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CARBON REMOVER AND METAL SURFACE CLEANING COMPOSITION

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This invention relates to the removal of undesirable foreign deposits from the metal surfaces. More particularly this invention pertains to the removal of hard carbonaceous materials, resins, varnish, lacquers, rust, abrasives, welded metal particles, and the like, from engines, turbines, industrial equipment and the like by applying thereto a novel chemical composition, each component thereof being within rather specific proportions, said composition having the ability of penetrating through the deposits, loosening it and facilitating in removing it from the metal surface, leaving the engine or other metal surfaces clean and undamaged.

The development of high power engines operating at relatively very high temperatures and heavy loads, such as internal combustion engines, Diesel engines, gasoline aircraft engines, jet engines, form, during their operation, carbon and sludge deposits which cause sticking, clogging, and wear of movable parts. This results in wear and corrosion of engine parts, and generally reduces the operating efficiency of the engine. Present developments in gas turbine engines which operate at such elevated temperatures as from 1100° F. to 1800° F. greatly accentuate this problem. Thus, gas turbine engine parts such as the compressor blades, and turbo-jet units such as turbo-supercharged engines, as well as other industrial units such as heat exchange elements, torque converter transmissions, air and gas compressor valves, etc., become coated within relatively short periods of time with thick layers of carbonaceous and other foreign deposits which must be removed. These deposits adhere so tenaciously to the surface that the only way to remove them at present is by hand scraping or by soaking in chemical solutions for long periods of time. Such drastic treatment usually results in damage caused by corrosion or pitting of the treated metal surface due to the chemical nature of the material used to remove the deposits, swelling or destruction of insulating and non-metallic parts, and chipping or cracking of metal surfaces due to hand scrubbing and cleaning. In addition present known deposit removers are highly toxic due to their high content of phenolic and/or halogen-containing materials which are a hazard and are detrimental to the health of the user. Known deposit removers also introduce a fire hazard problem due to the fact that such materials have low flash points but are only effective at elevated temperatures.

It is an object of this invention to provide a cleaning and deposit-removing composition which can be easily and readily applied to heavily carbon-coated metal surfaces at room or at slightly elevated temperatures and leave the surface clean. It is another object of this invention to provide a cleaning composition which is non-

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corrosive to the metal being cleaned and which is non-reactive with non-metallic parts with which it might come in contact. Still another object of this invention is to provide a cleaning composition which is safe to use within a relatively wide temperature range.

The above and other objects may be attained in accordance with the present invention by admixing, with a suitable hydrocarbon base, certain chemically active ingredients in rather specific proportions, each of which exerts a specific function and a co-ordinating one with the composition taken as a whole which results in a potent cleaning composition. The active ingredients of this invention comprise a hydrocarbon base admixed with specific types of detergent, wetting and coupling agents, a penetrant and water, all of which are essential. A criteria of compositions of this invention is that all ingredients which comprise it must be present at all times and in relatively specific proportional relationship to each other.

The base comprises essentially a hydrocarbon having a boiling point above that of room temperature and up to the boiling temperatures of mineral lubricating oil fractions. The selection of the type of hydrocarbon base to be used depends primarily upon the intended use of the composition. Thus, if the composition is to be used mainly as a carbon remover, a relatively light petroleum hydrocarbon fraction, such as kerosene, is preferred, although mineral seal oil, gas oil, various petroleum naphtha cuts, mineral spirits, kerosene SO_2 extracts, aromatic solvents, petroleum ether, aromatic hydrocarbons such as benzene, p-xylene, o-xylene, m-xylene, cumene, butylbenzenes; paraffinic hydrocarbons, e. g. normal hexane, dimethyl pentane, octane, iso-octane, undecane, dodecane; cycloparaffins, e. g. cyclohexane, methylcyclohexane, isopropylcyclohexane, can be used. In cases where compositions of this invention are to be used as flushing oils in addition to functioning as carbon and engine deposit removers, a petroleum hydrocarbon having some lubricating properties such as a mineral lubricating oil should be used. The amount of base used can vary from between about 12% to about 50% by weight, and preferably between about 12% and 20% by weight of the composition.

Detergents of this invention function both in a chemical and physical manner. Primarily they help to keep finely divided carbon and resinous particles formed during operation of internal combustion engines, turbines and the like or deposits already formed but loosened from a surface by suitable means, in a state of suspension thereby preventing their adherence to or build-up on a surface. This is due to the adsorptive action of the detergents, making the carbon parti-

cles and other deleterious matter with which they come in contact large enough and light enough so that their settling rate is greatly retarded and therefore they tend to remain in suspension. In addition the detergents co-act with other constituent materials of this invention so as to aid in loosening and removing deposits from surfaces and at the same time not interfere with the activity of other additives present. They are also relatively thermally stable and resist oxidation.

It has been found that particularly suitable detergents which have the above properties when employed in conjunction with other additives of this invention are non-hydroxy containing polyamine salts of organic and inorganic acids. The polyamines which can be used to form the detergent salts of this invention are the aliphatic polyamines which can contain substituent non-hydroxy groups such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, tetramethyl methylenediamine, propylene diamine, dipropylene triamine, N,N'-diethyl hexamethylene diamine, N-n-dodecyl diethylene triamine, N-n-tetradecyl diethylene triamine, N-n-tetradecyl diethylene triamine, N-n-hexadecyl triethylene tetramine, N-octyl ethylene diamine, N-2 ethyl hexyl N-hexadecyl triethylene tetramine, N-heptyl trimethylene diamine, N-tetradecyl tripropylene tetramine, 1.3 diamino propane, 3 diethyl amino propylamine, 1.3 diamino butane, 1,3 bis ethyl amino butane, 1.10 decylene diamine, phenyl ethylene diamine, di-o-tolyl ethylene diamine, and the like. Mixtures of such compounds consisting either of compounds derived from the same alkylene polyamine with different alkyl substituents, such as would result on treating ethylene diamine with mixed alkyl chlorides, or mixtures of varying degrees of alkylation or mixtures containing compounds derived from different alkylene polyamines with the same or different or mixed alkyl substituents are also contemplated for use herein.

Acids which can be used to combine with the above-mentioned polyamines to form detergent salts may include:

I. Aliphatic acids, e. g. capric, undecanoic, lauric, myristic, palmitic, stearic, arachidic, sorbic, oleic, ricinoleic, linoleic, linolenic, elaidic, erucic, brassidic, clupanodonic, mono, di and tri hydroxy-stearic, alkyl malonic, alkyl succinic, alkyl glutaric, alkyl maleic, alkyl malic, alkyl tartaric, alkyl citric, alkyl adipic, tartronic acids and the like. Also synthetic acids prepared by oxidizing hydrocarbons such as paraffinic wax can be used as well as fatty oils containing substantial amounts of free fatty acids. Among the fatty oils which can be used for this purpose are: olive oil, castor oil, peanut oil, rapeseed oil, cottonseed oil, sesame oil and the like.

II. Aromatic acids: Benzoic, salicylic, cinnamic, hydrocinnamic, phthalic, naphthoic, abietic, resinic, phenyl acetic to phenyl stearic, resorcylic, gallic, toluic, xylic, lauroxy and phenoxy benzoic acids and the like.

III. Cyclic acids: Naphthenic acids derived from petroleum hydrocarbons, cyclohexane carboxylic, tetrahydrophthalic, tetrahydrotoluic, camphane-3-carboxylic, cholic, cyclohexylacetic, cyclohexylbutyric, cyclohexylcaproic, cyclohexylvaleric acids and the like.

IV. Heterocyclic acids: Picolinic, nicotinic, isonicotinic, quinolinic, chinchomeronic, lutidinic, cynchomeronic, pyrole carboxylic, thiophene carboxylic, furan carboxylic, pyrrol carboxylic acids and the like.

V. Organic compounds containing inorganic acids: (A) Benzene sulfonic acid, toluene sulfonic acid, triisopropyl naphthalene sulfonic acid, diphenyl sulfonic acid, polyamyl naphthalene sulfonic acid, diwax benzene sulfonic acid, xylene sulfonic acid, benzene disulfonic acid, wax sulfo succinic acid, diwax naphthalene sulfonic acid, petroleum sulfonic acids derived from various petroleum fractions such as: gas oil, kerosene, light oil, turbine oil, mineral lubricating oil, petroleum waxes, petrolatum, etc.; (B) Phosphorus-containing acids, such as obtained by reacting P_2S_5, P_2O_5, P_4S_3, and the like with olefinic hydrocarbons, aromatic hydrocarbons, phenolic compounds, alcohols, organic acids as listed above and mixtures thereof and the like.

The oxygen atoms in the carboxyl radical of the acids under groups I to IV may be replaced by S, Se, and/or Te atoms resulting in the following acid radicals: CSOH, COXH, CXXH, where X is S, Se or Te. Also any of the above acids may contain non-polar and/or polar substituent groups such as: alkyl, mercapto, hydroxy, amino, cyano, isocyano, nitroso, nitro, alkoxy aroxyl and the like.

Specific polyamine salts which are preferred for use in compositions of this invention are:

Ethylene diamine oleate
Diethylene triamine oleate
Propylene diamine oleate
Dipropylene triamine oleate
Ethylene diamine stearate
Ethylene diamine palmitate
Ethylene diamine ricinoleate
Diethylene triamine stearate
Diethylene triamine palmitate
Diethylene triamine ricinoleate
Ethylene diamine hydroxy stearate
Ethylene diamine petroleum sulfonate
Propylene diamine petroleum sulfonate
Ethylene diamine trioctyl phosphate
Tripropylene tetramine oleate
N-n-dodecyl diethylene triamine oleate
N-n-dodecyl diethylene triamine ricinoleate
N-octyl ethylene diamine oleate
N-octyl ethylene diamine petroleum sulfonate
N-octyl ethylene diamine ricinoleate
N-octyl ethylene diamine caprylate
N-octyl ethylene diamine laurate
Ethylene diamine diisopropyl salicylate
Ethylene diamine dioctyl benzoate
Ethylene diamine naphthenate
Ethylene diamine phenyl stearate
Propylene diamine diisopropyl salicylate
Propylene diamine naphthenate
Ethylene diamine diwax naphthalene sulfonate, etc.

The amount of polyamine salt detergent which can be used in compositions of this invention may vary from about 2 to 15% and preferably is kept within range of between 4% to 8% by weight.

The function of good penetrant is to penetrate through interfering layers of deleterious materials and loosen them from the surface to which they adhere. To accomplish this a penetrant must possess low degree of volatility, low surface tension and high capillary or creeping properties so that once having penetrated through the foul matter adhering to a surface it can displace it therefrom and leave on said surface a protective oiliness film which if desired can be easily removed by flushing, for example, with steam and the like. The protective film acts as a boundary

separator between contacting surfaces thereby protecting them from wear and the like. Penetrants which are particularly suitable due to their co-ordinate action with other constituents of this invention so as to produce a product having maximum efficiency in removing foul matter from surfaces are halogenated aliphatic and aromatic compounds, e. g. trichloroethylene, 2,2-dichloroethylether, o-dichlorobenzene, dichloroisopropylether, etc; ketones, e. g. mesityl oxide, isophorone; and mixture of the above halogenated compounds and ketones. The penetrant generally comprises approximately 20% to 50% by weight of the composition.

To activate and improve the general properties of compositions under consideration a wetting agent is employed which co-acts with the above penetrants and wets the surface which has been rendered free of the deleterious materials by the active ingredients of this composition. The surface thus wetted is protected and foul matter is prevented from re-adhering to the cleaned surface. Wetting agents which are suitable for this purpose are the polyamines referred to previously and alicyclic alcohols, etc. These types of compounds can best be illustrated by such specific compounds as ethylene diamine, diethylene triamine, propylene diamine, dipropylene triamine, cyclohexanol, trimethyl-cyclohexanol and the like. The amines are particularly preferred, for in addition to acting as wetting agents, they react with acidic materials thereby continuously replenishing the detergent agent. The amount of wetting agent used ranges between about 2% and about 25% and preferably is kept within 8% to 20% by weight of the total composition.

Water is an essential component of the present composition. The exact function or mechanism of it is not understood, but in cases where water was eliminated as a component of the present composition the efficiency of the latter as a deposit remover was reduced to such a degree as to render it almost useless. It is noted that the wetting power of the composition is increased and the foreign matter is kept in a more permanent dispersion due to the presence of water. It therefore appears that water exerts a synergistic effect and also acts as a carrier for foreign deposits loosened from a surface. The amount of water used varies from between about 10% to about 20%, and preferably is kept between about 12% and 15% by weight.

In order to stabilize compositions under consideration so as to prevent separation and break down, a coupling agent is added. The preferable

coupling agents are polyhydric organic derivatives such as alkylene glycols; diglycols, e. g. dipropylene glycol, dibutylene glycol, diamylene glycol; triglycol, e. g. tripropylene glycol; ether alcohols containing up to 20 carbon atoms and more particularly glycol mono-alkyl ethers, e. g. the "cellosolves," e. g. ethylene glycol mono-ethyl ether, ethylene glycol mono-propyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-isobutyl ether, ethylene glycol mono-tert.butyl ether, ethylene glycol mono-hexyl ether, propylene glycol mono-ethyl ether, propylene glycol mono-isobutyl ether, etc.; diglycol mono-alkyl ethers such as the "carbitols," e. g. diethylene glycol mono-methyl ethyl normal and isopropyl ethers, diethylene glycol mono-butyl ether, diethylene glycol mono-decyl ether, etc.; also dipropylene glycol mono-isopropyl ether, dipropylene glycol mono-ethyl ether, dipropylene glycol mono-isoamyl ether, dipropylene glycol mono-heptyl ether, diisobutylene glycol mono-isopropyl ether, ethylene-propylene glycol mono-ethyl ether, ethylene-isobutylene glycol mono-isopropyl ether, etc.; also, glycerine mono or di-ethers of 6 or more carbon atoms such as glycerine mono- or dipropyl, butyl, amyl, etc. ethers; mono-esters of glycol or glycerine, etc. The amount of coupling agent used generally does not exceed 20% and is preferably kept in the range of 15 to 20%.

The above classes of additives which constitute the essential component parts of compositions of this invention have not been selected at random but have been selected after careful and painstaking research and because of their coordinating action in aiding to remove deleterious engine deposits as well as removal of undesirable foreign deposits from various surfaces in general.

To more fully illustrate the present invention the following are a few compositions which have been compounded, tested and found extremely efficient for removing deposits from metal surfaces and the like.

Composition, parts by weight

	Hydrocarbon	Detergent	Penetrant	Wetting Agent	Coupling Agent	Water
1	Kerosene, 20.	Ethylene diamine oleate, 4.4.	o-dichloro benzene, 40.	ethlenediamine, 5.6.	ethylene glycol monobutyl ether, 15.	15
2	Do.	do.	do.	ethylenediamine, 2.6.	do.	18
3	Do.	propylene diamine oleate, 4.5.	do.	propylene diamine, 2.5.	do.	18

To test the effectiveness of compositions of this invention as removers of carbon and other deleterious materials from various surfaces the following tests were performed and results compared with the best known commercial materials used for the same purpose and with compositions similar to these of the present invention except that for polyamine salts, aliphatic mono amine and alkylolamine salts were used. Such compositions comprised for example the following constituents:

Composition, parts by weight

	Hydrocarbon	Detergent	Penetrant	Wetting Agent	Coupling Agent	Water
4	Kerosene, 12.	Diethylethanol amine oleate, 5.6.	o-dichloro benzene, 40.	diethylethanol amine, 20.4.	ethylene glycol monobutyl ether, 10.	12
5	Kerosene, 19.	Isopropanol amine oleate, 6.3.	o-dichloro benzene, 47.	diethylethanol amine, 7.7.	ethylene glycol monobutyl ether, 11.	14
6	Kerosene, 12.	lauryl amine naphthenate, 6.4.	o-dichloro benzene, 40.	diethylethanol amine, 19.6.	ethylene glycol monobutyl ether, 10.	12

Example I.—Steel panels were sprayed with a solution of oil sludge in carbon tetrachloride and

baked at 220° C. in a forced draft oven. The steel panels were then removed from the oven, cooled and some were immersed in deposit remover compositions of this invention while others were immersed in commercial deposit remover X reported to contain chlorinated aromatic, water, butyl "cellosolve" and ethanolamineoleate and in compositions of Examples 4, 5 and 6. The time of initial deposit removal as well at time of complete removal were noted at a little above room temperature such as about 90° F.

Composition	Test Temp.	Time of Initial Removal, min.	Time of Complete Removal, min.	Remarks
	°F.			
Commercial Product	90	None after 60 Min.	None after 120 Min.	No effect, panel still heavily coated.
Composition of Ex. 1	90	0:30 min.	2:10 min.	Absolutely clean.
Composition of Ex. 2	90	0:50 min.	6:10 min.	Do.
Composition of Ex. 3	90	1:00 min.	8:10 min.	Do.
Composition of Ex. 4	90	2:00 min.	24:00 min.	Clean.
Composition of Ex. 5	90	3:45 min.	16:10 min.	Do.
Composition of Ex. 6	90			Ineffective at 90° F.
Composition of Ex. 6	185		60% at 10:00 min.	Substantial deposit left.

Compositions of this invention are excellent deposit removers such as are formed on pancake valves of catalytic hydrocarbon compressors where it is not uncommon to find hard carbon deposits of over one-half inch in thickness on said valves and other parts of such equipment such as the cylinder walls, pistons, bearings and the like.

In addition compositions of this invention are excellent removers for deposits which are formed during operation of gas turbine engines. They also effectively remove scales, rust and corrosion deposits from metal surfaces such as boiler tubes, evaporation pipes, machines and the like. They are excellent degreasing compositions and are effective dirt removers as well as paint and varnish removers. In addition to removing undesired deposits from metal surfaces they are equally effective for removing deposits from non-metallic surfaces.

Compositions of this invention are non-corrosive to metals, non-toxic and are not fire hazard. They have no harmful effect when in contact with the skin, rubber, plastic surfaces and the like, and can be applied by any known means such as spraying, immersing, dipping, swabbing and the like.

It is to be understood that while the features of the invention have been described and illustrated in connection with certain specific examples, the invention, however, is not to be limited thereto or otherwise restricted, except by the prior are and the scope of the appended claims.

We claim as our invention:

1. A cleaning composition comprising a mixture of:

	Per cent by weight
Kerosene	20.0
Ethylenediamine oleate	4.4
o-Dichlorobenzene	40.0
Ethylene glycol mono butyl ether	15.0
Ethylene diamine	5.6
Water	15.0

2. A cleaning compositon comprising a mixture of:

	Per cent by weight
Kerosene	20.0
Propylene diamine oleate	4.5
o-Dichlorobenzene	40.0
Ethylene glycol monobutyl ether	15.0
Propylene diamine	2.5
Water	18.0

3. A cleaning composition comprising a mixture of about 12% to about 50% by weight of kerosene, about 2% to about 15% by weight of ethylene diamine oleate, about 20% to about 40% by weight of o-dichlorobenzene, about 2% to about 25% by weight of ethylene diamine, about 10% to about 20% by weight of ethylene glycol monobutyl ether, and about 10% to about 20% by weight of water.

4. A cleaning composition comprising a mixture of from about 12% to about 50% by weight kerosene, from about 2% to about 15% by weight of ethylene diamine oleate, from about 20% to about 40% by weight of a chlorinated organic compound of the class consisting of o-dichlorobenzene, trichloroethylene, dichloroethyl ether and dichloroisopropyl ether, from about 2% to about 25% by weight of ethylene diamine, from about 10% to about 20% by weight of ethylene glycol monobutyl ether and from about 10% to about 20% by weight water.

5. A cleaning composition comprising a mixture of from about 12% to about 50% by weight of kerosene, of from about 2% to about 15% by weight of ethylene diamine oleate, from about 20% to about 40% by weight of o-dichlorobenzene, from about 2% to about 25% by weight of propylene diamine, from about 10% to about 20% by weight of ethylene glycol monobutyl ether, and from about 10% to about 20% by weight of water.

6. A cleaning composition comprising a mixture of from about 12% to about 50% by weight kerosene, from about 2% to about 15% by weight of a lower aliphatic diamine salt of a high molecular weight fatty acid having 10 to 18 carbon atoms and wherein the diamine is selected from the group consisting of ethylene diamine and propylene diamine, from about 20% to about 40% by weight of a chlorinated organic compound selected from the class consisting of o-dichlorobenzene, trichloroethylene, dichloroethyl ether and dichloroisopropyl ether, from about 2% to about 25% by weight of a lower aliphatic diamine selected from the group consisting of ethylene diamine and propylene diamine, from about 10% to about 20% by weight of an unsubstituted lower alkylene glycol monoalkyl ether of up to 20 carbon atoms and wherein the alkylene glycol is selected from the group consisting of ethylene glycol and propylene glycol and from about 10% to about 20% by weight water.

7. A cleaning composition comprising a mixture of about 12% to about 50% by weight of kerosene, about 2% to about 15% by weight of an organic amine soap selected from the class consisting of ethylene diamine oleate and propylene diamine oleate, from about 20% to about 40% by weight of o-dichlorobenzene, from about 2% to about 25% by weight of a lower aliphatic diamine selected from the class consisting of ethylene diamine and propylene diamine, from about 10% to about 20% by weight of ethylene glycol

monobutyl ether, and from about 10% to 20% by weight of water.

8. A cleaning composition comprising a mixture of about 12% to about 50% by weight of a light liquid petroleum hydrocarbon solvent, about 2% to 15% by weight of an organic amine soap selected from the class consisting of ethylene diamine soap of a higher fatty acid having 10 to 18 carbon atoms and propylene diamine soap of a higher fatty acid having 10 to 18 carbon atoms, from about 20% to about 40% by weight of o-dichlorobenzene, from about 2% to about 25% by weight of a lower aliphatic diamine selected from the class consisting of ethylene diamine and propylene diamine, from about 10% to about 20% by weight of ethylene glycol monobutyl ether, and from about 10% to 20% by weight of water.

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