claim 1 comprising also a lightly cross-linked, water-swellaable, polymeric substance to increase the viscosity of the resulting preparation.

6. A composition consisting essentially, in parts by weight, of

(1) from about 50 to about 3,000 parts of a water-soluble thickening promoter selected from the group

- consisting of water-soluble alkylene and polyoxyalkylene glycols wherein the alkylene moieties contain from 2 to 4, inclusive, carbons, alkyl and aryl monoethers of said glycols wherein the alkyl group contains from 1 to 4, inclusive, carbon atoms and the aryl group contains from 6 to 10, inclusive, carbon atoms, lower alkanols containing from 2 to 4, inclusive, carbon atoms, dimethylformamide, dimethylacetamide, dioxane, tetrahydrofuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, mono-, di-, and trialkanolamines in which each alkylene moiety contains from 2 to 4, inclusive, carbon atoms, and mixtures thereof;
- (2) from about 5 to about 1,000 parts of water dispersible salt of a polymer sulfonate resin having a molecular weight above 1,000 in which from about 50 to about 90 percent of the monomer units have neutralized sulfonate groups;
- (3) from about 15 to about 3,000 parts ammonium sulfate;
- (4) from about 10 to about 3,500 parts of a strongly alkaline inorganic electrolyte selected from the group consisting of ammonium hydroxide, an alkali metal hydroxide, an alkali metal carbonate, an alkali metal phosphate, and an alkali metal silicate;
- (5) from about 200 to about 4,000 parts of a chlorinated organic solvent selected from the group consisting of dichloromethane, 1,2-dichloroethane, 1,1-trichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane, trichloroethylene and tetrachloroethylene;
- (6) from about 2 to about 400 parts of a paraffin wax melting at a temperature in the range of from 100° to 150° F.;
- (7) from 0 to about 100 parts of an odorant agent; and
- (8) from about 3,000 to about 9,000 parts water.
7. Composition of claim 6 but further containing from about 5 to about 200 parts of an alkali metal nitrite.
8. Composition of claim 7 consisting essentially, to a close approximation, of
- (1) 500 parts monoethyl ether of diethylene glycol,
- (2) 500 parts triethanolamine,

- (3) 85 parts ammonium salt of a water-dispersible sulfonated lightly cross-linked polyvinyl toluene having an average molecular weight of at least about 3 million and of the recurring aromatic nuclei of which about 80 to 90 percent are sulfonate substituted,
- (4) 265 parts ammonium sulfate,
- (5) 250 parts sodium disilicate,
- (6) 2,000 parts dichloromethane,
- (7) 20 parts paraffin wax melting in the range of from 115° to 120° F.,
- (8) 50 parts sodium nitrite,
- (9) 5 parts odorant,
- (10) water to make a total of 10,000 parts.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,296,147

January 3, 1967

Eugene M. Gatz

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 16, line 72, beginning with "6. A composition" strike out all to and including "10,000 parts.", in line 12, column 18; in the heading to the printed specification, line 7, for "8 Claims" read -- 5 Claims --.

Signed and sealed this 24th day of October 1967.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents