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ALL-WEATHER SURFACE CLEANER

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This invention relates to the removal of soil from the surfaces of aircraft. In particular it is directed to products for cleaning aircraft which are suitable for use under varying temperature conditions; are especially useful under low temperature conditions; and are characterized by stability at temperatures as low as —65° F.; and methods of rinsing said products with organic solvents or aqueous media.

The soil deposited on the surfaces of operating aircraft generally can be characterized as oily-type and/or traffic film-type. The oily-type soil consists primarily of oil and carbonaceous substances originating from the engine and the points of lubrication. The traffic film-type of soil consists largely of air-borne dirt, salts, inert materials, etc.

Heretofore the removal of such soil has depended upon the use of detergent concentrates which are diluted with naphtha solvents prior to application. Such has been the practice in cleaning operations of both civilian and military aircraft. These compositions, in the concentrations used, are applied to the soiled surfaces and after an appropriate contact time are flushed off with a high pressure water spray. These systems function tolerably well at temperatures higher than 32° F., and preferably within the range of 65° F. to 125° F. However, they are not workable below the freezing point of water and exhibit reduced performance properties when used at temperatures below the preferred range. Because of such limitations, the surface cleaning of aircraft is now considered impractical in cold zones. In the arctic regions, cleaning operations are avoided; and in consequence thereof, the planes are flown to sites where the temperature conditions are more favorable for use of the detergents.

It has now been found that the cleaning of soiled aircraft surfaces can be accomplished at low temperatures by means of novel products and the wash-rinse systems in accordance with the present invention.

Accordingly, it is among the principal objects of this invention to provide means and methods for cleaning aircraft which are effective over a wide temperature range, and especially at low temperatures.

Another object of this invention is to provide products for use as cleaners for aircraft which are characterized by freeze-thaw stability over the range from —65° F. to room temperature, circa 75° F.

A further object is to provide products for use as cleaners within the ambit of the primary objectives just mentioned characterized by such features as: high flash point; low toxicity; non-injurious effect on the structural materials of aircraft such as the metals, transparent and laminated plastics, and standard finishes thereof; excellent freeze-thaw stability; and rinsability with organic solvents or water or aqueous solutions of suitable fluidity at operating temperatures.

The cleaning products which make the foregoing objects, as well as other objects and advantages, capable of accomplishment and which remove both oily- and traffic film-type soils when used above and below 32° F. consist of, or are based on, a fundamental or primary or basic cleaner, said primary or basic cleaner being rinsable by a hydrocarbon solvent. For use with aqueous rinses, that fundamental cleaner is supplemented with an addtional or supplementary component.

The basic cleaners are emulsion compositions consisting essentially of three components, to wit: (1) an organic solvent continuous phase, (2) an aqueous dispersed phase consisting of water and a freezing point depressant, and (3) an emulsifying agent. These basic cleaners may be rinsed off principally with a hydrocarbon solvent.

The organic solvent component of the basic cleaner dissolves and removes organic soils. It also contributes physically to the removal of solid soils such as dust and traffic film. The aqueous component of the basic cleaner facilitates the removal of solid soils such as dust and traffic film, and water-soluble inorganic soils, and contributes to the removal of inert particles by minimizing the redeposition thereof. The freezing point depressant of the aqueous component (dissolved in water prior to the dispersion thereof in the composition) prevents freezing of the water at temperatures down to 0° F. and maintains stability at temperatures as low as minus 65° F. The emulsifying component assists in removal of solid soil and provides means for incorporating water in the base solvent in such wise as to produce a sub-microscopically fine dispersion of the water in the base solvent.

For use with water or aqueous rinses, the cleaners consist essentially of the basic cleaners just described plus supplementary emulsifiers. The supplementary emulsifiers render the cleaners self-emulsifying with aqueous rinses. Where the temperatures are below 32° F. the water rinses include a freezing point depressant. These cleaners can also be rinsed off with hydrocarbon solvents.

These water- or aqueously-rinsable cleaners consist essentially of an amount of: about from 75 to 95 percent of the basic cleaner and about from 5 to 25 percent of the supplementary emulisifiers.

The organic solvent component of the basic cleaners is generally a naphtha having a suitably high flash point, as for example, 80° F. or higher. Illustrative thereof are products such as "Soltrol 170," a naphtha having a flash point of 180°–190° F., made by Phillips Petroleum Co., Bartlesville, Okla.; "Amsco 140," a naphtha having a flash point of 135°–145° F., sold by American Mineral Spirits Co., New York, N.Y.

The organic solvent may consist of a plurality of solvents or a mixture of one or more suitable naphthas and one or more chlorinated hydrocarbons such as methylene chloride or trichloro-ethanes such as 1,1,1-trichloroethane, etc.

Suitable for use as the emulsifying component of the basic cleaners are: amine soaps, or a plurality of amine soaps, as for example various amine oleates. They may be used either in the preformed state, or conveniently prepared in the course of manufacturing the cleaners. Among such amine oleates are those wherein the amine moiety is an alkyl radical having from 2 to about 8 carbon atoms, preferably from 3 to 6 carbon atoms. The suitability of an amine oleate may be readily ascertained by simple test in the laboratory to determine the ability thereof to form water-in-oil emulsions that are transparent or virtually transparent. The transparencies of such water-in-oil emulsions indicate that excellent dispersion of the dispersed phases is achieved; and in consequence thereof the emulsions possess great stability. Aqueous solutions of hydroxylated amine soaps such as oleates of triethanolamine, diethanolamine, ethanolamine, isopropanolamine, n-propanolamine, etc., i.e., hydroxylated lower alkylamines, are normally incompatible with naphtha solvents. However, it has been discovered that combinations of such hydroxylated amine soaps with unsubstituted amine soaps are capable of forming stable water-in-solvent systems. Accordingly the suitability of combinations of amine soaps and hydroxylated amine soaps to effectuate

the formation of stable water-in-oil compositions may readily be ascertained by a simple preliminary testing.

Suitable freezing point depressants are: methanol, ethanol, propanol, ethylene glycol, etc.

The total amount of amine soap required to form stable water-in-solvent systems depends upon the quantity of water to be emulsified and the particular amine soap or combination of amine soaps employed. Generally the minimum proportions of soap-to-water on a weight to weight basis ranges from 1:1 up to 7:1 as the water content of the cleaning composition increases from 0.5 percent to 3 percent. The amount of the soap required to form a stable water-in-solvent system can accordingly be readily ascertained by preliminary tests, the formation of a transparent composition being an excellent indicator of the desired stability.

It is advantageous to use the freezing point depressants in an amount approximately equal to that of the water.

In addition to the aforementioned emulsifiers, the amine and hydroxylated amine soaps, there may also be included other emulsifying or surface active agents, as for example anionic surface active agents such as sodium sulphate derivative of 3,9-diethyl tridecanol-6 (available commercially as "Tergitol 7," a product of Carbide and Carbon Chemical Co., New York, N.Y.)

Among the substances which may be used as the supplementary emulsifiers for addition to the basic cleaners are: fatty alkylol amide condensates, relatively high molecular alkyl primary amines, i.e., primary aliphatic amines whereof the carbon chain varies in length from 10 to 18, high molecular weight fatty diamines having the general structure $R—NH—(CH_2)_n—NH_2$, wherein R varies in chain length from C_{12} to C_{18} and "*n*" is 2 or 3. The fatty alkylol amide condensate is available as "Alrosol O," a product of Geigy Chemical Corporation, Ardsley, N.Y. Also, an alkyl primary amine, such as a tertiary alkyl primary amine is available as "Primene J M T," Rohm & Haas Co., Philadelphia, Pa. The "Primenes" are mixtures of high molecular weight amines principally in the 18 to 21 range of carbon atoms. They have excellent solubility in oils and petroleum hydrocarbons and are useful as stabilizers and sludge inhibitors in fuel oil and other light oils, and as detergent, antioxidant and corrosion inhibiting additives in all varieties of petroleum products. The supplementary emulsifier may be used in the form of a mixture of "Alrosol O" and "Primene J M T," or "Alrosol O" alone. The "Alrosol O" may also be used in admixture with the aforesaid primary or secondary amines and alkyl-aryl-polyether alcohols, such as for example "Triton X–100," Rohm & Haas Co., Philadelphia, Pa.; alkali salts of petroleum sulphonic acids, such as ammonium petroleum sulphonate, available as "Ammonium Petronate" and "Petronate," L. Sonneborn Sons, New York, N.Y., etc. Suitable replacements for "Alrosol" are non-ionic emulsifiers, especially water free, prepared by the condensation of secondary hydroxylated amines such as diethanolamine with fatty acids, having a carbon content of about 12 to 20 carbon atoms. These products are available commercially as "Emcol P 5100," "Emcol P 5130" from Emulsol Corporation; "Drew 1011," E. F. Drew Co.; "Hymolon K," Hart Products Corp., New York, N.Y.; "Ninol 201," Ninol Laboratories, Inc., Chicago, Ill., etc.

The supplementary emulsifiers may be incorporated with the basic cleaners to provide a finished composition at the time of manufacture, or the supplementary emulsifiers may be added to the basic cleaners when desired. By allowing for the addition to the basic cleaner, when desired, of a supplementary emulsifier, the user can select a wash-rinse system on the basis of operating temperatures and availability of rinse materials.

The following are examples of compositions in accordance with the instant invention.

Example 1

An all weather cleaner for aircraft suitable for use in connection with an organic solvent rinse (selected for its non-deleterious action on aircraft surfaces and attendant structural components, as e.g., kerosene, mineral spirits, Stoddard solvent, etc.) and its high flash point to minimize flammability hazards has the following approximate composition:

	Parts by weight
High flash naphtha, e.g., "Soltrol 170"	98.5
Isopropylamine Oleate	0.5
Water	0.5
Methanol	0.5
Total	100.00

The aforementioned ingredients may be combined in a single mixing tank. If desired a smaller tank, as for example one-tenth the size of the main tank, may be used for stoichiometric amounts of the isopropylamine with the oleic acid. With vigorous stirring the amine is added to the oleic acid. If desired some cooling may be used to dissipate the heat resulting from the interaction of the amines and the oleic acid. When cooled to room temperature, circa 75° F. or lower, a mixture of the water and methanol are added to the amine soap and thoroughly stirred to insure uniformity. The mass thus produced has a soft grease-like consistency. Then the naphtha is slowly stirred into the mass. The resulting product is ready for use.

Example 2

An all weather cleaner for aircraft suitable for use with an organic solvent rinse, prepared in accordance with the general procedure described in Example 1 has the following composition:

	Parts by weight
High flash naphtha, e.g., "Amsco 140"	88.3
Diethylamine oleate	3.0
Triethanolamine oleate	6.0
Water	1.5
Ethylene glycol	1.2

Example 3

An all weather cleaner for aircraft suitable for use with an organic solvent rinse, prepared in accordance with the general procedure described in Example 1 has the following composition:

	Parts by weight
High flash naphtha, e.g., "Amsco 140"	87.3
n-Butylamine oleate	5.0
Triethanolamine oleate	5.0
Water	1.5
Ethylene glycol	1.2

Example 4

An all weather cleaner for aircraft suitable for use with an organic solvent rinse, prepared in accordance with the general procedure described in Example 1 has the following composition:

	Parts by weight
Soltrol 170	87.0
Isopropylamine oleate	10.0
Water	1.5
Methanol	1.5

Example 5

An all weather cleaner for aircraft suitable for use with an organic solvent rinse, prepared in accordance with the general procedure described in Example 1 has the following composition:

	Parts by weight
Soltrol 170	59.0
Isopropylamine oleate	35.0
Water	3.0
Methanol	3.0

Example 6

An all weather cleaner for aircraft suitable for use with an organic solvent rinse, prepared in accordance with the general procedure described in Example 1 has the following composition:

	Parts by weight
Solvent, a blend of: a solvent naphtha having a boiling point within the range of 365°–410° F. and a flash point of 140°–142° F., e.g., Amsco 140, 75 volume percent and Methylene chloride, 25 volume percent	89.3
Diethylamine oleate	2.7
Triethanolamine oleate	5.3
Water	1.5
Methanol	1.2

Example 7

An all weather cleaner for aircraft suitable for use with an organic solvent rinse, prepared in accordance with the general procedure described in Example 1 has the following composition:

	Parts by weight
Solvent, a blend of: Amsco 140, 75 vol. percent and Methylene chloride, 25 vol. percent	88.7
Diethylamine oleate	2.6
Triethanolamine oleate	5.3
Water	0.3
Methanol	1.6
Ethylene glycol	1.5
Total	100.0

Example 8

An all weather cleaner for aircraft suitable for use with an organic solvent rinse, prepared in accordance with the general procedure described in Example 1 has the following composition:

	Parts by weight
High flash naphtha, e.g., "Soltrol 170"	86.84
Diethylamine oleate	4.54
Triethanolamine oleate	5.48
"Tergitol 7" (contains 75% water)	1.99
Ethylene glycol	1.15
Total	100.00

Example 9

An all weather cleaner for aircraft suitable for use with an organic solvent rinse, prepared in accordance with the general procedure described in Example 1 has the following composition:

	Parts by weight
Solvent, a blend of: Soltrol 170, 85.0 vol. percent and Chlorothene, 15.0 vol. percent	88.02
Diethylamine oleate	3.0
Triethanolamine oleate	5.97
Water	0.39
"Tergitol 7" (contains 75% water)	1.46
Ethylene glycol	1.16
Total	100.00

Example 10

In an all weather cleaner for aircraft suitable for use with an organic solvent rinse, prepared in accordance with the general procedure described in Example 1 has the following composition:

	Parts by weight
Solvent, a blend of: Soltrol 170, 75 vol. percent and Chlorothene, 25 vol. percent	88.02
Diethylamine oleate	3.00
Triethanolamine oleate	5.97
Water	0.39
"Tergitol 7" (contains 75% water)	1.46
Ethylene glycol	1.16
Total	100.00

Example 11

An all weather cleaner for aircraft suitable for use with aqueous rinses or organic solvent rinses has the following composition:

	Parts By Weight	Percent By Weight
Base Cleaner:		
Soltrol 170	67.95	
Diethylamine Oleate	3.55	
Triethanolamine Oleate	4.29	
Tergitol 7 (75% water)	1.56	
Ethylene Glycol	0.90	78.25
Supplementary Emulsifier:		
Alrosol O	18.26	
Primene J M T	3.48	21.75

The aforementioned ingredients may be combined in a single mixing tank. If desired, a smaller supplementary tank, as described in Example 1, may be used for the preliminary mixing of all the ingredients but the naphtha. Diethylamine, triethanolamine and oleic acid in stoichiometric proportions are mixed as described in Example 1. When cooled to a temperature of 120° F. or lower, there may then be added thereto Tergitol 7 and the ethylene glycol, and the mass then thoroughly stirred to insure uniformity. The mass has a soft grease-like consistency at this point. Then the Alrosol O and Primene J M T are added thereto. When that mixture becomes homogeneous, the naphtha may then be slowly stirred into the homogeneous mass to produce the final product.

This product may be removed (in the rinsing operations) from the surface by washing or flushing with aqueous solutions containing suitable freezing point depressants to enable the rinse to be fluid at the operating temperature. Thus, for example, an aqueous solution that can be used at very low temperature is a composition as follows: 40 parts by volume of ethylene glycol, 10 parts by volume of isopropanol and 50 parts of water.

Example 12

An all weather cleaner for aircraft suitable for use either with aqueous or organic solvent rinses, made in accordance with the procedure of Example 11, has the following composition:

	Parts By Weight	Percent By Weight
Base Cleaner:		
Solvent (75 vol. percent Amsco 140 25 vol. percent methylene chloride)	89.3	
Diethylamine Oleate	2.6	
Triethanolamine Oleate	5.3	
Methanol	1.2	
Water	1.5	90
Supplementary Emulsifier:		
Alrosol O	90	
Primene J M T	10	10

Example 13

An all weather cleaner for aircraft suitable for use either with aqueous or organic solvent rinses, made in

accordance with the procedure of Example 11, has the following composition:

	Parts By Weight	Percent By Weight
Base Cleaner:		
Amsco 140	88.8	
Diethylamine Oleate	2.7	
Triethanolamine Oleate	5.3	
Ethylene Glycol	1.2	
Tergitol 7 (25% water)	2.0	90
Supplementary Emulsifier:		
Alrosol O		
Primene J M T	10	10

Example 14

An all weather cleaner for aircraft suitable for use either with aqueous or organic solvent rinses, made in accordance with the procedure of Example 11, has the following composition:

	Parts By Weight	Percent By Weight
Base Cleaner:		
Soltrol 170	67.73	
Chlorothene	20.29	
Diethylamine Oleate	3.00	
Triethanolamine Oleate	5.97	
Tergitol 7 (75% water)	1.46	
Water	0.39	
Ethylene Glycol	1.16	90
Supplementary Emulsifier:		
Alrosol O	90	
Primene J M T	10	10

It will be understood that the foregoing description of the invention and the examples set forth are merely illustrative thereof. Accordingly, the appended claims are to be construed as defining the invention within the full spirit and scope thereof.

We claim:

1. A water-in-oil emulsion cleaning composition consisting essentially of:

(1) about 59.0% to 98.5% of a member of the group consisting of
  (*a*) naphtha having a flash point of at least about 80° F. and
  (*b*) a mixture of a solvent as defined in (*a*), and
  (*c*) a member of the group consisting of methylene chloride and trichloroethane, the proportion of *a*:*c* in volume percent ranging from 100:0 to 75:25,

(2) 1 to 6% of a dispersed phase consisting of approximately equal parts of water and a freezing point depressant which is selected from the group consisting of methanol, ethanol, propanol, and ethylene glycol, and

(3) 0.5 to 35.0% of an emulsifying agent selected from the group consisting of
  (*a*) an oleic acid soap of an alkylamine whereof the alkyl radical has from 2 to 8 carbon atoms and
  (*b*) a mixture of a soap as defined in (*a*) and an oleic acid soap of a hydroxylated lower alkylamine whereof the carbon chain has from 2 to 3 carbon atoms,

and wherein the minimum proportions by weight of soap-to-water are in the range of about 1:1 to 7:1 as the water content increases from the aforesaid minimum to maximum and wherein the amounts of the soaps in mixture 3(*b*) are proportioned to maintain stability of the water-in-oil emulsion.

2. The detergent composition of claim 1, wherein (1) is naphtha.

3. The detergent composition of claim 1, wherein (1) is
  (*a*) naphtha and
  (*b*) trichloroethane.

4. A water-in-oil emulsion cleaning composition consisting essentially of from 75 to 95% of a composition in accordance with claim 1 and from 25 to 5% of a supplementary emulsifier selected from the group consisting of:
  primary aliphatic amines whereof the carbon chain has from 10 to 18 carbon atoms, and
  a condensate of a fatty acid having from 12 to 20 carbon atoms with diethanolamine.

5. The detergent composition of claim 4, wherein (1) is naphtha.

6. The detergent composition of claim 4, wherein (1) is
  (*a*) naphtha and
  (*b*) trichloroethane.

7. A water-in-oil emulsion cleaning composition consisting essentially of:

	Parts by weight
High flash naphtha	88.3
Diethylamine oleate	3.0
Triethanolamine oleate	6.0
Water	1.5
Ethylene glycol	1.2

8. A water-in-oil emulsion cleaning composition consisting essentially of:

	Parts by weight
A blend of: High flash naphtha, 75 volume percent / Methylene-chloride, 25 volume percent	89.3
Diethylamine oleate	2.7
Triethanolamine oleate	5.3
Water	1.5
Methanol	1.2

9. A water-in-oil emulsion cleaning composition consisting essentially of:

	Parts by weight
High flash naphtha	86.84
Diethylamine oleate	4.54
Triethanolamine oleate	5.48
Sodium sulfate derivative of 3,9-diethyl tridecanol-6	0.50
Water	1.49
Ethylene glycol	1.15

10. A water-in-oil cleaning composition consisting essentially of:

	Parts by weight
High flash naphtha	98.5
Isopropylamine oleate	0.5
Water	0.5
Methanol	0.5

11. A water-in-oil emulsion cleaning composition consisting essentially of:

	Parts by weight
High flash naphtha	67.95
Diethylamine oleate	3.55
Tiethanolamine oleate	4.29
Sodium sulfate derivative of 3,9-diethyl tridecanol-6	0.39
Water	1.17
Ethylene glycol	0.90
A condensate of a fatty acid having from 12 to 20 carbon atoms with diethanolamine	18.26
Tertiary alkyl primary high molecular amine whereof the carbon content is from 18 to 21 carbon atoms	3.48

12. A method of cleaning aircraft which comprises washing the aircraft with a composition in accordance with claim 1, followed by the rinsing thereof with an organic solvent rinse selected from the group consisting of kerosene, mineral spirits and Stoddard solvent.

13. A method of cleaning aircraft which comprises washing the aircraft with a composition in accordance

with claim 4, followed by the rinsing thereof with a member of the group consisting of

(1) an aqueous rinse and

(2) an organic solvent selected from the group consisting of kerosene, mineral spirits and Stoddard solvent.

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