(1)

Serial Number 437,086

Filing Date 27 Oct 1982

Inventor Charles R. Hegedus

NOTICE

The Government-owned invention described herein is available for licensing. Inquires and requests for licensing information should be addressed to:

DEPARTMENT OF THE NAVY
Chief of Naval Research (Code 302)
Arlington, Virginia 22217

CLASS 106 SUBCLASS 634

Navy Case No. 66219
1-215-441-3000
Warminster, PA 18974

PREPARATION OF WATER-DISPLACING PAINT

STATEMENT OF GOVERNMENT INTEREST

BACKGROUND OF THE INVENTION

The present invention relates to paints and more particularly to a method of preparing an effective water-displacing paint having a lusterless finish and improved storage stability.

Corrosion of metallic surfaces, particularly those of vehicles, such as aircraft, ships and automobiles, is an important concern of maintenance personnel because of the adverse effect on structural integrity and operating performance caused by corrosive deterioration. As a result, corrosion control procedures are steadfastly and regularly performed as part of an overall preventive maintenance program on such vehicles. When such vehicles are located in marine environments and subjected to salt spray and high humidity associated therewith, corrosion control becomes even more critical a task and one which is made extremely difficult by the environmental conditions. A salt-laden

atmosphere is highly corrosive, requiring the immediate attention be provided to cracked or chipped paint by recoating or touching-up the exposed bare metal substrate. When touch-up of the exposed area is effected, moisture on or near the substrate, if not treated for removal, will cause voids in the applied coating and inadequate adhesion between the coating and the substrate, ultimately leading to additional corrosion and further maintenance problems.

Numerous coating compositions have been developed to prevent corrosion of metal substrates, some featuring water-displacing qualities that facilitate their effective use in humid environments. One such water-displacing coating composition is a paint formulation described in U. S. Patent Application Serial No. 288,598 filed on July 30, 1981 by Charles R. Hegedus and Kenneth G. Clark. This water-displacing paint formulation resolved the adverse effect previously evidenced on the water-displacing qualities of existing coating compositions upon their pigmentation, and in doing so, provided a more permanent and durable corrosion preventive coating able to be applied to bare metal substrates in moist environments without need of priming. It has been discovered, however, that during extended periods of storage, pigments included in the water-displacing paint have settled and been compacted, making re-dispersion difficult upon application of the paint. Furthermore, formulations of the paint, having lusterless finishes, preferred in the military

community for camouflage purposes, have not been found to be as effective at displacing water as glossy coatings due to an adverse affect on the water-displacing properties caused by pigments conventionally used to flatten the paint.

SUMMARY OF THE INVENTION

Accordingly, it is a general purpose and object of the present invention to provide an improved formulation and preparation of a water-displacing paint, particularly one having a lusterless finish.

Another object of the present invention is to provide a method of formulating and preparing a lusterless water-displacing paint that increases the stability of and thereby maintains pigment dispersion during extended periods of storage.

Still another object of the present invention is to prepare a stable and effective water-displacing paint formulation that, when applied to a metal substrate, provides an effective lusterless coating to prevent corrosion.

Briefly, these and other objects of the present invention are accomplished by an improved preparation of a lusterless water-displacing paint wherein solvents including ethyl acetate, aromatic mineral spirits and 1,1,1 trichlorotrifluoroethane are mixed in specific proportional amounts and a binder of silicone alkyd resin is completely dissolved therein. A small quantity of a titanate coupling agent is blended into the solution and milled along with selected amounts of pigments, including

titanium dioxide and zinc molybdate, to a predetermined Hegman grind range. Thereafter, respective amounts of an anti-settling agent, preferably an extremely pure fumed silica, and a low molecular weight petroleum sulfonate are added and blended separately, each for about 30 minutes. Finally, a synthetic silica for flattening the finish of the paint coating is added and the resultant formulation milled to a fine Hegman grind.

Other objects, advantages and novel features of the present invention will become apparent from the following detailed description thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the present invention, a water-displacing paint is formulated and prepared so that the paint, when applied to a metal substrate without a primer, air dries to deposit an adherent, flexible, and durable coating having a lusterless finish in a desired color. In storage, the paint formulation exhibits reduced pigment settling, maintaining a higher level of pigment dispersion that facilitates restoration of a uniform suspension after extended storage periods, such as in the range of about one year. The paint, formulated and prepared according to the present invention, has a low surface tension, typically less than 30 dynes per centimeter, permitting it to spread completely and readily upon the substrate, and displaces water from the substrate upon application

by adsorbing onto the metal and diffusing under water droplets. It should be noted that the paint is immiscible with water so that droplets cannot be entrapped in the coating after application.

The paint contains a significant portion of a silicone alkyd resin which serves as a binder for the paint composition and provides the paint coating with its important physical characteristics. The silicone alkyd resin provides a polymer film having good adhesion, high temperature strength and hardness, and excellent chemical as well as abrasion resistance. The silicone alkyd resin is characterized by a solids content of 50 weight percent, a minimum phthalic anhydride content of approximately 20 weight percent, and a minimum oil content, preferably linseed for its drying qualities, of about 25 weight percent. One such silicone alkyd resin suitable for inclusion in the paint according to the present invention is Varkyd 385-50E, manufactured by the McCloskey Varnish Company.

A relatively small portion of a low molecular weight petroleum sulfonate is included in the paint to serve as a corrosion inhibitor, providing chemical protection for the metal substrate, and as an adsorption agent. Small percentages of the petroleum sulfonate offer sufficient corrosion retardation and surface adsorption without adversely effecting the desirable physical properties provided by the silicone alkyd resin. The petroleum sulfonate employed in the paint formulation, prepared

in accordance with the present invention and detailed hereinafter, is a sodium petroleum sulfonate having a molecular weight of about 400 to 500 and a typical specific gravity of 0.980 at 77°F. The sodium petroleum sulfonate has an acid number, in accordance with ASTM-D-974, typically in the range of 6-10, and a saponification number, in accordance with ASTM-D-94, of between 16-25. One suitable sodium petroleum sulfonate is ALOX 904, manufactured by the Alox Corporation. Other low molecular weight petroleum sulfonates commonly employed as corrosion inhibitors, particularly those of barium and ammonium, are as equally effective as the sodium petroleum sulfonate contained in the present paint formulation.

Controlled portions of ethyl acetate, aromatic mineral spirits, and 1,1,1 trichlorotrifluoroethane are included in the paint formulation as solvents. Selected and combined on the basis of solvency, evaporation rate, and ability to displace water, the solvents promote water displacement, ensure water immiscibility, and control drying time of the paint coating. The ethyl acetate employed in the paint formulation is a commercially available organic compound, also known chemically as ethyl ester acetic acid. The aromatic mineral spirits, also known as aromatic hydrocarbon, is a standard petroleum distillate having a boiling range between 365°F and 410°F, a minimum flash point of 145°F, and a specific gravity range of 0.89 - 0.90 at 60°F. One such aromatic mineral spirit suitable

for inclusion in the paint is Solvent G, manufactured by the AMSCO Division of Union Oil Company of California. The 1,1,1 trichlorotrifluoroethane included as a solvent in the paint is a widely known and generally available fluorohydrocarbon, one suitable trichlorotrifluoroethane being Freon TF, manufactured by the DuPont Company.

An organo-titanate of the monoalkoxy type is included as a coupling agent in the paint in small percentages to promote surface adhesion of the paint coating. The titanate employed in the present formulation is isopropyl, tri (N ethylamino-ethylamino) titanate in a 4.5% (by mass) solution with isopropyl alcohol. One suitable such titanate is KR-44S, manufactured by Kenrich Petrochemicals, Inc.

Desired coloring of the paint is provided by the addition of standard tinting pigments in appropriate amounts. Selected portions of commercially available compounds of rutile titanium dioxide and zinc molybdate are combined in the present paint formulations to impart a white color to the paint. One suitable titanium dioxide compound commercially available is R-960, manufactured by the DuPont Company. An effective zinc molybdate compound suitable as a white pigment is MOLY-WHITE 101, manufactured by Sherwin Williams Chemicals. It should be understood that alternate colors can be obtained by decreasing the portion of titanium dioxide in the white paint formulation and adding the appropriate tinting pigments to impart the desired

color to the paint.

A commercially available anti-settling agent is included in the paint formulation in a small percentage to reduce the extent of pigment dispersion occurring during storage. The most effective anti-settling agent employed in the paint formulation is an extremely pure (>99.8%) fumed silica in very fine powder form having an amorphous X-ray structure and hydrophobic characteristics. One suitable such fumed silica is AEROSIL R972, manufactured by the Degussa Corporation. Another effective anti-settling agent is a high molecular weight, unsaturated polycarboxylic acid. One particular polycarboxylic acid found suitable for the present invention is BYK-P-104, manufactured by Byk-Mallinckrodt.

To flatten the desired color of the paint coating and thereby provide the paint with a lusterless finish, a selected amount of synthetic silica extender pigments are included in the paint formulation in accordance with the present invention. These synthetic silica pigments having oil absorption ranging from 140 to 180 pounds per 100 pounds of linseed oil were found to reduce the 60 and 85 degree gloss effectively when measured according to ASTM method D-523. One such effective synthetic silica is Syloid 74, manufactured by W. R. Grace and Company.

A most effective example of the paint formulated and prepared according to the present invention is set forth below on a weight percent basis.

TABLE I

Silicone Alkyd Resin	36.3%
Ethyl Acetate	18.1%
Aromatic Mineral Spirits	10.8%
1,1,1 Trichlorotriflouroethane	7.1%
Rutile Titanium Dioxide	10.3%
Zinc Molybdate	6.3%
Isopropyl, Tri (N-ethylamino-ethylamino) Titanate (4.5% in isopropyl alcohol)	2.1%
Fumed Silica	0.8%
Sodium Petroleum Sulfonate	2.1%
Synthetic Silica	6.4%

In accordance with the present invention, the foregoing paint formulation is prepared by first mixing the solvents, ethyl acetate, mineral spirits and 1,1,1 trichlorotrifluoroethane, respectively, while stirring continuously. The silicone alkyd resin is then added to the solvent mixture and stirred until the resin is completely dissolved. Thereafter, the organo-titanate coupling agent is blended into the resin solution, typically stirring for approximately 5 minutes. The resultant solution is then placed in a conventional ball mill along with the titanium dioxide and zinc molybdate, and milled to a Hegman grind ranging from 6 to 7. Thereupon, respective amounts of the

fumed silica and petroleum sulfonate are added separately, milling for about 30 minutes after each addition. Finally, the synthetic silica is added and the resultant formulation milled until the Hegman grind is consistently between 3 and 5.

Evaluation of the paint formulation included testing of its storage stability and pigment settling under accelerated conditioning. In the storage stability test, performed in accordance with ASTM D-869, a sample of the foregoing paint formulation was stored in a clear glass jar under ambient laboratory conditions for a period of 120 days, and evaluated periodically for pigment condition both visually and physically by penetration of the pigment sediment layer with a glass stirring rod. In the accelerated pigment settling test, a sample of the paint formulation was placed in a centrifuge at 750 rotations per minute for 2 one-hour periods per day for 4 days to approximate the amount of pigment settling normally produced in one year of storage. Evaluation of both test samples evidenced an improved pigment settling condition and greater ease of pigment re-dispersion after agitation, either by hand or preferably using an automatic paint conditioner, such as a paint shaker.

To evaluate the water-displacing ability of the present paint formulation, steel test panels inclined at a 30° angle from the horizontal were sprayed liberally with red-dyed synthetic sea water so that fine droplets completely covered the panels.

Thereafter, one milliliter of the paint formulation was poured along the upper edge of the panel using a pipette and, after being suspended vertically for one minute, the panels were placed horizontally, painted side up, in a closed dessicator at 70 $\pm$ 5°F(21$\pm$3°C) and 100% static relative humidity. Immediately following the application of the paint formulation to the panels, the paint coating was uniform with no indication of water remaining on the panels. After four hours in the dessicator, the panels exhibited no corrosion demonstrating the effectiveness of the formulation as a water-displacing, anti-corrosive agent.

In extended atmospheric exposure testing, the present paint formulation was applied to bare specimens of an aluminum alloy 2024-T3 cleaned and treated in accordance with Military Specification MIL-C-81706 to produce a chemical conversion coating thereon conforming to MIL-C-5541. After seven days, the painted specimens were scribed through the respective coatings and into the aluminum substrate. Two groups of specimens were then exposed separately to a harsh naval environment for a period of eight months and an "acid rain" environment for a period of fifteen months. Following the exposure periods, both groups of specimens were evaluated and exhibited no substrate corrosion in the unscribed area while minimal substrate corrosion was evidenced in and along the scribe.

It should be understood that the foregoing paint formulation can be applied by spray techniques and may be

packaged in a pressurized spray container using dichlorodifluoromethane (Freon-12) as a propellant. Effective spray application of the paint is achieved by combining approximately 250 milliliters of the paint, formulated in Table I and prepared according to the present invention, with approximately 115 milliliters of the propellant in a standard 16 ounce (473 ml) pressurized spray container.

Upon the metal substrate to be coated, it is recommended that the paint formulation be applied to a dry film thickness of 35 $\pm$ 5μ (1.3 $\pm$ 0.2 mils). Upon application, the organic solvents begin to evaporate into the atmosphere and the silicone alkyd polymer reacts with oxygen in the air causing oxidation and crosslinking to occur. Such reaction results in formation of a flexible, pigmented coating which is initially soft but which hardens in time, typically in about 8 hours, to produce a hard, durable and lusterless finish for long-term corrosion protection of the metal substrate.

Therefore, it is now apparent that the disclosed invention provides an improved formulation and preparation of a corrosion preventive paint for coating metal substrates. In particular, the disclosed preparation of a corrosion preventive paint formulation provides a lusterless coating that effectively displaces water on the surface of the metal substrate being coated. Furthermore, the disclosed method of preparing a lusterless water-displacing paint increases the stability of and

thereby maintains pigment dispersion during extended periods of paint storage. In addition, the disclosed preparation of a lusterless, water-displacing paint is safe and easy to use, and economical to manufacture.

ABSTRACT OF THE DISCLOSURE

An improved preparation of a lusterless water-displacing paint is disclosed wherein solvents including ethyl acetate, aromatic mineral spirits and 1,1,1 trichloro-trifluoroethane are mixed in specific proportional amounts and a binder of silicone alkyd resin is completely dissolved therein. A small quantity of a titanate coupling agent is blended into the solution and milled along with selected amounts of pigments, including titanium dioxide and zinc molybdate, to a predetermined Hegman grind range. Thereafter, respective amounts of an anti-settling agent, preferably an extremely pure fumed silica, and a low molecular weight petroleum sulfonate are added and blended separately, each for about 30 minutes. Finally, a synthetic silica for flattening the finish of the paint coating is added and the resultant formulation milled to a fine Hegman grind.