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PROTECTIVE COATING FOR FERROUS TYPE METAL

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This invention relates to a method of preparing a rust preventive coating on ferrous metals. More particularly, this invention is concerned with a method of forming a dark blue, rust preventive coating on ferrous metal through the use of soluble oils of selected formulation and other mineral oil compositions containing water, and emulsifier and a coupling agent.

Soluble oils comprise homogeneous mixtures of oil and emulsifiers and constitute a well recognized type of oil. Soluble oils have the ability to form oil-in-water emulsions when added to water in various concentrations, commonly 1:1–1:100 ratios of oil-to-water. Because of their cooling and lubricating characteristics, soluble oils find extensive application in such industrial processes as metal working operations, including cutting, shearing, grinding, grooving, extruding, cold drawing and the like. Soluble oils are known under various names such as emulsifiable cutting oils, certin types of spray oils, rust proofing oils and the like.

Staining of ferrous metals by soluble oil emulsions containing high percentages of water has been observed heretofore. Such a staining of the ferrous metal is considered objectionable where the ferrous metal is to be subjected to further surface treatment, such as burnishing, and in operations where the final finish of the metal must be bright. The prior art is directed to ways for preventing the formation of a stain during contact of the freshly ground surfaces of the ferrous metal with the soluble oil emulsions.

We have now discovered a method of producing a rust-resistant, blue, protective coating on ferrous metals through the application of soluble oils rather than soluble oil emulsions under suitable conditions, including specified water concentrations in the soluble oils. This invention also applies to any mineral oil composition which contains an emulsifier, water in a specified concentration and a sufficient amount of a coupling agent to prevent emulsification of the oil and phase separation. This blue coating is of an adherent, long-lasting nature and serves to protect the ferrous metal surface against corrosion and oxidation under usual conditions of use. Furthermore, it may be utilized for its decorative color and appearance.

It is therefore, an object of our invention to provide a method of uniformly producing a corrosion-resistant, adherent coating on ferrous metal surfaces.

It is another object of our invention to utilize a soluble oil or soluble oil blend, or other mineral oil composition, rather than a soluble oil emulsion or other mineral oil emulsion in the preparation of a corrosion-resistant, rust-preventive, long-wearing, ferrous metal coating.

It is also an object of our invention to form a dark blue, protective coating on ferrous metal surfaces through the use of a soluble oil blend of low total water concentration.

It is a further object of our invention to provide a method for producing a corrosion-resistant, long-wearing, rust-preventive, dark blue coating of adherent nature on the surface of ferrous-containing metals and alloys through the use of a mineral oil composition, particularly a soluble oil, which may be re-used after the coating treatment without reconstitution.

A particular point of novelty in our invention lies in the uniform production of a valuable protective coating for ferrous metals through the use of selected mineral oil compositions, particularly soluble oil formulations, containing at least about 1% total water, an emulsifier and a coupling agent while said oils are in an essentially unemulsified condition and without substantial phase separation.

The soluble oils which may be utilized in the process of our invention are soluble oils of the usual type of formulation, that is, containing an emulsifier, a mineral lubricating oil, a small amount of alkali metal hydroxide, a coupling agent and optionally an extender and/or an extreme pressure addend. However, other mineral oil formulations comprising mineral oil, an emulsifier, a coupling agent and water may be used.

The emulsifier may be any suitable emulsifier which may be dispersed or dissolved in the lubricating oil in proper proportions. The emulsifiers are of two general classes, namely, (1) the alkali metal soaps and other salts of fatty acids, rosin acids, naphthenic acids, oil-soluble sulfonic acids, tall oil acids and the like, and (2), polyethylene glycol, mono-esters and alkyl mono-esters of the aforementioned acids. Mixtures in a single soluble oil composition are suitable. Preferably the emulsifier is an alkali metal soap of a fatty acid of C_{16}–C_{18} carbon chain length, or alkali metal soap of one or more petroleum mahogany sulfonic acids, or alkali metal soap of petroleum naphthenic acids. The alkali metal portion is preferably sodium or potassium. The emulsifier may be present in a concentration of about 7–30% by wt. of total formulation.

The extender may, for example, be sodium resinate and not only provides a cheap means of formulating the soluble oil by reducing the necessary concentration of more expensive emulsifier, but also in the case of sodium resinate gives better hard water stability. Other conventional extenders may be used. The concentration for the extender is about 0–15% by wt. of total formulation.

The mineral lubricating oil which may be used comprises any oil boiling in the lubricating oil boiling range but in the case of soluble oils should be a neutral lubricating oil fraction with or without additional phenol extract, that is the extract obtained during the refining of a lubricating oil fraction with phenol. The neutral may be of 80–200 SUS viscosity at 100° F., for example, Gulf Coast 100 viscosity neutral oil, Mid-Continent conventionally refined (acid refined) 100 viscosity neutral oil, and 80 viscosity East Texas solvent refined neutral oil in equal proportion with phenol extract of 80–250 viscosity neutral oil. The mineral lubricating oil may be used in any concentration, preferably about 20–85% by wt. of the total soluble oil formulation.

The alkali metal hydroxide is either potassium hydroxide, which is preferred, or sodium hydroxide and is present in a concentration of about 0–0.3%. The hydroxide is not essential in the event that the other constituents have a very low acid number and sufficient emulsifier in soap form is already present.

The coupling agent is any agent which makes miscible two immiscible agents, and has the effect of keeping the

various constituents of the blend, particularly oil and water, in homogeneous solution. It may be hexylene glycol, diethylene glycol, ethylene glycol or a similar coupling agent. The coupling agent may be present in any suitable concentration, particularly in soluble oils in an amount of 4% by wt. of total formulation or less.

The total water of the oil formulation which may be present depends upon the particular constituents of the formulations and in any case is at least about 1% by total wt. of formulation and less than that which would cause the constituents of the soluble oil or other mineral oil blend to separate into phases and the oil to emulsify to an appreciable extent. With the usual soluble oil formulation not more than about 3% total water may be present without causing the above conditions. Our range for water then is about 1–3% for soluble oils and, preferably, about 2–3%. This total water includes water present in the formulation as an impurity in the emulsifier and/or other constituents of the soluble oil, and any water added thereto after the soluble oil or other oil composition has been prepared.

The extreme pressure addend may be, for example, the sulfurized methyl esters of animal fatty acids, preferably of C_{16}–C_{18} carbon chain length, is an optional additive, and when present may be found in a concentration of up to 30% by wt. of total formulation.

Our process comprises contacting a soluble oil or other mineral oil composition of the above general formulation and a ferrous-containing metal or metal alloy article and maintaining the contact between the oil and metal for a sufficient time to produce the desired, dark blue, corrosion-resistant, rust-preventive coating on the metal surface. The exact nature of the dark blue metal coating is unknown but the following reactions are suggested as a possible explanation for the blueing phenomenon:

(1) Metallic iron undergoes oxidation and solution into the water present in the soluble oil:

$$Fe+2H_2O \rightarrow Fe(OH)_2+H_2$$

(2) Ferric iron is formed, probably as a result of the oxidation of ferrous hydroxide by air:

$$4Fe(OH)_2+O_2+2H_2O \rightarrow 4Fe(OH)_3$$

(3) The ferric iron concentration increases to a point where blueing occurs on the iron surface. The presence of both ferrous and ferric iron in the blue stain suggests the following reactions:

$$2Fe(OH)_3+Fe \rightarrow 3Fe(OH)_2$$

and

$$2Fe(OH)_3+Fe(OH)_2 \rightarrow FeOFe_2O_3+4H_2O$$

The blue coating is therefore tentatively classified as a ferrous oxide-ferric oxide mixture or complex. As seen from the above suggested reaction, water is again available for further blueing of the metal at the end of the sequence of reactions. The metal is preferably blued after the metal surface has been freshly polished, so as to facilitate adhesion of the coating to the metal surface. Any interfering oxide films present on the metal are scoured therefrom.

As stated above, the water concentration of the soluble oil formulation must be at least about 1% and may be up to about 3% or up to the limit of water concentration which may be present without causing substantial phase separation of the soluble oil. The following tables demonstrate that the blueing effect increases with time, with temperature and water concentration, and that satisfactory blueing can be effected in 24 hours with temperatures varying from room temperature to about the boiling point of water, preferably substantially higher than 180° F., under no increased pressure and preferably with total water concentrations of 2–3% present.

The metal is placed in the oil composition in a sealed container or similar apparatus so that the water evaporation is rendered substantially nil, or alternatively, the water concentration is maintained at the desired level by continuous or intermittent addition of make-up water to the soluble oil as the water evaporates from the soluble oil formulation. The soluble oil may be concomitantly exposed to an oxygen-containing gas phase during the period of blueing to facilitate conversion of ferrous hydroxide to ferric hydroxide in the solution. The oxygen may also be made available to the solution by being bubbled up therethrough. The tests below were usually conducted in a closed container at room temperature with the metal partially immersed in the soluble oil formulation, and with air present above the liquid level. In all the cases, blueing occurred only on the surfaces of the metal immersed in the soluble oil.

The exact procedure for performing the tests is as follows:

A test specimen of SAE 1020 steel was prepared as specified in the tentative test method for rust-preventive characteristics of steam-turbine oil in the presence of water (ASTM D665–53T). The test specimen was placed in each case in a 4 oz. sample jar containing 100 cc. of the soluble oil. The jar was sealed and the soluble oil brought to the pre-determined test temperature. The jar was then unsealed to relieve the pressure and resealed to prevent excess water loss. The test strip was inspected without opening the jar at 24 hr. intervals up to a total time of 336 hrs. for evidence of blueing.

In tests set forth in Tables I, II and III, soluble oil A of the following formulation was utilized:

SOLUBLE OIL A

Constituents:	Percent by weight
Sodium mahogany sulfonates [1]	10
Oleic acid	2
Potassium hydroxide (100% assay)	0.3
Diethylene glycol	1.7
Water	1.4
Total water	About 1.7
100 viscosity SUS at 100° F. Gulf Coast pale neutral petroleum lubricating oil	85.

[1] A mixture of sodium mahogany sulfonates prepared from petroleum oil and having the following approximate assay:

Acid No. (1948 method)	less than	0.03
Water	percent	5.0
Sulfated ash	do	11.4
API gravity		6.7
Lbs./gal.		8.527

In Table IV below, soluble B was tested:

SOLUBLE OIL B

Constituents:	Percent by weight
Sodium mahogany sulfonates [1]	15.00
Sodium resinate [2]	9.00
250 SUS at 100° F. Gulf Coast neutral lubricating oil	52.73
Potassium hydroxide (100% assay)	0.21
Water added	0.21
Total water	2.00
Hexylene glycol	2.85
Sulfurized methyl esters of animal fatty acids [3]	20.00

[1] A mixture of sodium mahogany sulfonates prepared from petroleum oil and having the following approximate assay:

Acid No. (1948 method)	less than	0.03
Water	percent	5.0
Sulfated ash	do	11.4
API gravity		6.7
Lbs./gal.		8.527

[2] Mixture of metal resinates of the following assay:

Acid No. (1948 method)		12.2
Water	percent	10.8

[3] Methyl esters of animal fatty acids (as oleic) of the following assay:

API gravity		28.7
Color ASTM (NPA)		3+
Pour point, ° F		+50
Vis. SUS at 100° F		46.7
Sap. No. 197, water-trace, free fatty acids	percent	4.59
Iodine number		65.5

Table I.—Time-temperature relationships of blueing on ferrous metals

[Test soluble oil—Soluble oil A.[1] Test metal—ASTM turbine oil rust test strip—SAE 1020 steel.]

Temp. (° F.)	Time (Hrs.)						
	24	48	72	96	120	144	168
Room (75–80° F.):							
Sample 1	Clear	Clear	Clear	Clear	Clear	Clear	Clear.
Sample 2	do	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Slight Blueing Extreme Tip.
Sample 3	do	do	do	do	do	do	Do.
120° F.:							
Sample 1	do	do	do	do	do	do	Strip ¼ Blued.
150° F.:							
Sample 1	do	do	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing. Extreme Tip.
Sample 2	do	do	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.
180° F.:							
Sample 1	do	do	do	do	do	do	Do.
Sample 2	do	do	do	do	do	do	Do.

Temp. (° F.)	Time (Hrs.)						
	192	216	240	264	288	312	336
Room (75–80° F.):							
Sample 1	Clear	Clear	Clear	Clear	Clear	Clear	Clear.
Sample 2	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Slight Blueing Extreme Tip.
Sample 3	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Strip ½ + Blued.	Strip ½ + Blued.
120° F.:							
Sample 1	Strip ⅛ Blued	Strip ½ Blued	Strip ½ Blued	Strip ½ Blued	Strip ½ Blued	Strip 100% Blued.	Strip 100% Blued.
150° F.:							
Sample 1	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.	Slight Blueing Extreme Tip.
Sample 2	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.
180° F.:							
Sample 1	do	do	do	do	do	do	Do.
Sample 2	do	do	do	do	do	do	Do.

[1] No water added.

Table II.—Time-temperature relationships of blueing on ferrous metals

[Test soluble oil—Soluble oil A.[1] Test metal—ASTM turbine oil rust test strip—SAE 1020 steel.]

Temp. (° F.)	Time (Hrs.)				
	24	48	72	96	120
Room (75–80° F.):					
Sample 1	Strip ⅛ Blued	Strip ¼ Blued	Strip ½ Blued	Strip ¾ Blued	Strip 100% Blued.
Sample 2	do	do	do	do	Do.
120° F.:					
Sample 1	Clear	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.
Sample 2	Strip ⅞ Blued	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.
150° F.:					
Sample 1	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Slight Blueing Extreme Tip.
Sample 2	Trace Blueing Tip and Sides.	Trace Blueing Tip and Sides.	Trace Blueing Tip and Sides.	Trace Blueing Tip and Sides.	Trace Blueing Tip and Sides.
180° F.:					
Sample 1	do	do	do	do	Do.
Sample 2	do	do	do	do	Do.

[1] Plus ½% added water.

Table III.—Time-temperature relationships of blueing on ferrous metals

[Test soluble oil—Soluble oil A.[1] Test metal—ASTM turbine oil rust test strip—SAE 1020 steel.]

Temp. (° F.)	Time (Hrs.)							
	24	48	72	96	120	144	168	192
Room (75-80° F.):								
Sample 1	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.
Sample 2	do	do	do	do	do	do	do	Do.
Sample 3	do	do	do	do	do	do	do	Do.
120° F.:								
Sample 1	do	do	do	do	do	do	do	Do.
Sample 2	Clear	Clear	Trace Blueing Extreme Tip.	Trace Blueing Extreme Tip.	Strip ¼ Blued	Strip ½ Blued.	Strip ¾ Blued.	Do.
150° F.:								
Sample 1	Strip ¾ Blued.	Strip ¾ Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Do.
Sample 2	Strip 100% Blued.	Strip 100% Blued.	do	do	do	do	do	Do.
180° F.:								
Sample 1	do	do	do	do	do	do	do	Do.
Sample 2	do	do	do	do	do	do	do	Do.

[1] Plus 1% added water.

Table IV.—Time-temperature relationships of blueing on ferrous metals

[Test soluble oil—Soluble B.[1] Test metal—ASTM turbine oil rust test strip—SAE 1020 steel.]

Temp. (° F.)	Time (Hrs.)							
	24	48	72	96	120	148	168	192
Room (75-80° F.):								
Sample 1	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Trace Blueing.
Sample 2	do	do	do	do	do	do	do	Do.
Sample 3	do	do	do	do	do	do	do	Do.
120° F.:								
Sample 1	do	do	do	do	do	do	do	Do.
Sample 2	do	do	do	do	do	do	do	Do.
150° F.:								
Sample 1	do	do	do	do	do	do	do	Do.
Sample 2	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.	Strip 100% Blued.
180° F.:								
Sample 1	do	do	do	do	do	do	do	Do.
Sample 2	do	do	do	do	do	do	do	Do.

[1] No additional water added.

As seen from the above, the water content of the soluble oil is an important factor in producing the blue coating of the ferrous metal. Where the water content is low, the blueing effect occurs more slowly and may or may not be complete after 336 hours. The effect of temperature on the rate of blueing from room temperature up to 180° F. as tested, is not predictable, sometimes a temperature increase increasing the blueing/unit time and sometimes having an opposite effect. If, during processing at a certain temperature the blueing effect is not proceeding at a desired rate, a temperature increase may, at least in some cases, cause the blueing to occur more completely and/or more quickly. However, where water appears in a high concentration in the soluble oil, the effect of temperature is minimized. This addition of water to the soluble oils was restricted by the capacity of the blend to accept water without subsequent phase separation and without substantial formation of an emulsified condition in the oil.

It has also been found in further tests with the above metal that where the soluble oil is present in the form of a gel with water in a total concentration of 1–3%, the blue deposit on the surface of the SAE 1020 steel can be obtained even more rapidly than under similar conditions but with the oil in liquid form rather than in gel form.

Sample 1 of Table I tested at room temperatures showed no blueing effect due to the fact that this test was carried out in an open container and excessive evaporation of water to below a total concentration than less about 1% is believed to have occurred.

Test pieces of the metal which have been blued have been found to retain the blue protective coating for periods up to 3 years or more and the portions of the metal so coated were rust-free. The metal, SAE 1020 steel is known to rust on exposure to oxygen for an appreciable length of time.

Our process, therefore, comprises blueing a ferrous-containing metal through contact with an oil of the above defined formulation, typified by soluble oils having at least about 1% total water but less than that concentration of water which would cause phase separation in the oil composition.

Modifications of our process and the apparatus for carrying it out as are within the skill of one versed in the art are contemplated as being within the scope of this invention.

We claim and particularly point out as our invention:

1. The process for the formation of an adherent, corrosion-resistant coating on a ferrous metal surface which comprises contacting said ferrous metal with a substantially water-emulsion-free mineral oil composition consisting essentially of a mineral oil boiling in the lubricating oil boiling range, an emulsifier, a coupling agent in which water and mineral oil are mutually soluble and at least about 1%, by wt. of total composition, of total water but less than that amount which causes substantial phase separation and emulsification of said oil composition, for a time sufficient to coat the surface of said metal with a corrosion-resistant, adherent coating.

2. The process of claim 1 in which said contacting is

carried on in the presence of an oxygen-containing environment.

3. The process of claim 2 in which said coupling agent is present in a concentration of not more than about 4% by wt. of said composition.

4. The process of claim 3 in which said mineral oil composition is a soluble oil, said emulsifier is present in an amount of about 7–30%, by wt. of said composition and said mineral oil is present in an amount of about 20–85%, by wt. of said composition.

5. The process of claim 4 in which said coupling agent is selected from the group consisting of hexylene glycol, diethylene glycol and ethylene glycol, said mineral oil is selected from the group consisting of neutral oils and solvent extracts thereof and said emulsifier is selected from the group consisting of petroleum mahogany sulfonates, petroleum naphthenates and soaps of fatty acids.

6. The process of claim 5 in which said total water is present in an amount of not more than about 3%, by wt. of said composition and said contacting is carried out for at least about 24 hrs.

7. The process of claim 6 in which said total water is present in an amount of about 2–3%, by wt. of said composition and said contacting is carried out at about 33–210° F.

8. The process of claim 7 in which said contacting is carried out at about 65–180° F.

9. The process for the formation of an adherent, corrosion-resistant protective coating on a ferrous metal surface which comprises contacting said ferrous metal in the presence of an oxygen-containing environment with a substantially water-emulsion-free emulsifiable oil composition comprising about 10–15%, by wt. of total composition, of sodium mahogany sulfonates, about 50–85%, by wt. of total composition, of a petroleum mineral neutral oil, about 1–3%, by wt. of total composition, of a coupling agent selected from the group consisting of ethylene glycol, diethylene glycol, and hexylene glycol, and about 2–3%, by wt. of total composition, of total water, for at least about 24 hrs. at at least about 65° F. until a corrosion-resistant, adherent protective coating is formed on the surface of said metal.

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