Patented Jan. 23, 1940 2,188,140

UNITED STATES PATENT OFFICE

2,188,140

CLEANING PREPARATION

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No Drawing. Application May 8, 1933, Serial No. 669,938

4 Claims. (Cl. 87—5)

This invention relates to cleaning preparations of the kind used about the household. Cleaners of this type generally contain alkalis having a detergent value, and soap, but heretofore the principal materials in such cleaners have been pumice, volcanic dust (sometimes known as volcanic ash or pumicite) feldspar and quartz, all of which are vitreous in structure and particle surface and harder than most of the ware on which they are used. Such materials are abrasive to the ware even when so finely divided as to operate inefficiently in loosening grease and dirt thereon. Cleaners of this type are generally limited in their uses for aluminum ware because of the corrosive and discoloring action, on the metal, of the alkalis contained in the cleaner. The principal object of the present invention is to devise a cleaner which will operate efficiently in removing dirt and grease without appreciable abrasion of glazed and porcelain coated ware, aluminum ware and other household utensils and articles, and which will not corrode or objectionably discolor the surface of aluminum.

The invention consists principally in a cleaner whose principal ingredient consists of particles of relatively soft mineral adapted to become plastic when wet and containing particles of sufficient size to operate efficiently to abrade softened dirt and grease. It also consists in the preparations hereinafter described and claimed.

The principal part of my cleaner consists of fine particles of limestone, of which a considerable proportion are small enough to pass a No. 325 U. S. Bureau of Standards sieve, a portion of said particles being too large to pass through a No. 200 U. S. Bureau of Standards sieve and any remaining particles being of intermediate sizes. It is noted that there are many cleaning preparations in the market in powder form. In all cases that I have found, their particles were small enough to pass through a No. 50 U. S. Bureau of Standards sieve; and, with one exception, their particles were small enough to pass the No. 80 sieve. Accordingly, "small particles," as used herein, is intended to indicate particles small enough to pass a No. 60 sieve.

In all instances herein, the number of a sieve refers to the standard of the U. S. Bureau of Standards. I have found that, when used in a household cleaner, the particles small enough to pass the said No. 325 sieve are not adequately effective in loosening softened dirt and grease, and that the abrasive ability, to loosen such soft dirt and grease, of the limestone particles too large to pass the No. 325 sieve increases approximately as the product of the two largest dimensions of the particle under consideration. Hence approximately the same degree of abrasive cleaning action may be obtained by taking a small proportion of large particles or a large proportion of relatively smaller particles retained on the No. 325 sieve, or by an intermediate quantity of varying sizes. For example, a suitable mixture of the sizes of the limestone particles may be made by taking ninety percent by weight of those particles, of a finely pulverized mass of limestone which has been reduced by normal commercial methods, which are small enough to pass the No. 325 sieve and adding thereto ten percent by weight of particles all of which are small enough to pass a No. 100 sieve and too large to pass a No. 140 sieve. Likewise a suitable mixture of sizes may be made by taking forty percent by weight of commercially ground particles small enough to pass the No. 325 sieve and adding thereto sixty percent by weight of particles all of which will pass the No. 200 sieve and are too large to pass the No. 230 sieve. However, such mixtures are not normal products of the regular processes of reducing the mineral particles, and they are therefore relatively expensive on account of the necessity of screening out the desired particles from normally ground material. My preferred proportions of the various sizes of limestone particles, and which may be produced by normal processes of pulverizing are: less than one percent large enough to be retained on the No. 100 sieve, about ten percent passing the No. 100 sieve and retained on the No. 200 sieve, and about ten percent passing the No. 200 sieve and retained on the No. 325 sieve, all the remaining limestone particles passing the No. 325 sieve. Satisfactory results are also obtained by proportioning the particles so that from five to thirty-five percent are too large to pass a No. 200 U. S. Bureau of Standards sieve and upwards of fifty percent will pass a No. 325 sieve, the remaining particles passing the No. 200 sieve but being retained by the No. 325 sieve. Satisfactory results are also obtained when from one to five percent of the particles are retained on the No. 100 sieve and upwards of sixty percent pass a No. 325 sieve, about five to thirty-five percent being sizes that pass the No. 100 sieve but are retained by the No. 325 sieve. The proportions here cited are given by way of illustration.

As set out hereinafter, it is of value that the

cleaner be plastic when wet. By "plastic" is meant having the faculty of absorbing moisture and retaining the same under pressure to such an extent that the mass coheres and is capable of flowing without rupture. A widely accepted theory of the reason for plasticity is the existence of colloids in the mass and their faculty for adsorbing water. Particles of most relatively soft minerals when reduced to colloidal size have the colloidal characteristic of adsorbing water. Of the particles of limestone which are small enough to pass the No. 325 sieve, a small proportion are of colloidal size and together with the next larger particles should be present in sufficient quantity to make the mixture plastic when wet. In natural impurities of the limestone, such as phosphates, metallic oxides, clayey matter and the residue of conchiolin of the prehistoric marine animals which are the origin of most limestones, there are generally present, in the finer particles and assisting to make the mixture plastic, small quantities of colloids. Mineral mixtures normally deficient in colloidal particles may be improved by the addition thereto of extraneous substances containing colloids; the amount added of such colloidal substance being regulated with respect to the degree of deficiency in said mixture and the nature of the added material. Such added material may be of varied forms and may be either inorganic, as for example finely divided colloidal clay, or it may be organic. In the latter case such organic material may be selected in kind and quantity not only for its colloidal content but also for its suitability as a diluent. For example, finely ground cereal is suitable because it contains colloidal matter and is comparatively nonabrasive and by its added bulk reduces the relative proportion of the larger mineral particles in the composition. Such added foreign colloidal matter may have either a detergent value or none. As used herein, "detergent" means a compound soluble in water and having the ability in the presence of water to emulsify oils. Detergents suitable for use in my preparation include soap and soluble alkaline salts of the alkali metals.

The largest particles form a relatively small proportion of the mineral matter. I have observed, when the larger particles are present in small proportion, the smaller particles cohere to the surface thereof and stabilize the mixture in such a way that the larger particles of minerals and the particles of other desirable substances added thereto remain scattered throughout the mixture even after long jarring, such as is incident to transportation. This cohesion of the particles of limestone and other relatively soft minerals having rough particle faces is generally greater than that of particles having vitreous faces. Likewise, I have observed, when the larger particles are used in relatively small proportion, the mixture as a whole remains plastic.

My composition contains also a small percentage of substantially dry soap particles or of one or more other suitable substances easily soluble in water and having a detergent value, or preferably a small quantity of suitable soap together with such other detergent substance. An important purpose of both soap and other detergent content is to soften dirt or grease so that the larger particles previously mentioned may loosen such softened material. As used herein, "soap" means a compound comprising at least one of the fatty acid salts of the alkali metals.

Carbonates of sodium are common as chemical agents in cleaners of this type and, to a less degree, so also is trisodium phosphate. Both have recognized detergent value. However the suitable softening of dirt and grease of obstinate nature with these substances requires the presence of such amounts of them as to create solutions of relatively high sodium oxide content, whereas even comparatively low concentrations of sodium oxide content obtained from these substances in the manner previously used, adversely affect aluminum surfaces. My invention also comprises new combinations of these detergents and also of other suitable substances, devised, through their embodiment in cleaning compositions, to permit the use even at high temperature, without injury to aluminum, of solutions of greater sodium oxide content and pH values than hitherto feasible. These combinations are described later herein.

In operation my cleaner is moistened with water, for instance, by application of a wet cloth, and rubbed on the surface to be cleaned. The finer particles serve to act in different ways. They serve to polish the surface of the ware and, suspended in and in conjunction with rinsing water, they serve to carry off the loose dirt, any suds present aiding in the latter action. The finer particles also serve as a plastic vehicle and lubricant for the larger particles, whose principal function is to scrape loose the coarse dirt softened by soap or other detergents, such loosened dirt being carried off with the plastic mass by rinsing. The plastic mass of particles serves also to hold the component constituents in proper distribution when wet, and furthermore, on encountering stiff resistance of dirt or grease, the mass flows plastically sufficiently to permit the larger particles of mineral to engage the dirt and grease to be removed. To more effectively soften particularly obstinate dirt or grease, it is feasible to put a quantity of my cleaner in a vessel containing water to make a solution which can be boiled so as to permit intimate contact at high temperature between the detergents and the material to be removed. Thus a greasy vessel may have its grease softened or a smaller greasy object may be boiled in the said vessel.

In the foregoing description, it is obvious that my invention admits of considerable variation in the preparation and proportions of its ingredients and I do not wish to be limited to any particular numerical proportions.

My preferred composition is as follows: about eighty-nine percent by weight of particles of sedimentary limestone of organic origin and meeting the specifications as to relative proportions of various sizes hereinbefore set forth as the preferred mixture of mineral particles, to which are added about two or three percent by weight of small particles of soap, together with about nine percent by weight of particles of sodium salts easily soluble in water and having appreciable detergent value, of which salts about one or two percent by weight consists of metasilicate of sodium.

Limestone as used herein refers to a rock consisting essentially of calcium carbonate, whether in the form of calcite or in the form of aragonite. When pure, limestones are soft rocks having a hardness generally of about 3. They occur in many varieties. Some may be of compact granular structure, some earthy or incoherent, whilst others may be crystalline limestones or marbles.

Although the calcite of limestones has a hardness of about 3, aragonite has a hardness of about 3.5 to 4 and is found in small proportions in most sedimentary organic limestones, the proportion increasing in the younger rocks. Small proportions of volcanic dust, quartz and other mineral impurities occur in some limestones. Likewise different forms of limestones and stones from the same quarry and even parts of the same stone commonly have particles of different degrees of friability. I have found that under pressure of rubbing, as in the cleaning operation, a considerable number of the calcite particles meeting substantial resistance will break up along cleavage planes and thus danger of scratching the ware is further reduced. With such a mixture, the soft and more friable particles are sufficient to deal with loose and soft dirt that yields to short rubbing, while the harder and less friable particles are brought into play to deal with the harder and more obstinate dirt. Where the hardness or softness of minerals or mineral particles is mentioned herein, either by a numerical designation or otherwise, I have reference to the hardness of such minerals as established in Mohs scale.

The calcium carbonate of limestone is soluble in many organic acids and in dilute solutions of most inorganic acids. The organic acids of household wastes when passed through the drains therefore act to dissolve the residue of my cleaner and reduce the danger of clogging drains and sewers. Dilute inorganic acids, such as dilute hydrochloric acid, may be used specifically for dissolving such residue; and when so used in suitable concentration, such acids are substantially harmless to the metal of the drains.

Although the sedimentary limestones of organic origin are described hereinbefore as containing small proportions of impurities and having other characteristics of value in my composition, I have found that many other minerals, which are essentially calcium salts, and also other minerals softer than about 4.5 and substantially insoluble in water have in varying degree characteristics in common with the preferred limestone, and while I have hereinbefore described the insoluble mineral matter of my composition as being limestone, it is feasible to substitute therefor other calcium salts softer than about 4.5 or other relatively soft suitable mineral substantially insoluble in water. It is noted that limestone, fluorspar and all other materials mentioned herein are harder than 2.5. Fluorspar having a hardness of about 4, has particle faces, which are vitreous rather than rough, and shows no substantial plasticity; nevertheless it splits very easily along cleavage planes and being brittle may easily be very finely ground with but small proportions of the particles above the No. 325 sieve, and the abundance of very fine particles and the ease with which its particles split along cleavage planes, compensate for the lack of plasticity sufficiently to also make fluorspar an acceptable substitute for limestone in my composition. Although I describe minerals as the principal constituent of my composition, it is obvious that substantially insoluble particles of manufactured salts of similar chemical composition to the minerals described may be used in lieu thereof.

While I have hereinbefore described the mineral matter of my composition as being entirely of relatively soft materials, it is feasible to use such soft material for the particles too large to pass a No. 325 sieve, in mixture with finely ground harder material of a kind commonly used, such as pumice, volcanic dust, feldspar and quartz. While such harder materials are abrasive to the ware due to their hardness and the sharpness of their particles even in finely divided form, a mixture thereof with larger particles of softer mineral matter enables the cleaning to be done rapidly and with less abrasion than with any similarly effective mixture of such hard minerals alone. Conversely, although not so desirable, it is feasible to use finely ground harder minerals such as pumice, volcanic dust, feldspar and quartz too large to pass the No. 325 sieve in connection with limestone or other suitable relatively soft mineral particles for all or part of the smaller particles, provided the mixture contains a sufficient quantity of the very fine particles to make the mixture plastic when wet. Likewise in the composition there may be large and small particles of the group of suitable soft minerals together with large and small particles of the group of harder minerals, provided the mixture contains about ten percent or more by weight of the finer particles of the softer minerals. For example: feasible compositions may comprise substantially insoluble mineral particles of which from about twenty percent to about sixty percent by weight consist of large and small particles of the soft minerals suitably sized as above described with the remainder suitably sized large and small particles of the harder minerals. When available mineral matter, otherwise suitable, contains too large particles or too great a proportion of suitably sized large particles, it is also feasible to reduce the relative proportion of these large particles and to mask their excessive abrasive action by adding finely divided relatively insoluble organic matter preferably adapted to become slippery when wet.

Frequently the contents of a cooking vessel are burned on it due to evaporation of the liquid. Such matter and cooked grease may be as hard as the surface of the vessel or harder. To soften such cooked material, a high concentration of sodium oxide content in hot solution is desirable. In an aluminum vessel, such high concentrations of sodium oxide content, in the combinations of sodium salts commonly used, will cause a chemical reaction to corrode or objectionably discolor the aluminum. Buffered salts offer desirable features in all types of cleaners since buffered solutions expend their detergent value relatively uniformly over the cleaning period; but such salts offer other advantages as pointed out immediately hereafter. For example, while a phosphate of sodium does not prevent a solution containing a sodium carbonate from injuring aluminum, it does react favorably in this connection in combination with suitable proportions of a silicate of sodium; and a silicate of sodium in suitable proportions similarly reacts favorably on either sodium carbonates or phosphates of sodium. This action with respect to the protection of aluminum consists in a protective film or coating formed by colloidal matter in the silicate. In chemical combinations as described, there should be not more than thirty (30) parts of sodium carbonate to each part of a silicate of sodium; there should be not more than eight (8) parts of a silicate of sodium to each part of a phosphate of sodium; and there should be not more than ten (10) parts of a phosphate of sodium to each part of a silicate of sodium. My preferred mixture of detergents other than soap is, about one-half part by weight of tri-

sodium phosphate, about one or two parts by weight of sodium metasilicate and about seven (7) parts by weight of sodium carbonate and when used for industrial duty requiring high sodium oxide concentration or high pH value, the water added thereto may be as little as about one hundred (100) parts by weight. By using proportions as described directly above, a concentration in water of as high as ten percent of sodium oxide content can be boiled in an aluminum vessel without injury to the surface. Such a concentration is about five times stronger than is usually necessary for household cleaning; so it is evident that not only is careful control of the concentration of sodium oxide content not necessary when the described combination of chemical agents is used in a cleaner of this type, but that this feature of my invention is of further value in solutions for use in industrial cleaning of aluminum or other metals, in which solutions insoluble mineral particles may or may not be necessary for the cleaning operation but where high sodium oxide concentrations and high pH values are of advantage. The addition of about two or three parts by weight of soap in suitable form is helpful in some cleaning operations, but not essential, and since sodium silicates are not only good detergents, outstanding as wetting agents but also act as dispersers, they help, without serious adverse effect on the plasticity of the mass of a cleaner of the type first described, to hold in solution, particularly in the rinsing operation, loosened particles of dirt.

Many cleaners, whose principal ingredient or ingredients are mineral, contain soap, for example, tallow soap, vegetable oil soap or tallow rosin soap, either singly or combined. I prefer to include in my cleaner a tallow soap or a vegetable oil soap to the extent of from about one percent to about fifteen percent of the total weight of the cleaner; and it is desirable for such soap (whether tallow or vegetable oil) to contain sodium silicate to the extent of about fifteen percent or more of the total weight of such soap or, say, from about one-half percent to four percent of the total weight of the cleaner. I have found that such silicate soap serves to prevent corrosive action and objectionable discoloration of aluminum when used in a cleaning composition provided that such composition contains not more than about ten percent by weight of a suitable carbonate of sodium nor more than about five percent by weight of trisodium phosphate. When a silicated soap, as described, together with suitable proportions of the other chemical agents as previously described, is used in a cleaner, the sodium silicate content of the soap when added to the cleaner in the proportions previously described herein for sodium silicates is sufficient to similarly protect aluminum.

Powdered rosin in combination with a sodium compound, such as sodium carbonate in the proportion of about 100 parts by weight of rosin to about 15 parts by weight of sodium carbonate, forms a sodium rosinate which has detergent value similar to soaps made from animal fats or vegetable oils. This union of rosin and sodium carbonate is generally carried out in the presence of substantial heat either by melting the rosin and adding the sodium carbonate and a small amount of water and heating the mixture, or by boiling a solution of the sodium carbonate and water and adding the rosin thereto gradually. This process as described usually requires the addition of a small quantity of sodium hydroxide to complete the action and the entire process involves considerable labor. I have found that by the addition of suitably powdered rosin to my composition containing sodium salts, such as sodium silicates or sodium carbonate, there is a chemical reaction as previously described, which takes place in the water of and during the cleaning operation, and which, while not instantaneously completed for all the rosin content, still furnishes appreciable detergent value and sufficient suds to aid in carrying away the loosened particles of dirt. The addition of rosin to the composition in the manner described may be in the presence of other soap to increase the suds. Similar resinous substances may be used in lieu of the rosin, such as rosin, abietic acid, pimaric acid and kindred acids.

What I claim is:

1. A cleaning preparation of substantially dry materials consisting mainly of crushed limestone particles of which upwards of fifty percent by weight are small enough to pass a No. 325 U. S. Bureau of Standards sieve, from five percent to thirty-five percent by weight of said particles being too large to pass a No. 200 U. S. Bureau of Standards sieve, the remainder of said particles being small enough to pass the No. 200 sieve and large enough to be retained on the No. 325 sieve.

2. A cleaning preparation of substantially dry materials consisting mainly of crushed limestone particles of which upwards of sixty percent by weight are small enough to pass a No. 325 U. S. Bureau of Standards sieve, from one percent to five percent by weight of said particles being too large to pass a No. 100 U. S. Bureau of Standards sieve, the remainder of said particles being small enough to pass the No. 100 sieve and large enough to be retained on the No. 325 sieve.

3. A composition of substantially dry materials adapted for use as a cleaner when rubbed with water directly on the surface to be cleaned, consisting principally of particles of crushed limestone with which are mixed particles of detergent easily soluble in water, between five and thirty-five percent by weight of said limestone particles being too large to pass a No. 200 U. S. Bureau of Standards sieve and upwards of twenty percent by weight being small enough to pass a No. 325 U. S. Bureau of Standards sieve, said detergent belonging to the group which consists of soaps and soluble alkali metal alkaline salts.

4. A cleaning composition consisting of about eighty-nine percent by weight of particles of sedimentary limestone of organic origin, about two to three percent by weight of small particles of soap, and about nine percent by weight of particles of sodium salts easily soluble in water and having appreciable detergent value, of which salts about one to two percent by weight consists of metasilicate of sodium, less than one percent of the limestone particles being large enough to be retained on a No. 100 sieve, about ten percent passing the No. 100 sieve and retained on the No. 200 sieve, about ten percent passing the No. 200 sieve and retained on the No. 325 sieve, and the remaining limestone particles passing the No. 325 sieve.

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