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(54) Title: WATER BASED COATING FOR ROUGHENED METAL SURFACES

(57) Abstract

An emulsion of an amine neutralized hydrocarbon oxidate composition including alkali metal e.g. sodium petroleum sulfonates is applied to metallurgically prepared roughened surfaces, e.g. carbonitrided steel, to form corrosion preventive films.

* See back of page

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WATER BASED COATING FOR ROUGHENED METAL SURFACES

Cross reference to Related Applications

Applications 6277NUS, now U.S. 4,748,055; 6277PUS, USSN 199,975; RI-6277QUS, USSN 057,677; and RI-6277RUS, USSN 243,957, cover siloxane compositions on roughened metals.

Background of Invention

The invention pertains to the field of corrosion protective coatings generally classified in U.S. Patent and Trademark Office class 427, subclasses 292, 409, 240, 421, 428, 429, and 435.

Description of the Prior Art

U.S. 2,528,535 to Merker teaches phosphating oil-in-water systems for lubricating compositions preferably with oxidation inhibitors and mentions the possibility of adding rust/corrosion inhibitors, preferably less than 3% by weight.

U.S. 4,737,385 to Pekar (assigned to Texo Corporation), teaches di-phase oil coatings which are applied to surfaces which have been conventionally phosphated to improve corrosion resistance. Components are siloxane compositions, water based siloxane compositions mixed with water-reducible epoxy-esters and then baked to produce the final coating.

U.S. 4,135,043 to Davis (assigned to Lubrizol), oil-soluble dispersants with dimercaptothiadiazole, to

suppress copper activity and "lead paint" deposition in lubricants.

U.S. 4,606,945 to Itoh (assigned to Nissan), coatings to protect the surface of automobiles and other articles.

U.S. 4,629,753 to Quinn (assigned to Lubrizol), uses water dispersed compositions comprising solid metal containing colloidal particles and liquid dispersing medium, and hydrophobic-polar organic molecules.

U.S. 4,198,285 and 4,186,077 to Carlos et al. (assigned to Ashland), discuss the preparation of hydrocarbon oxidates using amines and sulfobetains which are useful in preparing corrosion inhibiting compositions in solvent systems.

U.S. 4,479,981 to Winters et al. (assigned to Ashland), discusses the preparation of waterborne corrosion preventive compositions including amine salts of oxygenated waxes.

None of the above patents disclose the waterbased, air-dryable compositions of the present invention for use over metallurgically-prepared ("roughened") metallic surfaces to provide demonstrated high salt-spray resistance.

Summary of the Invention

I. General Statement of the Invention:

According to the present invention, metallic work pieces are protected from corrosion, e.g. ASTM B-117 salt spray tests, by the steps of:

(a) roughening the surfaces of the work pieces, e.g. by sand blasting, by nitrocarburizing, by oxynitriding, by nitrocarburizing and oxidizing, by phosphating, or by other metallurgical processes which provide an expanded, porous surface having sufficient strength to retain a coating onto the metallic work piece surface; and

(b) applying to said expanded surface a waterborne self-healing corrosion protective coating composition capable of application to metallic surfaces; said composition comprising in combination:

1. An oxygenated hydrocarbon composition produced by the partial oxidation of an aliphatic petroleum fraction to a total acid number in the range of about 10 to about 90, said oxidate having been neutralized with an aliphatic amine to render it capable of being emulsified. Further this composition comprises the addition of an alkali/alkaline earth metal sulfonate to further improve corrosion protection and aid in emulsification. Preferred oxygenated hydrocarbon composition is Aqualox 2268 commercially available from Alox Corp., Niagara Falls, New York.

2. Optionally an alkali substituted organic amine such as dimethylethanolamine, triethylamine, triethanolamine, or others.

3. Water

4. Optional thickeners, pigments, fillers, dyes, odorants, oils, cosolvents, extreme pressure (E.P.) additives and other optional additives well known to those skilled in the art.

Utility of the Invention

This invention provides extreme corrosion protection of a level previously usually obtained only by expensive electroplate,e.g. cadmium or even chromium plating, at a small fraction of the cost of such plating. An attractive black surface can be provided to fit the prevailing fashion for black surfaces in the automotive industry.

Brief Description of the Drawing

Figure 1 is a graph of salt spray resistance (days to failure) for several inventive and conventional formulations.

Figure 2 is a schematic diagram of a manufacture according to the invention.

Figure 3 is a schematic diagram of a process of the present invention showing nitrocarburizing followed by dip coating into the emulsion compositions of the invention.

Description of the Preferred Embodiments

1. Starting Materials:

(a) metallurgically preparing the work piece surfaces;

Surface Treatment Processes

Surface treatment processes can be conventional such as chromate, and particularly preferred nitriding or phosphating.

See generally Kirk and Othmer, "Encyclopedia of Chemical Technology", 2nd ed., vol. 18 (1969), pp.282-303 and the later editions.

Phosphating can be accomplished by the conventional techniques such as those set forth in "Practical Phosphate Coatings", Mangill Company, and U.S. Patents 3,967,948, 2,465,247, 3,686,031, 4,419,199, 4,539,051, and 4,540,637 and references thereto. For automotive uses, preferred phosphating is to a thickness of at least 2,000-3,000 mg Zinc Phosphate/ square foot of work piece.

"Nitrogen-treatment" can be either salt bath or fluidized bed nitriding, such as the commercial processes "Tuff Tride", "Melonite", "QPQ" (Quench-Polish-Quench, in which salt bath nitriding is followed by quench in an oxidizing salt bath,followed by mechanical polishing, and a second quench), or fluidized bed nitriding as described in "Fluidized Bed Furnace Heat Treating Applications for the Dye Casting Industry", JAPKA, May-June 1983, Dye Casting Engineer. Other miscellaneous nitrogen treatment processes which may be employed with the invention include Procedyne's "Dyna-case Surface Hardening Treatment". deep case carburization in a fluidized furnace by adding methanol which is vaporized and mixed with nitrogen and a small

amount of natural gas to form a synthetic endothermic atmosphere within the treating furnace at about 899-1010 C(1650-1850F) for 10 minutes- 1 hours, followed by quenching; nitriding by adding nitrogen from raw ammonia onto the surface of the material at 510-593°C (950-1100°F) to provide a case of 0.001-0.015 inches deep; nitrocarburizing providing a case of 0.005-0.0020 inches deep by contacting mixtures of natural gas and raw ammonia in a fluid bed furnace at 566-621°C (1050-1150°F) for 0.5-2.0 hours; steam blueing in a fluid bed furnace at 343-538°C (650-100°F) for 20 minutes-1 hour to provide a blue or black surface, oxynitriding or even combinations of these conventional surface treatment processes.

Nitrocarburizing and oxynitriding are particularly preferred.

(b) application of the compositions of the invention;

Application: The formulations of the present invention may be applied to substrates to be protected by conventional application techniques, such as spraying, brushing, dipping,flow-coating, dipspinning, "Filwhirl", or airless spraying. Coating thickness can be varied by changing the formulation, the number of coats,or the amount applied per coat but in general will be in the range from about 0.1 to 5 mils, more preferably 0.1 to 2 mils, after drying.

1. Oxygenated hydrocarbon composition

The oxygenated hydrocarbon composition will be produced according to the techniques commonly known to those experienced in the art of preparing oxidized

petrolatums or hydrocarbon waxes. U.S. 4,198,285 and 4,186,077 to Carlos discuss the preparation of hydrocarbon oxidates. These oxidates will have a total acid number in the range of about 10-90, more preferred 15-70, and most preferred 20-60, and preferably will contain an amount of alkali substituted organic amine (see below). Typical viscosity of said oxidate will be in the range of about 10-70 centstokes at 100C. Charge stocks for the preparation of said oxidates are normally of the C30-C80 chain length. Chain lengths of oxidates vary due to oxygen attack on secondary carbons with the formation of low molecular weight acids such as formic, butyric, acetic, propionic, etc. These lower molecular weight acids are undesirable and will be removed from oxidate composition by washing or stripping with air or nitrogen. Equally higher molecular weight acids consisting of C5+ to C80 chain lengths are formed along with esters, aldehydes, ketones, lactones, alcohols, peroxides, and various other hydroxy acids formed during the oxidation process. Normally saponification values are 1-3 times greater than the acid value formed during oxidation due to free fatty acids. Such amine/oxidate compositions are described in U.S. 4,479,981 to Winters et.al.. Further the composition will contain about 0.1 to 50.0 % by weight of an alkali/alkaline earth metal organic sulfonate.

Most preferred of the compositions commercially available are those currently available under the brand name "Aqualox 2268" from Alox Corp. of Niagara Falls, New York.

About 0.5 to 45, more preferred 1.0 to 30, and most preferred 10-25 parts by weight of the oxygenated hydrocarbon composition will be used in the composition of the invention.

Stated differently, the Aqualox composition may be described as an partially neutralized amine soap of an oxidized petrolatum to which an amount of alkali earth metal organic sulfonate has been added to provide a mixture which is capable of being either solvent dispersed or emulsified into an oil in water emulsion.

About 1 to 30, more preferably about 3 to 20, and most preferably about 4 to 10 parts by weight of a alkali metal or alkaline earth metal sulfonate can be added. Such sulfonate will preferably have a total base number of about 0.5 to 200, more preferably about 1 to 100, most preferably 5 to 50. Preferred sulfonates are alkali metal sulfonates, more preferably sodium sulfonate, and most preferably Lubrizol 5363 from Lubrizol Corp., Wickliffe, Ohio.

2. Additional Alkali substituted aliphatic amine (Optional)

In addition to any alkali substituted, aliphatic amine contained in the oxidized hydrocarbon composition can optionally be added so that the total composition contains about 0.5 to 30, more preferred 1 to 25 and most preferred 2 to 10 parts by weight of a neutralizing amine chosen from the group consisting of morpholine, monoethanolamine, dimethylamine, trimethylamine, dimethylethanolamine, triethanolamine, or AMP-95(2-Amino-2-Methyl-1-Propanol). Most preferred is triethylamine available from Union Carbide Corp., Danbury, Connecticut. "Amine" as used herein also includes aqua ammonia which can function as an amine in these formulations. The amine can be used to adjust pH to the preferred range of about 7 to 11; more preferably about 8 to 9.5.

3. Water

Water employed in the formulation is most preferred as deionized or distilled but is not critical as normal tap water may be employed. Water added should not be in excess of that which produces a dried film of the desired thickness. Compositions will preferably contain about 5 to 95, more preferably 50 to 90, and most preferably 60 to 85% water. Concentrates may be shipped for dilution at point of use.

2. Concentrate Preparation

Apparatus: The apparatus for the present invention will be that conventionally utilized in the preparation of coatings compositions, e.g. kettles and mixing tanks having flow metering or measuring devices and agitation means, e.g. pumps mounted on side-arms connecting with the main vessel, internal stirrers, contra-rotating shearing devices and any of the other available devices which are well known to the art.

Temperature: The temperature during mixing may be different during different stages in the formulation. These temperatures are not narrowly critical and will vary to provide faster mixing or better compatibility of ingredients according to observation of those skilled in the art. For example, pressure vessels may be utilized for the purpose of raising ingredient boiling points,where useful, in order to provide better dispersion of difficult-to-mix ingredients.

Mixing Procedure: While the formulation of the present invention may be manufactured continuously if desired, batch techniques will be more usually employed. The oxygenated hydrocarbon-amine-sulfonate emulsions are

mixed thoroughly under constant agitation, after which the formulation is drawn off into shipping containers, e.g. tank cars, tank trucks, drums, or smaller cans and containers.

Quality Control: The finished formulation, prior to packaging, will generally be checked for viscosity, pH, non-volatiles, weight per gallon, freeze thaw stability, corrosion protection under accelerated conditions and other tests utilizing techniques well known to the coatings industry.

3. Emulsion Preparation

The concentrate(e.g. prepared according to Example 1) is diluted with 0 to 80, or more preferably 0 to 55, and most preferably 0 to 30 parts by weight of water to form the emulsion which is applied to the work pieces. The solution is preferably applied at 25C(77F).

4. Batch or Continuous Basis

While the examples describe the invention on a batch basis, it may come, of course, to be practiced on a continuous basis with continuous flows of starting materials into the mixing vessel and with continuous coating techniques, e.g. roller coating continuous conveyor or even continuous work piece, e.g. sheet steel moving continuously through a dip tank.

EXAMPLE 1

(Formulation according to the invention providing excellent salt spray resistance and shelf life.)

To a conventional steam jacketed mixing kettle equipped with a rotary stirrer are added 80 parts by weight of water. Agitation is started and the water is heated to a temperature of 150-160F(65-71C). To the hot water are added 20 parts by weight of a hydrocarbon oxidate, amine, and sulfonate composition. This preferred composition is known as Aqualox 2268 available from Alox Corporation, Niagara Falls, New York. Agitation and heating are continued until the complex becomes molten and the homogeneous emulsion is formed. Heating is at this point discontinued and the material is sampled for quality control testing. This emulsion, once testing is completed, can be applied to metallurgically prepared parts, e.g. phosphated, nitrocarburized or carbonitrided,to give soft oily films which give outstanding corrosion protection.

The resulting formulation is tested for corrosion protection by applying it to a ferrous work piece which has been previously nitrocarburized by conventional techniques, e.g. those of U.S. 4,496,401, Dawes, or U.S. 4,756,774 to Fox, by dipping the work piece into the emulsion formed. After drying 24 hours, the test work piece is subjected to a 5% neutral pH salt(NaCl) spray at a temperature of 35C(95F) according to ASTM B-117. Test parts resist failure (corrosion) for 4200 hours.

A sample of emulsion shows no significant separation (e.g., less than 2% "cream") upon standing at room temperature for 24 hours.

When a work piece as previously described is dipped into the above formulation and allowed to dry at room temperature at approximately 50% relative humidity, the coating is dry to touch in 0.5 to 2 hours. but is cured for 24 hours. The coating remains soft and oily to touch

but remains self healing, i.e., a scratch made with a scribe heals to protect the metal.

For comparison, a similar phosphated work piece coated with Aqualox fails in 48 hours and a similar but uncoated nitrocarburized work piece fails in 72 hours of salt spray. Thus, the combination of the nitrogen-treated surface plus the coating compositions of this invention provides dramatically longer protection.

EXAMPLES II TO V

(according to Table I)

When various differing compositions are prepared according to Example I using ingredients according to Table 1, the results are as shown in Table 2.

Modifications

Specific compositions, methods, or embodiments discussed are intended to be only illustrative of the invention disclosed by this specification. Variation on these compositions, methods, or embodiments are readily apparent to a person of skill in the art based upon the teachings of this specification and are therefore intended to be included as part of the inventions disclosed herein. For example, the formulation may contain additional corrosion inhibitors, biocides, antifoamers, dyes, pigments, antiwear additives, EP (extreme pressure) additives, perfume or odor masking agents, etc.

Reference made in the other specification is intended to result in such patents or literature being expressly incorporated herein by reference including any

patents or other literature references cited within such patents.

What is claimed is:

TABLE I

Examples

Ingredients	I. INV B1754-58B	II. B1646-199E Polysiloxane 4,748,055	III. COMP B1646-200A Joncryl 614	IV. COMP B1646-192B SACI 445W	V. COMP B1646-200D Joncryl 639
Aqualox 2268	20.00				
NitroCoat 801		20.00			
Joncryl 614			100.00		
SACI 445W				100.00	
Joncryl 639					100.00
Water	80.00	80.00		80.00	
Total Parts	100.00	100.00	100.00	180.00	100.00
(1) Days Till Failure	175 days No Rust	29 days 40% Failure	0.4 days 100% Failure	9 days 60% Failure	3 days 100% Failure
Film Integrity	Oily	Oily	Firm	Tacky	Firm

(1) All blends evaluated at 20% weight non-volatile.

NitroCoat is a registered trademark of Ashland Oil, Inc.

CLAIMS

1. A method for protecting metallic work pieces from corrosion, comprising in combination the steps of:

A. roughening the surfaces of said work pieces by sandblasting, oxynitriding, nitrocarburizing, nitrocarburizing plus oxidizing, phosphating or other metallurgical process to provide an expanded porous surface, and

B. applying to said expanded surface a corrosion protective coating composition capable of application to metallic surfaces; said composition comprising in combination:

1. oxygenated hydrocarbon composition having acid number of about 10 to 90, and viscosity of about 10 to 90 centistoke;

2. aliphatic amine;

3. alkali metal sulfonate and/or alkaline earth metal sulfonate; and

4. water

2. A method according to Claim 1 wherein said hydrocarbon oxidate is a hydrocarbon wax oxidate, a petrolatum oxidate, or mixtures thereof having an acid number ranging from about 10 to 90 and wherein said hydrocarbon oxidate is produced by mixing the corresponding hydrocarbon wax and petrolatum and then oxidizing the mixture.

3. A method according to Claim 1 wherein said aliphatic amine comprises amines selected from the group consisting of morpholine, monoethanolamine, dimethylamine, triethylamine, dimethylethanolamine, triethanolamine, 2-Amine-2-Methyl-1-Propanol, aqua ammonia or mixtures thereof, and wherein said alkali or alkaline earth metal sulfonate contains calcium, barium, sodium, magnesium, zinc, lithium, strontium, cadmium, aluminum, cesium, rubidium, tin, or bismuth.

4. A method according to Claim 2 wherein said alkali or alkaline earth metal sulfonate contains sodium.

5. A method according to Claim 1 wherein said coating composition comprises Aqualox 2268.

6. A method according to Claim 1 wherein composition consists essentially of water and dispersed within said water:

A. A film forming amount of an oxygenated hydrocarbon composition produced by the partial

oxidation of aliphatic petroleum fractions neutralized with aliphatic amine and blended with alkali metal petroleum sulfonates having a melting point in the range of about 40-70°C (104-158°F), said alkali metal sulfonate having a total base number in the range of 0.05 to about 200.

B. substituted aliphatic amine or amines.

7. A manufacture comprising a ferrous metal work piece having a surface prepared by sandblasting, oxynitriding, nitrocarburizing, nitrocarburizing plus oxidizing, phosphating or other metallurgical process to provide an expanded porous surface, said surface being coated with a composition comprising in combination:

1. oxygenated hydrocarbon composition produced by partial oxidation of aliphatic petroleum fractions neutralized with aliphatic amine or amines and blended with alkali metal petroleum sulfonates with said mixture having a melting point of about 40-70°C (104-158°F), said alkali metal sulfonate having a total base number in the range of about 0.05 to about 200;

2. optionally a substituted aliphatic amine

3. water

8. A method according to Claim 1 wherein said composition additionally comprise an alkali substituted aliphatic amine selected from the group consisting of morpholine, monoethanolamine, dimethylamine, triethylamine, dimethylethanolamine, triethanolamine, 2-Amine-2-Methyl-1-Propanol, ammonium hydroxide, and mixtures therein.

9. A method according to Claim 1 wherein said composition comprises:

A. about 0.5 to 45 wt.% oxygenated hydrocarbon composition,

B. about 0.5 to 30 wt.% alkali-substituted aliphatic amine,

C. about 0.5 to 30 wt.% alkali/alkaline earth metal sulfonate;

D. about 5 to 95 wt.% water.

10. A manufacture comprising a ferrous metal work piece having a surface prepared by sandblasting, oxynitriding, nitrocarburizing, nitrocarburizing plus oxidizing, phosphating or other metallurgical process to provide an expanded porous surface, and coated with a composition comprising in combination:

A. oxygenated hydrocarbon composition produced by partial oxidation of aliphatic petroleum fractions neutralized with aliphatic amine and blended with alkali metal petroleum sulfonates having a melting point in the range of about 40-70°C (104-158°F), said alkali metal sulfonate having a total base number in the range of about 0.05 to about 200;

B. a fatty acid having an acid value in the range of about 80 to about 250, and saponification number in the range of from about 80 to about 250, and having an iodine number in the range of about 110 to 160.

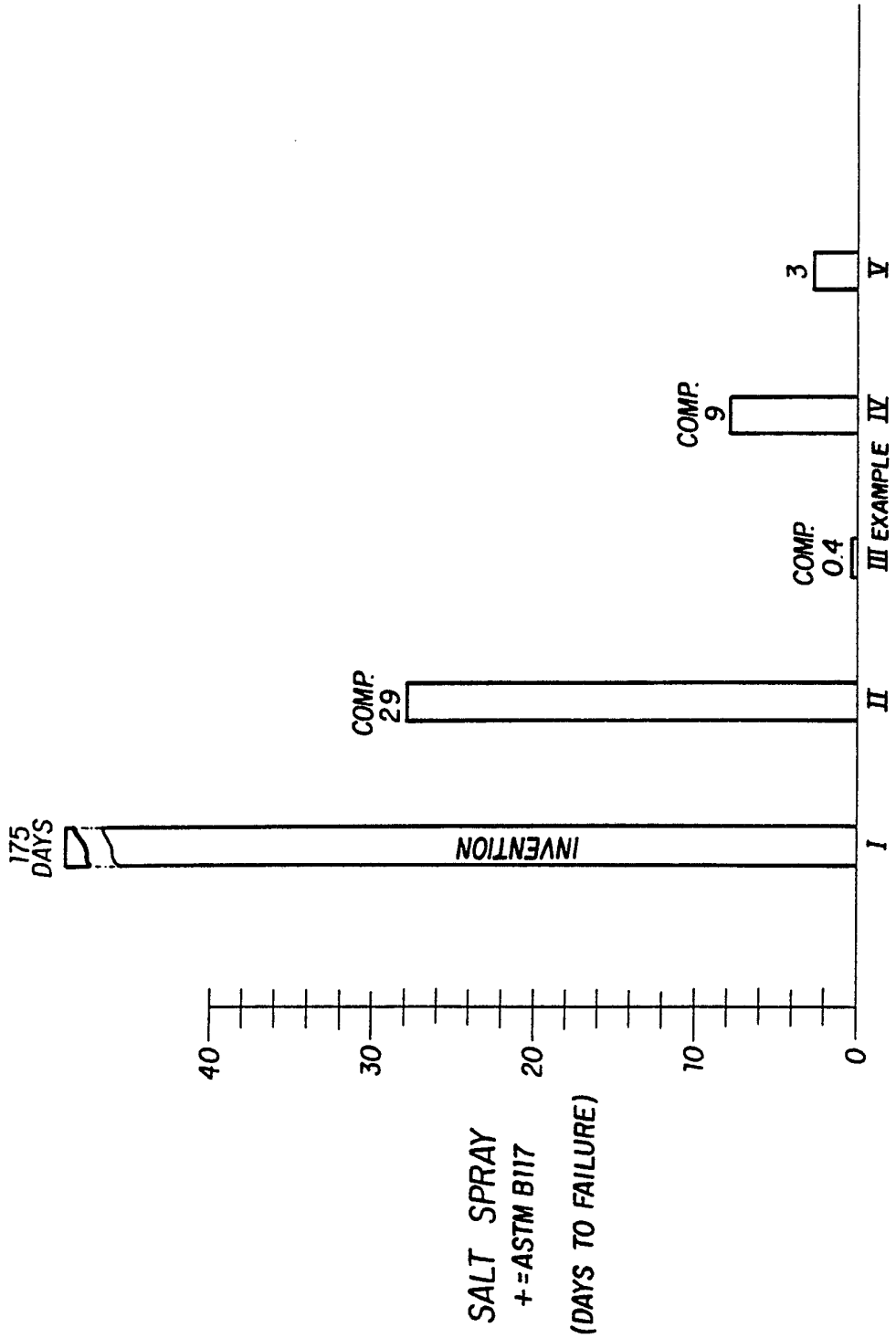
SALT SPRAY
+=ASTM B117
(DAYS TO FAILURE)
0
10
20
30
40
175 DAYS
INVENTION
I
COMP. 29
II
COMP. 0.4
III
EXAMPLE
COMP. 9
IV
3
V

FIG. 1

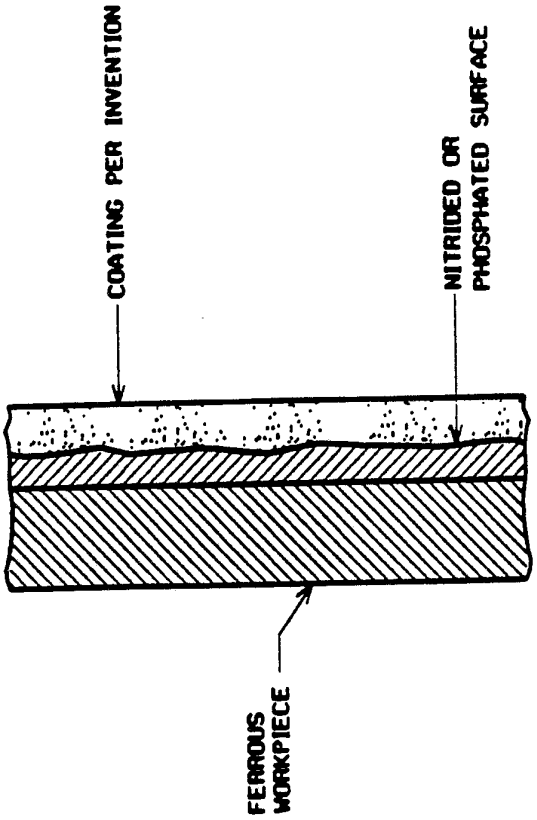
COATING PER INVENTION
NITRIDED OR PHOSPHATED SURFACE
FERROUS WORKPIECE

FIG.2

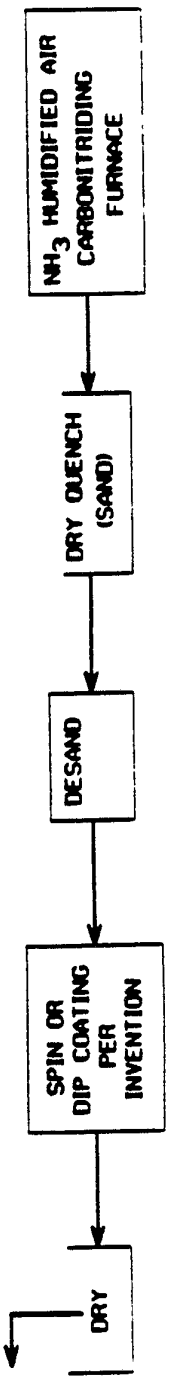
NH_3 HUMIDIFIED AIR CARBONITRIDING FURNACE
DRY QUENCH (SAND)
DESAND
SPIN OR DIP COATING PER INVENTION
DRY

FIG.3