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COMPOSITION AND PROCESS FOR CLEANING ALUMINUM SURFACES

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This invention relates to a composition and process useful for the cleaning of metallic surfaces and particularly such metallic surfaces as those found on aluminum aircraft.

In the maintenance of aircraft, it has been the practice to protect the surface of the aircraft from corrosive elements and provide esthetic appeal by either painting the surface or maintaining the surface in a bare metallic condition but cleaning the surface frequently to remove unsightly ad corrosive materials.

It has been generally recognized that a painted surface affords the best protection from the elements, however the increased weight resulting from the necessary thickness of coating to provide adequate protection has increased the dead weight of the aircraft in some instances up to several hundred pounds. Therefore in instances where fuel or payload is of primary concern, it has been the practice to avoid painting of the aircraft and rely on frequent cleaning and brightening of the aircraft skin to remove corrodants and unsightly soils.

Numerous cleaning compositions have been used for this application but to date all compositions used for this purpose have some serious shortcomings. One composition frequently used for the cleaning and brightening of aircraft surface has been an acid composition based on the use of phosphoric acid or acid phosphate salts usually combined with wetting agents and solvents. Although this composition when properly used has produced results which are appealing to the eye, the very basis of its effectiveness, that of removal of the metallic oxides produced by atmospheric oxidation of the metal by the acidic ingredients, also results in the corrosion of the metallic surface. Although the amount of metal removed generally on the surface is small for each cleaning operation, repeated cleanings have resulted in appreciable reduction in thickness of the metal skins with the resultant weakening of the aircraft structure. It has also been generally recognized that all the acid constituents cannot be removed from areas around rivets and between faying surfaces with the result that the acid continues to corrode in these highly stressed areas, often weakening the stress member sufficiently to cause a rupture. If the aircraft is inadequately rinsed, the reaction product of the phosphoric acid and aluminum results in an unsightly and corrosive film of acidic metallic phosphate, such as aluminum phosphate on the surface.

Another method of cleaning generally practiced is the use of petroleum solvents with or without emulsifying agents. This method is far less corrosive than the phosphoric acid method but the surface cleanliness leaves something to be desired. The petroleum solvents have no effect on the inorganic soils such as dust and metallic oxides and an oily film is retained on the surface, whether or not an emulsifier is used with the solvent. This film is highly attractive to dust and other soils resulting in rapid resoiling of the aircraft surface. The solvents employed are flammable and their use is restricted for this reason. It has also been an objection to the use of solvent cleaners of this type that the solvents attack asphalt ramps and cleaning area floors and such cleaning operations can only be conducted on concrete ramps. The disposal of the used solvents has also presented a problem as such solvents cannot be run into municipal sewage lines and storage in open basins presents a serious fire hazard.

Still another method of cleaning has been the use of an aqueous system incorporating wetting and emulsifying agents, water soluble solvents such as aliphatic alcohols, peptizing agents such as alkali metal silicates. Although numerous compositions of this type have been used, all contain the alkali metal silicates which act as corrosion inhibitors in this alkaline system. Although the silicates are excellent inhibitors, particularly for aluminum, they have one pronounced shortcoming which is inherent in their mechanism of corrosion protection which is the deposition of a thin silicate film on the aluminum surface. When the surface dries, the silicate film appears as a white, powdery deposit which is often streaky and unsightly.

Accordingly, it is the object of the present invention to provide a composition which will clean all metallic surfaces of an aircraft without corroding the metal.

It is a further object of this invention to provide a cleaning composition and process which is nonflammable and largely eliminates the use of organic solvents which are both toxic and require special disposal methods.

It is a further object of this invention to provide a composition which is completely water soluble and which does not react with the metal to produce an insoluble product which deposits on the surface and presents an unsightly appearance.

It is a further object of the invention to provide a composition which is mildly alkaline to dissolve alkaline soluble materials on the aircraft surface which may exist as a soil or which may have been placed upon the surface to act as a temporary protective coating for the aircraft surface.

It is still a further object to provide a composition which is relatively inexpensive so that it can be an economical replacement for former conventional cleaning processes and a composition which is stable for long periods of time so that it can be stored and used when needed.

It has long been known that amines are effective cleaning agents for aluminum surfaces; however, because of their cost they have not been used without dilution for the purpose of aircraft cleaning. It has been found practical to use organic amines with petroleum type solvent diluents but when dissolved in water the amines become corrosive to aluminum surfaces. The corrosion is evidenced by an etching of the aluminum surface or the deposition on the surface of a dark film which is believed to be the reaction product of the amine with the alloying constituents of the various aluminum alloys.

I have discovered that when an aliphatic amine of sufficient alkalinity is mixed in aqueous solution with a chromate that the solution is surprisingly stable and non-corrosive to aluminum. It is believed that this surprising phenomenon is a result of the fact that the high alkalinity of the amine reduces the oxidation potential of the chromate to a state where it is insufficient to oxidize the amine but still retains sufficient oxidation potential to prevent corrosion of the aluminum.

The amines which I have found to be stable in the presence of chromate ion and which have sufficient alkalinity to provide good cleaning of aluminum when dissolved in water and which are non-corrosive to aluminum in the presence of chromate ion are the aliphatic amines which when dissolved in water at a concentration of twenty-five percent by weight will have an alkaline pH of 12.5 or over when measured by the standard glass electrode at a temperature of 25° C.

Among the aliphatic amines which I have found which are stable to the presence of chromate ion and which satisfy the pH limitation, cleaning requirements and are

non-corrosive to aluminum in the presence of chromate are the following.

Amine:	pH of 25% solution at 25° C.
Ethyl amine	12.6
Diethyl amine	12.5
N-butyl amine	12.5
Ethylene diamine	12.8
Diethylene triamine	12.5
Triethylene tetramine	12.5

All of these amines were tested by preparing a water solution of the amine compounded as follows:

Example I

	Percent
Amine	5.0
Sodium chromate	0.5
Water	94.5

Example II

	Percent
Amine	25.0
Potassium chromate	0.5
Water	74.5

Examples I and II above were tested for stability by storing at room temperature for a period of two weeks. It was found there was no significant color change to indicate reduction of the chromate to the tri-valent state. Tests were also conducted to determine the cleaning characteristics of the composition on aluminum. It was found all materials satisfactorily removed normal surface films without staining or etching the aluminum when the aluminum was exposed to the cleaning solution for a period of ten minutes.

Several intermediate ranges of concentration of the chromate and amine were tested and were found to produce comparable results.

The tests of Examples I and II above were made with chromate ion supplied from sodium and potassium chromate; the chromate ion would also function as well if supplied in the form of any water soluble chromate, dichromate, or chromic acid if the latter two sources were used at the low end of the range of concentration of chromate to amine and the quantity used was not of sufficient concentration to appreciably decrease the pH of the system.

The range of concentration of the amine to the water which I have found satisfactory is from about 3 to about 25 parts of amine to 100 parts of solution. The range of the ratio of concentration of chromate ion to amine which has proven successful is about 1:5 to about 1:50.

I have further found that the compositions of Examples I and II above are materially improved, particularly with regard to the removal of oily type soils and organic residues by the addition of a water soluble solvent and particularly, the class of compounds generally known as the glycol ethers.

The glycol ethers employed in the invention are of the type $RO(R'O)_nX$ where R is alkyl of 4 carbon atoms or less or monocyclic aryl, R' is an alkylene radical of 4 carbon atoms or less, n has a value of one or more and X is alkyl, monocyclic aryl or hydrogen. Examples of these are:

Ethylene glycol ethyl ether
Ethylene glycol methyl ether
Dipropylene glycol mono methyl ether
Dipropylene glycol mono ethyl ether
Dipropylene glycol mono isopropyl ether
Tripropylene glycol mono methyl ether
Tripropylene glycol mono ethyl ether
Ethylene glycol mono phenyl ether
Triethylene glycol dipropyl ether

All of these compounds are sufficiently soluble in water and all are stable to the chromate ion in the presence of the amine. This group of chemical compounds has been found to have outstanding solubility for solvents and oils and when used in combination with the amine and chromate water solution. The following tests were run to determine the effectiveness of the glycol ethers in this combination.

Example III

An aluminum panel was cleaned with a standard petroleum solvent based emulsion cleaner of the following composition:

	Percent
Kerosene	80
Potassium oleate	10
Petroleum sulfonate (oil soluble)	5
Pine oil	3
Hexylene glycol	2

The panel was then rinsed with water and was found to have an oily residue on the surface. Sections of the panel were then cleaned with the following composition:

	Percent by Weight				
	A	B	C	D	E
Ethylene diamine	10	10	10	10	10
Water	89.8	69.8	69.8	69.8	69.8
Potassium chromate	0.2	0.2	00.2	0.2	0.2
Dipropylene glycol mono methyl ether	------	20	------	------	------
Triethylene glycol dipropyl ether	------	------	20	------	------
Isopropyl alcohol	------	------	------	20	------
Ethylene glycol	------	------	------	------	20

It was found that the panels washed with Compositions A, D and E still retained the oily character whereas the areas washed with Examples B and C were completely free of oily residues.

The quantity of glycol ether which I have found effective in improving the cleaning characteristics of the amine-chromate-water composition is from about 3 to about 20% of the composition. Below about 3% there is little or no effect on the addition of the glycol ether to the amine-chromate-water composition and above about 20% there is no improvement in the cleaning results although additions greater than 20% do not reduce the effectiveness of the cleaning composition.

Wetting agents may also be added to the composition to reduce the surface tension of the liquid and promote spreading of the cleaning compound on the surface of the aluminum. Among the compounds which have been found effective for this purpose are the chromate stable non-ionic wetting agents and water soluble petroleum sulfonates. Examples of this class of wetting agents are the following:

(1) Alkyl phenyl polyethylene glycol ether, a product of Carbide and Carbon Chemical Company, sold under the trade name of Tergitol NPX.
(2) Iso octyl phenol polyethylene glycol ether, a product of Rohm and Haas Company, sold under the trade name of Triton X–100.
(3) Sodium dodecyl benzene sulfonate.

The wetting agents may be employed at a concentration of about 0.1% to about 5% of the composition. Below about 0.1% there is little or no noticeable improvement.

In some instances it may be desirable to employ a solution with higher viscosity than that characterized by the mixture of amine, chromate, water, polyglycol ether and wetting agent. The purpose of the increased viscosity is to provide a heavy bodied material to cling to vertical surfaces. Materials which may be added for this purpose are chromate stable thickening agents such as bentonite or carboxy methyl cellulose. These examples are made by way of explanation and not limitation as a number of well known thickening agents have been found useful in the art. The only limitation on the type of thickening agent is that it be dispersible in the aqueous amine-

chromate solution and that it is not decomposed by this system. The concentration of thickening agent which has been found effective is from about 0.5% to about 6% of the concentration of the solution.

Therefore, the following are examples of compositions which I have found to be very effective aluminum cleaning compositions from the standpoint of cleaning results, non-corrosiveness and stability:

Example IV

	Percent
Ethylene diamine	5.0
Potassium chromate	1.0
Carboxy methyl cellulose	1.0
Dipropylene glycol mono methyl ether	5.0
Iso octyl phenol polyethylene glycol ether	2.5
Water	84.5

Example V

	Percent
Diethylene triamine	10.0
Sodium chromate	2.0
Carboxy methyl cellulose	0.5
Sodium dodecyl benzene sulfonate	1.0
Dipropylene glycol mono isopropyl ether	15.0
Water	71.0

The composition of Example IV was tested for cleaning an aircraft that had been soiled in service. One half of the aircraft was cleaned with petroleum solvent emulsion cleaner as disclosed by Example III; the other one-half of the aircraft was cleaned with the composition of Example IV. The part of the aircraft cleaned by the petroleum solvent emulsion cleaner presented an oily surface; no stains or oxidation had been removed and although the surface was improved in appearance over the uncleaned surface, the results were not satisfactory as compared to the other one-half which had been cleaned with the composition of Example IV. This latter one-half was free from oily residues as rinse water uniformly sheeted over the surface and exhibited no water breaks which is characteristic of an oily surface. All powdery residues of soil and oxidation had been removed and the surface showed no evidence of darkening, staining or corrosion.

The composition of Example IV was also tested for the removal of alkali soluble organic protective coatings. These coatings are composed largely of alkali soluble or disintegrable resins such as polyvinyl alcohol resin or phenol formaldehyde resins. It was found in test that the composition effectively removes such coatings in about the same time as a five percent solution of sodium metasilicate in water used at room temperature but without the deleterious effect of the alkali silicate composition.

While I have described a specific embodiment of my invention for purposes of explanation, it is to be understood that various modifications may be made within the spirit of the invention as set forth in the following claims.

I claim:

1. A composition for cleaning aluminum surfaces in the form of a hydrocarbon-free aqueous solution consisting essentially by weight of 3 to 25 parts of a water soluble, aliphatic amine of pH of at least 12.5 when dissolved by weight of the solution at a concentration of 25% in water; a chromate ion supplied by a member of the class consisting of water soluble chromate and dichromate, and chromic acid, in the range of 1 part of chromate ion to 5 parts of amine to 1 part of chromate ion to 50 parts of amine; and a major portion of water; based on 100 parts by weight of the composition.

2. The cleaning composition of claim 1 wherein the aliphatic amine is ethylene diamine.

3. The cleaning composition of claim 1 wherein the aliphatic amine is ethylene diamine and the chromate ion is supplied by sodium chromate.

4. A composition for cleaning aluminum surfaces, consisting essentially of the following ingredients:

	Percent
Ethylene diamine	5.0
Potassium chromate	1.0
Dipropylene glycol mono methyl ether	5.0
Iso octyl phenol polyethylene glycol ether	2.5
Carboxy methyl cellulose	1.0
Water	84.5

5. A composition for cleaning aluminum surfaces in the form of a hydrocarbon-free aqueous solution consisting essentially by weight of 3 to 25 parts of a water soluble aliphatic amine of the class consisting of ethyl amine, diethyl amine, N-butyl amine, ethylene diamine, diethylene triamine, and triethylene tetramine; chromate ion supplied by a member of the class consisting of alkali metal chromate, alkali metal dichromate and chromic acid, said chromate ion being present in the range of 1 part of chromate ion to 5 parts of amine to 1 part of chromate ion to 50 parts of amine; and a major portion of water; based on 100 parts by weight of the composition.

6. A composition for cleaning aluminum in the form of a hydrocarbon-free aqueous solution consisting essentially of 3 to 25 parts by weight of a water soluble aliphatic amine which when dissolved in water at a concentration of 25% by weight of the solution has a pH of at least 12.5; a chromate ion supplied by a member of the class consisting of water soluble chromate and dichromate, and chromic acid, in a concentration range of 1 part of chromate ion to 5 parts of amine, to 1 part of chromate ion to 50 parts of amine, by weight; a glycol ether of the general formula $RO(R'O)_nX$ in which R is a member of the group consisting of an alkyl radical of less than 4 carbon atoms and phenyl, R' is an alkylene radical of from 2 to 3 carbon atoms, n is an integer of from 1 to 3, and X is a member of the group consisting of an alkyl radical of less than 4 carbon atoms, phenyl and hydrogen, said glycol ether being present in a concentration of 3 to 20 parts by weight; and a major portion of water; based on 100 parts by weight of the composition.

7. The cleaning composition as defined in claim 6, wherein said glycol ether is selected from the group consisting of ethylene glycol ethyl ether, ethylene glycol methyl ether, dipropylene glycol mono methyl ether, dipropylene glycol mono ethyl ether, dipropylene glycol mono isopropyl ether, tripropylene glycol mono methyl ether, tripropylene glycol mono ethyl ether, ethylene glycol mono phenyl ether, and triethylene glycol dipropyl ether.

8. A composition for cleaning aluminum surfaces in the form of a hydrocarbon-free aqueous solution consisting essentially by weight of 3 to 25 parts of a water soluble aliphatic amine of pH of at least 12.5 when dissolved in water at a concentration of 25% by weight of the solution; chromate ion supplied by a member of the class consisting of water soluble chromate and dichromate, and chromic acid, in the range of 1 part of chromate ion to 5 parts of amine to 1 part of chromate ion to 50 parts of amine; and water.

9. In a process for cleaning aluminum surfaces, the step which comprises contacting said aluminum surfaces with the aqueous composition defined in claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS

1,765,344	Pietzsch et al.	June 17, 1930
2,509,197	Borus et al.	May 30, 1950
2,516,685	Douty et al.	July 25, 1950
2,540,003	McCoy	Jan. 30, 1951

FOREIGN PATENTS

719,671	Great Britain	Dec. 8, 1954
729,329	Great Britain	May 4, 1955