

- [54] **METHOD AND COMPOSITION FOR CLEANING SURFACES**
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[57] ABSTRACT

A method and formulations for cleaning painted aluminum siding and other metal, organic resin and the like surfaces comprising applying to the surface a layer containing a water-insoluble finely divided absorbent material and an oxide remover solution such as an aqueous acidic solution containing a phosphate radical and after the first layer has dried applying thereover a second layer which contains water-insoluble finely divided solid absorbent material in a liquid mixture including a water-soluble organic solvent and a compound selected from the group consisting of sodium nitrite, soluble silicates, and a water-insoluble organic solvent and after the first layer has been absorbed through the first layer removing the layers as by washing with water. The invention has special utility for cleaning and preparing architectural aluminum siding for refinishing with paint or other protective coatings.

11 Claims, No Drawings

METHOD AND COMPOSITION FOR CLEANING SURFACES

This invention relates to a method and formulations for cleaning metal, organic resin and the like surfaces. The invention has particular utility for cleaning aluminum siding, as is presently in common use in home and other building construction, and hence will be described chiefly with reference thereto. However, the invention also has utility for cleaning other surfaces of metal, organic resin and the like — for example awnings and similar structures formed of fiberglass reinforced polyester resin. In this connection it should be mentioned that the term "organic resin" surfaces as used herein comprehends not only surfaces of structures formed entirely of organic resin but also surfaces consisting of paint, lacquer, enamel or similar coating materials. Further in this connection the term "aluminum siding" will be used herein to mean not just unpainted aluminum sheet or siding but also, and most generally, aluminum siding which is coated with a decorative finish of paint or enamel such as is used for home construction and other architectural purposes.

Aluminum siding has become a very popular material for building construction, particularly private homes, because of its reputation for being quite durable and relatively maintenance free. The home builder, given the choice between painted wood siding and aluminum siding, frequently chooses the latter simply because with wood siding there must be repainting every four or five years whereas with aluminum siding it is expected that no repaintings or other refinishing will be necessary for perhaps ten years. From the standpoint of resistance to corrosion, rot or other serious deterioration it is indeed a fact that aluminum siding generally outlasts, with minimum maintenance, other materials such as painted wood. Further, for a home built in a rural area far away from the smoke and grime of an urban or industrial community, the aluminum siding will generally also retain a clean and pleasing appearance for many years. However, for homes within or close to an urban or industrialized area the difficulty is that the aluminum siding, while not rotting or otherwise seriously deteriorating structurally, nevertheless can become unsightly because of accumulations of dirt and grime and because of oxide accumulations the formation of which can be stimulated by deleterious impurities in the air.

There has been reference above to the fact that some of the surface deterioration and resulting unsightly appearance of aluminum siding after a few years is due to oxide formation. Of course, just as is the case with any paint or enamel exposed to the sunlight and outside environment, so with the paint or enamel used as the coating on aluminum siding there is a certain amount of oxidation, over the years, of the paint or enamel constituents such as the organic resins and with this, in turn, loosening of some of the pigment. But what is a particular source of appearance deterioration, due to oxide formation, in the case of aluminum siding in the presence of pin holes, scratches and the like through the paint or enamel which thereby exposes the aluminum. Theoretically, there should be no such bare spots exposing the aluminum; however, as a practical matter they are almost invariably present at least by the time the aluminum siding is in place on the home. This occurs not only because of scratching and other marring in the handling of the siding subsequent to its manufac-

ture but also, as is usually the case, because of various manufacturing irregularities, even though perhaps of a minor nature, in the production coating of the aluminum at the factory. In addition to the oxide formation which occurs, there is of course, also staining and soiling of the aluminum siding over the years from grease, asphalt, tar, oil, smoke, rust stains from adjacent nails or other ferrous metal members, and general soil resulting from the atmosphere, along with splash marks and the like.

Hence, though aluminum siding does have excellent durability from the standpoint of resisting serious structural deterioration, nevertheless, it is subject to developing an unsightly appearance over the course of just a few years, particularly in urban and industrial environments. The real problem has been that, until the present invention, there has not been available a relatively simple, safe and low cost method for efficiently cleaning aluminum siding. Various methods have been used but all have marked deficiencies.

One method for cleaning siding is that of abrading or blasting with abrasive materials. This is commonly used on stone or brick structures though it is quite messy and requires considerable equipment. But even aside from these deficiencies, the method is inferior for the cleaning of aluminum siding because aluminum siding simply does not have the structural rigidity of brick or stone and, further, there is the hazard that the abrasive will deteriorate the paint or enamel such that even though the surface might be cleaned it is degraded by way of the loss of the protective coating. Also, abrasive blasting or other abrasion techniques are not particularly effective in the removal of stains and deposits of organic materials such as grease, oils, tar or the like.

Chemical methods have been used for the cleaning of aluminum siding but such methods as have heretofore been used have been time consuming and hence expensive. For example, one such method which can be used is to first remove the organic deposits and stains by washing the siding with one or more organic solvents, then thoroughly washing the siding and thereafter applying any of various mineral acid solutions for the removal of oxide accumulations. This is then followed by a second washing operation. A reverse procedure can also be used, i.e., removal of oxide accumulations by the use of acid solutions, washing, removal of the organic stains and deposits with organic solvents and then a second washing. In addition to the aforesaid disadvantages of such procedures there is the difficulty that there can easily occur brush marks or streaking of the aluminum siding by way of the brushing and scouring used in the application and removal of the various cleaning materials.

It is an object of the present invention to provide a simple, inexpensive, safe and efficient method for the cleaning of metal, organic resin and the like surfaces — and especially for the cleaning of aluminum siding.

A second and attendant object of the invention is the provision of formulations for the practice of the method, which formulations can conveniently and safely be applied to the surface to be cleaned by the workmen at the work site.

Briefly, these objects are accomplished in accordance with the invention, in its broadest scope, by a method wherein there is first applied to the surface to be cleaned a coating of a slurry of water-insoluble finely divided solid absorbent material in an aqueous

solution of oxide remover, applying over this first coating a second coating comprising organic solvent and preferably also containing finely divided solid material, and thereafter removing the coatings. In the much preferred embodiment of the invention the oxide solution is an aqueous acidic solution containing phosphate radical, ideally phosphoric acid, the solution also having dissolved therein chelating agent, a surfactant and preferably also an inhibitor to prevent excessive attack by the solution on unoxidized metal surfaces. Further in accordance with the most preferred embodiment of the invention, the second layer or coating which is applied comprises a slurry containing finely divided solid absorbent material, an aqueous cleaning enhancer solution and an organic solvent, ideally a mixture of various organic solvents, as will hereinafter be discussed in detail. The aqueous cleaning enhancer solution contains sodium nitrite as well as certain other ingredients herein after discussed; and, in certain cases the sodium nitrite may be replaced in whole or part by soluble silicates. In practice, after the first coating is applied it is allowed to dry slightly or "set" which takes only a short period, after which the second coating is applied and then, after another short period, both coatings are removed as by simply washing them away from the surface with a hose. The method can be effectively practiced by a workman after a short period of training and the cleaned surface resulting from the use of the method is so very clean and bright as to be as favorable in appearance as the aluminum siding at the time of its initial installation.

It might be expected that it would be preferred to incorporate the organic solvent into the initial layer applied to the siding to the end of dispensing with the need for the application of a second layer. But, to the contrary, I have found that if the organic solvent is included in the oxide remover slurry it interferes with the function of the slurry in the removal of oxides and in loosening surface dirt. When, in accordance with the present invention, the organic solvent is in a coating applied subsequent to and over the first coating, the solvent is absorbed through the first layer sufficiently slowly that by the time the solvent reaches the surface being cleaned, the oxide remover formulation has already sufficiently performed its intended function of removing oxides and loosening surface dirt to the end that the solvent can then readily perform its function of dissolving the organic deposits and stains. As alluded to above, the most preferred embodiment of the invention, wherein the layers applied contain additional ingredients is especially effective toward the attainment of a very clean surface with minimum difficulty and trouble.

Other objects, features and advantages of the invention will appear more clearly from the following detailed description, chiefly referenced to the preferred embodiments thereof. But before proceeding further it should be mentioned that whereas in the practice of the invention only two coatings need be applied as described above, I have found that there are advantages to shipping the formulations for the practice of the invention to the site where it is to be used not in the form of a two-package system — one for the first coating and the other for the second coating — but instead in a three-package or four-package system. That is, one package is the material for application of the first coating, another of the packages is the aqueous solution

containing all the water-soluble ingredients for the second layer, and the third package contains the waterinsoluble organic solvent for incorporation into the second layer. The solid infinitely divided absorbent material for the second layer can be shipped separately or incorporated into either of the second or third packages. The detailed description of the preferred embodiments of the invention describes the various formulations largely in terms of the make up of these packages.

FORMULATION FOR THE FIRST LAYER

As mentioned above, the first coating of layer applied to the surface to be cleaned comprises a slurry of water-insoluble solid absorbent material in an aqueous oxide remover solution.

Oxide Remover Solution

The preferred oxide remover comprises an aqueous acidic solution containing phosphate radical, a chelating agent and a surfactant.

The phosphate radical is preferably supplied by phosphoric acid and is the main active component in the removal of oxides. Also, it imparts some brightness to the cleaned surface, particularly if the surface is a metal such as aluminum. Ordinary commercially available orthophosphoric acid of technical grade and a concentration of 75% to 85% is excellent for preparation of the solution, it simply being a matter of adding the other ingredients along with water thereto in order to attain the concentration desired. The final solution should contain from about 10 to 70 parts, and preferably about 20 to 40 parts, by weight of phosphate (i.e., phosphate radical) per 100 parts by weight of solution. Since PO_4^{116--} , HPO_4^{116-} , $\text{H}_2\text{PO}_4^{116}$ and H_3PO_4 are so similar in their molecular weights, this means that where, as is preferred, phosphoric acid is used to prepare the solution, the amount should be such as to provide the aforesaid 10 to 70, and preferably 20 to 40, parts by weight phosphoric acid (on a dry weight basis) per 100 parts by weight of the solution. Though disadvantageous, particularly from the standpoint of cost, other compounds can be used to supply the phosphate radical, examples being: metaphosphoric acid, pyrophosphoric acid and sodium dihydrogen phosphate.

A chelating agent is employed in the solution to assist in the removal of oxides, particularly metal oxides. Suitable chelating agents include the aliphatic carboxylic acids, preferably the aliphatic polycarboxylic acids. Among the many acids which may be employed are the mono, di, or tricarboxylic acids such as lactic, tartaric, or citric acid, either separately or in combination. Also, glycolic acid and the sugar based chelating acids, such as gluconic or glucoheptanoic acid may be used separately or in combination with other acids mentioned above. It is preferable to employ from about 2.5 to 4.0 parts by weight of such chelating acid or acids per 100 parts by weight of the oxide remover solution. In all cases, however, it is preferable that the total amount of chelating acid or acids in the solution be from about 10 to 15% by weight of the phosphoric acid (dry weight basis) employed in the solution.

The surface active agent in the oxide remover solution acts as an emulsifier, thus assisting in cleaning of other surface dirt by emulsifying oily components thereof. It is preferred to use a nonionic surfactant; and a preferred series of nonionic surfactants is sold under the trademark Igepal by General Aniline and Film Cor-

poration of New York, N.Y. This is a series of biodegradable nonionic surfactants comprising alkylphenoxypoly (oxyethylene) ethanols, resulting from the combination of a alkyl phenol with ethylene oxide. The general formula is $RC_nH_{4n}O(CH_2CH_2O)_nCH_2CH_2OH$ in which R may be C_8H_{17} or a higher homologue and $n = 7-9$. A suitable member of this series is Igepal Co 630 which is nonyl phenoxypoly (oxyethylene) ethanol. Other commercial surfactants of this composition are also sold by Rohm and Haas Company of Philadelphia, Penn. under the trademarks Triton X 100 and Triton X 101. It is preferred that from about 1 to 3 parts by weights of the nonionic surfactant per 100 parts by weight of the oxide remover solution be employed. Best results are obtained by using about 1.5 parts by weight of the surfactant per 100 parts by weight of the solution.

Although not necessary, an effective inhibitor may be employed in the acidic oxide remover to prevent attack by the acid solution on unoxidized metal surfaces and to prevent pitting and dulling. The use of such an inhibitor is particularly desirable when the surface being treated is not one which has previously been protected or coated, i.e., one which is an exposed surface of metal, or a surface having numerous scrapes or abrasions thereon which expose the bare metal surface. Numerous inhibitors are available commercially and their selection would be within the skill of the artisan and depend upon the particular type of metal surface being cleaned. As is well-known, the composition of inhibitors varies widely. Numerous by products such as sludge acid from oil refineries, waste animal material, waste sulfite cellulose liquor, etc. have been employed. However, synthetic inhibitors are preferred since they afford greater uniformity and effectiveness. Among the synthetic inhibitors available are complex structures of amines, aldehydes, mercaptans and other organic compounds as well as organic nitrogen bases and their derivatives, particularly those linked with the heterocyclic ring, such as pyridine and quinidine. Many of these compositions are available commercially under proprietary names. Particularly effective inhibitors for use in the instant acidic oxide remover are those which contain a thiocarbonyl group. Therefore, thiourea or one of its esters such as diethylthiourea or a combination thereof is preferred. These inhibitors form an addition compound on the surface of the metal, thus preventing excess erosion and, thereby, lowering the consumption of acid. The amount of inhibitor employed depends on the workpiece composition, the particular acidic oxide remover formulation, the temperature of use and the nature of soil being removed. Generally, however, the amount of inhibitor may be conveniently varied from about 0.5 to 2 parts by weight of the oxide remover solution.

The pH of the oxide remover solution may range from about 2.2 to 3.4.

The following is a typical formulation of the oxide remover solution which may be employed in the process of this invention, the parts by weight being based upon 100 parts by weight of the oxide remover solution:

phosphoric acid, dry weight basis	20 to 40 parts
citric acid	2 to 4 parts
lactic acid	1 to 2 parts
thiourea	0.5 to 1 part
diethylthiourea	0.5 to 1 part

-Continued

nonionic surfactant
water1 to 3 parts
75 to 49 parts

A specific example of an oxide remover solution useful in this invention is as follows, the parts by weight once again being based upon 100 parts of the solution.

phosphoric acid	26 parts
citric acid	3 parts
lactic acid	1 part
thiourea	0.75 parts
diethylthiourea	0.75 parts
Igepal CO 630	1.50 parts
methyl alcohol	2 parts
water	65 parts

Absorbent Material For First Layer

A finely divided water-insoluble solid absorbent material is blended with the oxide remover solution discussed above and forms a slurry therewith.

The solid absorbent material is a micron or submicron sized absorbing agent, preferably a colloidal silica compound. Many such absorbing agents are available commercially, including those containing distomaceous earth. A preferred submicron sized solid absorbent is sold under the trademark Cab-O-Sil by Cabot Corporation of Boston, Mass. This absorbent comprises colloidal silica particles sintered together in chain-like formations, the surface area thereof ranging from 50 to 400 square meters per gram, depending upon the grade employed.

The viscosity of the slurry may be increased or decreased by changing the ratio between the oxide remover solution and the micron or submicron sized absorbing agent. The selection of a suitable viscosity for the slurry will, of course, depend upon the particular surface to be treated. For example, when aluminum siding is being cleaned it is necessary that the slurry have a viscosity sufficient to allow it to stay on the vertical surface; and a preferred slurry for cleaning aluminum siding may be prepared by blending from about 80 to 100 grams of the water-insoluble finely divided solid material with one gallon of oxide remover solution.

Generally between about 1 and about 6 parts by weight of absorbent based on the total weight of the first layer formulation may be used and will produce a slurry having a viscosity of 800-2000 cps. A slurry containing from about 2.5 to 3 parts per 100 parts of the formulation is preferred.

FORMULATION FOR SECOND LAYER

The slurry which forms the second coating or layer contains, in accordance with the most preferred embodiment, an aqueous cleaning enhancer solution, water-insoluble organic solvent and finely divided solid absorbent material.

CLEANING ENHANCER SOLUTION

The cleaning enhancer solution employed in the instant invention preferably contains either sodium nitrite, soluble silicates or mixtures thereof, and also contains certain inorganic and organic components to emulsify and separate oily soil and dirt from surfaces

such as aluminum or organic resins without damaging or pitting the same.

The preferred cleaning enhancer solution contains as its active component sodium nitrite. Such an enhancer is particularly useful when the surface to be cleaned is a painted surface such as painted aluminum siding or other organic resin surface such as reinforced polyester. When the cleaning enhancer containing sodium nitrite is applied to the first layer formulation containing the acidic oxide remover solution, the sodium nitrite therein will react with the acids in the first layer formulation, e.g., the phosphoric acid and the organic acids, and form nitrous acid. The reaction begins slowly initially and then increases in rate such that the components of the two layers are put in motion or stirred up. Thus, the nitrous acid itself serves to enhance the cleaning function of the first layer by providing further acid cleaning. Also the motion or stirring up of the materials in the two layers, due in part to the decomposition of the nitrous acid, aids in the cleaning of the surface by allowing greater exposure of the cleaning materials to the surface being cleaned. The sodium nitrite may be employed in an amount from about 0.1 to 10 parts by weight of the cleaning enhancer solution. However, 1.5 parts of sodium nitrite per 100 parts of cleaning enhancer solution is preferred.

The cleaning enhancer solution also contains a chelating agent which is preferably a complex phosphate. For example, tetrasodium pyrophosphate, sodium tripolyphosphate, sodium hexametaphosphate and other complex phosphates which are conventionally employed as chelating agents may be used. The complex phosphates will enhance the cleaning action of the material while at the same time solubilizing metallic oxide contaminations by forming coordination complexes with metallic ions in solution. If it is preferred to use phosphate-free chelating agents, conventional chelating agents such as ethylenediaminetetraacetic acid, nitrilotriacetic acid or sodium salts of these as well as mono, di, or tricarboxylic acids discussed above may be used. The amount of chelating agent in the solution preferably varies between about 2 and 5 parts by weight per 100 parts of the cleaning solution.

The cleaning enhancer solution also includes a surfactant which may be of the anionic, cationic or nonionic type. Among the anionic surfactants which may be employed are: sodium, ammonium, potassium or amine salts of linear alkyl aryl sulfonic acids (C_8-C_{18} , and in particular C_{12}); sodium, ammonium, potassium, or amine salts of dodecyl benzyl sulfonic acids; sodium, ammonium, potassium or amine alkyl sulfates (C_8-C_{22} ; and, in particular, $C_{12}-C_{14}$); sodium, ammonium, potassium or amine salts of ethoxylated fatty alcohol sulfates; sodium, ammonium, potassium or amine salts of alkyl (C_8-C_{14}) phenoxy poly (oxyethylene) sulfates; and many others. Suitable cationic surfactants which may be employed include: dialkyl (C_8-C_{18}) dimethyl ammonium chloride; alkyl (C_8-C_{18}) trimethyl ammonium chloride; alkyl benzyl ammonium chloride; substituted imidazolines such as 2-alkyl (C_8-C_{18})-1 (ethyl beta oxypropanoic acid) imidazolines as well as amine, alkali or acid salts thereof; ethoxylated fatty acid amines; and many others.

The nonionic surfactants are the preferred class of surfactants for the instant invention and should preferably be present in the amount of 1 to 5 parts by weight per 100 parts by weight of the cleaning solution. In gen-

eral, the same class of nonionic surfactants as employed in the oxide remover solution discussed above may be used in the cleaning enhancer solution. In particular the preferred surfactant may be an octyl or nonyl phenoxy poly (oxyethylene) ethanol in which the compound shall contain 7 to 9 moles of ethylene oxide. Commercial surfactants of this composition are available from GAF (Igepal Co 630) or by Rohm Hass (Triton X 100 or X 101) and from many others. Also, the hydrophobic group in the nonionic surfactant may be changed to a primary or secondary linear alcohol having a carbon chain of 8-18; in other words, the surfactant may be polyalkylene ether of a primary or secondary alcohol (C_8-C_{18}). Surfactants of this composition are available from Union Carbide as Tergitol 15-S-7 or 15-S-9, a polyethylene glycol ether of a linear secondary alcohol (containing 7-9 moles of ethylene oxide).

The cleaning enhancer solution also contains a water soluble organic solvent. The water-soluble organic solvent preferably is selected from the group consisting of mono, di, or triethylene glycol ethers of primary alcohols. For example, primary alcohol ethers of ethylene glycol or diethylene glycol such as ethylene glycol monethyl, monomethyl, or monobutyl ethers of diethylene glycol ethyl, methyl or butyl ethers may be employed. The two best solvents for the purpose of the invention are ethylene glycol ethyl or butyl ethers. Although the above solvents are preferred, it has been found that any conventional water-soluble organic solvent having a boiling point sufficiently high so as to not flash off upon being applied to a heated surface such as sunlight heated aluminum siding may be employed. Thus, such common solvents as alcohols, including ethanol, isopropanol and methanol, as well as acetone, Cellosolve (2-ethoxyethanol) and many others are suitable. The solution should contain between 3 and 10 parts by weight of the water-soluble solvent per 100 parts by weight of solution.

A typical formula for a suitable cleaning enhancer solution containing sodium nitrite is as follows, ranges being indicated in parts by weight per 100 parts by weight of the solution:

45	sodium nitrite	0.1 - 10.0 parts
	sodium tripolyphosphate or	
	ethylenediaminetetraacetic acid	1.0 - 5.0 parts
	butyl cellosolve	5.0 - 20.0 parts
	nonionic surfactant	2.0 - 8.0 parts
	water	91.9 - 57.0 parts

50 An analysis of a specific example of a cleaning solution which may be employed is as follows:

55	water	79.5 parts
	sodium nitrite	1.5 parts
	sodium tripolyphosphate	2.0 parts
	butyl cellosolve	12.0 parts
	nonyl phenoxy poly (oxyethylene)	
	ethanol	5.0 parts

60 When the surface to be cleaned is unpainted aluminum or painted aluminum with significant portions of exposed aluminum, it may be preferable to employ an enhancer solution wherein the sodium nitrite has been replaced in whole or in part by an alkaline builder material such as sodium or potassium compounds including carbonates, phosphates, silicates, hydroxides, and the tetraborates. The silicates are, however, most suitable for use in this alternative cleaning enhancer solu-

tion, particularly when the surface to be cleaned is a metal such as aluminum since it is known that silicates protect aluminum surfaces against corrosion. Sodium orthosilicate, sodium metasilicate and sodium sesquiosilicate are excellent emulsifiers, good buffers and hold soils in suspension. Sodium metasilicate is the silicate most preferred for use in this alternative cleaning enhancer solution, the metasilicate being more versatile than the other silicates since the ratio of Na_2O to SiO_2 can be adjusted easily over a wider range than the others by simply adding sodium hydroxide. Such a cleaning enhancer solution may contain between about 2.5 and 6 parts by weight per 100 parts by weight of solution. A typical formula for a suitable alkaline cleaning enhancer solution is as follows, ranges being indicated in parts by weight per 100 parts by weight of the solution:

sodium metasilicate anhydrous	2.5 - 6.0 parts
sodium tripolyphosphate or ethylenediaminetetraacetic acid	1.0 - 5.0 parts
ethylene glycol butyl ether	3.0 - 10.0 parts
nonionic surfactant	1.0 - 5.0 parts
water	92.5 - 74.0 parts

An analysis of a specific example of a cleaning solution which may be employed is as follows:

water	86.0 parts
sodium metasilicate anhydrous	2.5 parts
sodium tripolyphosphate	2.5 parts
ethylene glycol butyl ether	7.0 parts
nonyl phenoxy poly (oxyethylene) ethanol	2.0 parts

Total solids: 14 parts, pH(.5% sol):9.1:pH(1% sol.):9.45

Water Insoluble Organic Solvent Solution

The solvent solution comprises one or more water-insoluble organic solvents and a nonionic emulsifier. Of primary importance in the selection of a suitable solvent and the amount thereof is the type of soil to be removed and the temperature of the surface to which the solvent will be applied. For example, in the instance wherein aluminum siding, which is disposed on the face of a building, is to be cleaned, it is necessary to select a solvent or solvents with a boiling point which is sufficiently high so that it will not flash off during application to the hot surface. Among the known solvents which may suitably be employed either alone or in combination are chlorinated hydrocarbons which are suitable are chloroform, methylene chloride, perchloroethylene, 1, 1, 1 trichloroethane, trichlorethylene and trichlorotrifluoroethane. Any of the well-known aromatic solvents may be employed, with the important consideration once again being the temperature at which the solvent will flash off during application. Generally, when cleaning aluminum surfaces which have been exposed to the sun, all aromatic solvents from those having a boiling point as low as Toluene on up may be employed. It should further be appreciated that solvents which will dissolve the paint or enamel surface to be cleaned should not be used.

The nonionic emulsifier employed in the solvent solution may be selected from the same group as the nonionic surfactant employed in both the oxide remover and the cleaning enhancer solutions discussed above. Thus, Igepal Co (630 as well as Triton X 100 or X 101

are preferred surfactants for use in this solution. The amount of nonionic surfactant used may range from about 5 to 15 parts per 100 parts of the solvent solution.

Absorbent Material For Second Layer

There are two types of water-insoluble finely divided solid absorbent material employed in the second coating or layer. The first is a micron or submicron sized solid absorbent material such as described above and the preferred absorbent material is also Cab-O-Sil as above. The second water-insoluble finely divided solid absorbent material for use in the second coating or layer preferably contains natural, finely ground insoluble silicates which include diatomaceous earth as well as a group of finely divided hydrated synthetic calcium silicates. Included in this latter group is that solid under the trademark Micro-Cel E by Johns-Manville Products Corporation of New York, N.Y. The chemical composition of Micro-Cel E in parts by weight is as follows:

SiO_2	54.3 parts
CaO	25.1 parts
Al_2O_3	3.6 parts
FeO	1.2 parts
MgO	0.5 parts
Na_2O	1.3 parts
Water	14.0 parts

In general, Micro-Cel E then is 75.0% calcium silicate and 5.0% aluminum silicate. The average particle diameter of this absorbing agent is less than 40 microns with 96% of the particles being finer than 40 microns and approximately 65% of the particles being between 6 and 20 microns in diameter.

The amount of water-insoluble finely divided solid absorbent material used in the formulation of the second layer may be varied as necessary to achieve a sufficient viscosity such that the second layer will remain on the surface to be cleaned. In general, the second layer formulaion may include up to about 2 parts by weight of the micron or submicron sized absorbent material such as Cab-O-Sil and between about 5 and 15 parts by weight of the finely ground insoluble silicate such as Micro-Cel E. It is preferred that the amount employed be sufficient to produce a fluid, stable dispersion having a viscosity of between about 800 and 3,000 cps. and most preferably between 1,500 and 2,200 cps. A formulation having this viscosity may be easily sprayed or pumped if desired.

Examples of Formulations For Second Layer

Although the individual constituents of the formulation of the second layer can be varied as above noted, the following formulation, with parts by weight of the various constituents being based on 100 parts by weight of the dispersion or slurry, is preferred for use in the process of this invention:

Cleaning Enhancer Solution	24.5 parts
Water	51.8 parts
Micro-Cel E	11.0 parts
Cab-O-Sil	0.5 parts
Solvent Solution	12.2 parts

Reference to the above formulation will indicate that approximately 50 parts of the final second layer formulation is water other than that included in cleaning en-

hancer solution. It should be appreciated that the second layer may be formulated with various such amounts of water ranging from no dilution (0 parts) up to approximately 80 parts of water other than that included in other solutions. However, the 50 parts dilution is preferred.

A specific example of a preferred formulation for the second layer useful for cleaning painted aluminum siding, with parts by weight once again being based on 100 parts of the formulation, is as follows:

water	71.2 parts
Micro-Cel E	11.0 parts
xylene	7.6 parts
1, 1, 1 trichloroethane	3.8 parts
butylcellosolve	3.0 parts
nonionic surfactant	2.0 parts
sodium tripolyphosphate	0.5 parts
Cab-O-Sil	0.5 parts
sodium nitrite	0.4 parts

THE PROCESS

The disclosed process for cleaning painted aluminum siding and other metal, organic resin and the like surfaces utilizes the formulations set forth above.

These formulations may be prepared in advance and merely vigorously shaken or stirred prior to use at the work site to evenly distribute the finely divided solid absorbent material and form a uniform slurry. In some instances, however, it may be convenient or desirable to prepare the formulations for layers 1 and 2 for practice of the process at the work site. In such a case, the formulation for the first layer is prepared by blending the finely divided water-insoluble solid absorbent material with the oxide remover solution to form a slurry. The formulation for the second layer is prepared on the site by three steps. First, the micron or submicron sized solid absorbent material such as Cab-O-Sil is blended with the solvent solution such as by using a conventional stirring apparatus for a sufficient time to intermix the components thereof and create a slurry. Generally, two to five minutes is recommended. Next, the very fine solid absorbent silicate material such as Micro Cel E is blended with the cleaning enhancer solution either in an undiluted state or diluted with water as noted above such that up to 80 parts by weight of the final second layer formulation is water other than that included in the enhancer solution. The degree of dilution will vary, of course, depending upon the cleaning operation to be performed. Finally, the solvent slurry is blended with the cleaning enhancer solution containing the finely divided silicate absorbent material. This completes the on-site properties of both formulations.

Whether prepared in advance or at the work site the above discussed formulations are applied in accordance with the process in layers to the surface to be cleaned. First, the formulation for the first layer is applied to the surface. This slurry may be applied by a suitable mechanical means known to the art which, of course, may vary depending upon the particular type of surface being cleaned. Exemplary of the means of applying such a coating are brush, roller, dipping, doctor blade, etc. In the case wherein aluminum siding is to be cleaned it is preferable to apply the oxide remover solution by means of a roller.

The use of a slurry serves to allow the relatively slow removal of oxides and, thus, prevents undesirable discoloration and pitting of surfaces such as aluminum.

Also, the slurry allows the solution to slowly absorb the surface soil and keep it in suspension. Thus, the micron or submicron sized solid absorbent material serves not only to prepare the formulation for the first layer, but also enhances soil removal. After the slurry is applied to the surface to be cleaned, it should remain thereon for a time sufficient to effect removal of oxides as well as the loosening of surface soil. The necessary time, of course, will depend upon the particular type of soil accumulated and the amount of oxide to be removed. In the case of aluminum siding, the slurry preferably should remain on the surface between 15 and 60 minutes. If maintained thereon for such a time, it will form a near dry film.

Next, the formulation for layer 2 is applied to the previously coated surface. This dispersion or slurry may be applied in any suitable manner such as by spraying, brush, roller etc. However, in the preferred embodiment, and in particular when the surface to be cleaned is aluminum siding, the formulation is coated on top of the dry oxide remover film with a cellulose sponge. One gallon of the formulation will cover 600 to 750 square feet adequately under normal conditions. This second layer should remain on the surface for a sufficient additional time to effect cleaning of the surface in conjunction with the first coating layer. Therefore, the necessary time required will vary depending upon the nature of the surface to be cleaned and the type of soil present thereon. In the preferred embodiment, when aluminum siding is being cleaned, it has been found that 10 to 45 minutes, depending upon the condition of the aluminum and the outside temperature, is sufficient. The rate of removal of aluminum oxide and surface soil is proportional to the temperature of the atmosphere in which the coatings are applied. The following chart reflects this temperature-rate relationship and is based upon the use the preferred specific examples of each of the formulations recited above. The metal surface employed in running these tests was a heavily oxidized and soiled aluminum panel.

	34°F	50°F	72°F	90°F
Time necessary for total oxide removal with Blend No. 1	50 min.	40 min.	27 min.	21 min.
Additional time for total soil removal with Blend No. 2 while Blend No. 1 stays on	35 min.	25 min.	20 min.	15 min.

After the required period of time, the layers are removed from the treated surface, preferably by the use of a spray of water under mild pressure, for example 10-30 pounds per square inch. The pH of the layers washed away from the surface will generally be between 2.7 and 3.3. The exposed surface will exhibit a surface which is free of oxides, soils and stains and painted surfaces will be completely free of general soils and water solid residues while being of a higher gloss than before.

The exact mechanism by which the above process operates is not fully understood. However, the fact is that the process described herein does provide outstanding results which have not been attainable heretofore. The solvents employed, that is the water-soluble solvent and the water-insoluble solvent, keep in solu-

tion all the possible soil forming matters of organic origin such as oil, tar, etc. The nonionic detergents or surfactants assist the solvents and the absorbing agents in forming a stable dispersion of the removed oxides and soils of inorganic and organic origin. The sodium nitrite, as discussed previously, is converted to nitrous acid and aids in cleaning by providing additional acid and also by stirring up the components of the two layers. The soluble silicate, which may be present in the cleaning enhancer solution in place of all or some of the sodium nitrite, helps in the removal of soil while primarily serving as an addition corrosion preventive agent on metal surfaces. The finely divided solid absorbent materials such as Micro-Cel E and Cab-O-Sil assist in maintaining a distinct film of layer 2 on layer 1. These absorbent materials allow only a very small amount of chemical interchange between the acidic film of layer 1 and the film of layer 2. It is believed that capillary action occurs by result of the presence of the various absorbing agents in the two layers and that this capillary action aids in soil pick up and absorption.

The water-insoluble solid absorbent material such as Cab-O-Sil and Micro-Cel E or products of similar chemical properties discussed above also act, it is believed, as very mild abrasives during the wash down period. The micron or submicron sized solid absorbent materials such as Cab-O-Sil in the first layer formulation acts as a mild abrasive in removing soil from the surface to be treated while the solid absorbent material in the film of the second layer formulation, and in particular Micro-Cel E, acts as an abrasive during the wash down period in helping to remove the film of layer 1. Thus, these solid absorbent materials assist in providing a higher gloss on painted, coated or uncoated surfaces.

Subsequent to the cleaning of the metal surfaces and after the surface is completely dry, a protective coating may be applied to prevent any oxidation of an exposed metal surface or the discoloration of paint. Several formulae, particularly suitable for the protective coating of aluminum surfaces such as aluminum siding are disclosed in the technical literature.

In fact, it has been found that the cleaning process of this invention in particularly adapted for the preparation of aluminum surfaces prior to the application thereto of a protective coating. This is because by use of the method and formulations of this invention not only can the surface grime, grease and the like be removed, but also there can be effected removal of "chalk" resulting from deterioration of the existing paint along with accumulated oxides and the like. Further, the method and formulations effect a controlled slight etching of any bare aluminum or the like metal surface to improve the adhesion of the refinishing protective coating thereto.

CHANGES AND MODIFICATIONS

While the invention has been described specifically with reference to certain embodiments thereof, various changes and modifications may be made all within the purview of the invention in its broadest scope. For example, the oxide remover solution may be any of the known compositions for removing oxides from surfaces, the compositions varying depending on the surface being cleaned. Thus, although the composition set forth in detail above is much preferred, the initial oxide cleaning composition may be selected from a variety of mineral and organic acids and solutions of acid salts,

either with or without surfactants, inhibitors and solvents. Known acid cleaning solutions which may be used, although inferior to the oxide remover detailed above, are inorganic (mineral) acid solutions, organic acid solutions, mixtures of mineral and organic acids, acidsolvent mixtures and solutions of acid salts. Thus, acids such as citric, tartaric, acetic, oxalic, gluconic, sulfuric, nitric, hydrochloric, hydrofluoric, and chromic, to name but a few, may be useful in various oxide remover solutions. Exemplary of useful acid salts are sodium bisulfate and sodium bifluoride.

A further modification within the intended scope of the invention is the addition of acids such as nitric or sulfuric directly to the preferred oxide remover solution. Such acids, added in minor amounts, will enhance the cleaning power of the oxide remover slurry. However, such acids should be added just prior to application since they will react with the organic acids in the solution such as lactic acid.

It is still further within the scope of the invention and, in fact preferred if it is desired to use nitric or sulfuric acids in combination with the phosphoric acid formulation of layer 1, to add these acids to the cleaning enhancer solution in place of either some of all of the sodium nitrite or the soluble silicate.

Still other changes and modifications which will be apparent to one skilled in this art may be made all within the full and intended scope of the claims which follow.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for cleaning a surface comprising applying to the surface a first coating of a slurry of a water-insoluble finely divided solid absorbent material in an aqueous acidic solution containing phosphate radical, a chelating agent and a surfactant; after said slurry has dried applying to said coating a coating of a second slurry of water-insoluble finely divided solid absorbent material in a liquid comprising a mixture of (a) a second aqueous solution comprising a chelating agent, a surfactant, water-soluble organic solvent and a compound selected from the group consisting of sodium nitrite, soluble silicates and mixtures thereof, and (b) water-insoluble organic solvent; and after said second coating has been absorbed through said first coating removing said coatings.

2. The method of claim 1, wherein the phosphate radical is supplied by phosphoric acid.

3. The method of claim 2, wherein the chelating agent of the first slurry is an organic chelating acid selected from the group consisting of aliphatic carboxylic and aliphatic polycarboxylic acids.

4. The method of claim 2, wherein the chelating agent of the second slurry is selected from the group consisting of complex phosphates, ethylenediaminetetraacetic acid, nitrilotriacetic acid, sodium salts of ethylenediaminetetraacetic acid and nitrilotriacetic acid and mono, di, or tricarboxylic acids.

5. The method of claim 2, wherein the surfactants of both slurries are nonionic and are selected from the group consisting of alkylphenoxypoly (oxyethylene) ethanols resulting from a combination of an alkylphenol with ethylene oxide and having the general formula $RC_6H_4O(CH_2CH_2O)_n^{CH_2}CH_2OH$ in which R may be C_8H_{17} or a higher homologue and $n = 7-9$.

6. The method of claim 2, wherein the water-soluble solvent is selected from the group consisting of mono-, di-, or triethylene glycol ethers of primary alcohols.

7. The method of claim 1, wherein the compound of the second aqueous solution is a soluble silicate selected from the group consisting of sodium and potassium silicates.

8. The method of claim 1, wherein the compound of the second aqueous solution is sodium nitrite.

9. The method of claim 1, wherein the aqueous acidic solution contains in parts by weight 10-70 parts of phosphate radical, 2.5-4.0 parts of chelating agent and

1-3 parts of surfactant.

10. The method of claim 9, wherein the second aqueous solution contains in parts by weight 2.5-6.0 parts of soluble silicate, 2-5 parts of chelating agent, 1-5 parts of surfactant and 3-10 parts of water-soluble organic solvent.

11. The method of claim 9, wherein the second aqueous solution contains in parts by weight 0.1-10 parts of sodium nitrite, 2-5 parts of chelating agent, 1-5 parts of surfactant and 3-10 parts of water-soluble organic solvent.

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