

UNITED STATES PATENT OFFICE

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SLUSHING OIL

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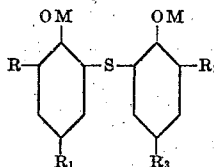
This invention relates to corrosion-preventing coating compositions of the type known as slushing oils.

Slushing oils, as generally known, consist of heavy body mineral oils, petroleum jelly, lanolin, tallow oil, etc., which may be thinned with a volatile solvent if necessary. These oils are employed as liquid coating compositions to provide protection of metal surfaces against corrosion by water and atmospheric gases. When finished or semi-finished metal objects such as machinery, machine tools, engines, gun barrels, sheet steel, etc., particularly when fabricated of iron or steel, are to be stored or shipped over salt water or in tropical climates they are generally treated with a heavy coating of a slushing oil to prevent corrosion. Slushing oils are also employed to prevent corrosion of fine steel products such as razor blades which must be touched with the workmen's hands during manufacture and inspecting operations.

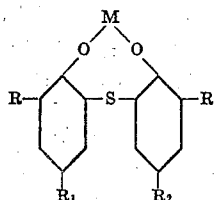
Ordinary slushing oils such as described are satisfactory for their intended purpose if they contain no corrosive substances and as long as they remain on the metal surface and protect it from contact with water, acids, air and other gases which tend to promote corrosion. Unfortunately, however, ordinary slushing oils do not adhere to metal surfaces as well as desired and are easily rubbed off during shipping and handling. Various substances such as natural and synthetic resins have been added to slushing oils with the intention of causing them to adhere more firmly to the metal surface. This practice has obvious disadvantages especially when the oil is applied to some objects and later on when it is to be removed. Other suggestions have been made to increase the adherence of the oil on the metal surfaces but in general the principal attempts have been made to provide an oil which has the inherent qualities of adherence so much desired.

We have found that slushing oils may be prepared which retain the advantages of slushing oils heretofore employed and at the same time are of much greater effectiveness because of the great tenacity with which they adhere to metal surfaces and also because of other properties which will be presently described. Our improved slushing oils of the present invention are pre-

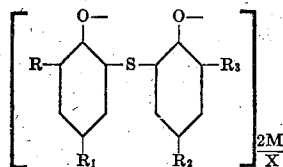
pared by adding to slushing oils of any desired type such as those outlined above certain dialkyl diphenol sulfide metal salts having the general formula



in which R, R₁, R₂ and R₃ are alkyl radicals having 4 or more carbon atoms in each alkyl group and M is a metal. When M is a divalent metal such as barium the formula may become



and when a polyvalent metal such as aluminum or chromium is used the resulting salts are complex in nature. The dialkyl phenol sulfide of our invention may therefore be defined broadly by the formula



in which R, R₁, R₂ and R₃ are alkyl radicals as defined above, M is a mono- or polyvalent metal, and X is the valence of M.

The effectiveness of our new slushing oils is due, we believe, to the particular chemical structure and properties of the dialkyl diphenol sulfide salts added thereto. Although we do not wish to be bound by any particular theoretical explanation it appears from the evidence before us at present that the superior properties of our slushing oils are due to a number of specific and interrelated factors contributed by the dialkyl diphenol sulfide salts acting in conjunction with

the oil comprising the remainder of the composition. It will be observed from the structural formula given above that the phenol hydrogen has been replaced with a metal. The metal surface to be protected from corrosion by the slushing oil and the metal radical, or radicals, of the dialkyl diphenol sulfide salt are believed to have an affinity, or attraction, for each other and when slushing oils containing such dialkyl diphenol sulfide metal salts are applied to a metal surface the dialkyl diphenol sulfide metal salt is believed to be very firmly attached to the metal surface with the metal radical forming a firm bond between the metal surface and the remainder of the dialkyl diphenol sulfide molecule. In other words it appears that the dialkyl diphenol sulfide metal salt is plated out on the metal surface in a continuous film one or more molecules in thickness.

The non-metallic portion of the dialkyl diphenol sulfide metal salt contains alkyl groups of sufficient length to be easily soluble in the oil portion of our improved slushing oil composition. These alkyl groups are held close to the metal surface to form a closely packed outer layer which, being chemically similar to the oil, promotes the formation of a second film, consisting of oil, over the metal surface. Since the alkyl groups of the dialkyl diphenol sulfide metal salt and the oil portion of the slushing oil are similar in character and are both non-polar it will be seen that they are mutually soluble and will not be easily separated by water which is always present in a corrosive atmosphere. Accordingly the dialkyl diphenol sulfide metal salts cause a protecting oil film to be formed on the metal surface which is not easily removed.

The dialkyl diphenol metal salts themselves are not water-soluble and they are not removed by solvent action should the metal article be subjected to the washing action of large volumes of water. It is also pointed out that these compounds are hydrolyzed only with difficulty owing to the insolubility of the compounds and also to the fact that both ortho positions in each benzene nucleus are substituted and the metal radical is thus protected from the action of water. Even if some hydrolysis should occur, as in the presence of carbonic acids, sulfurous acids and other dilute acids found in corrosive atmospheres, the metal radical which is split off as a result of the hydrolysis will, particularly in case of the alkaline earth metals, tend to neutralize the acid and prevent its action on metal surfaces. The dialkyl diphenol sulfide metal salts are thus seen to have a double function in slushing oils in the prevention of corrosion.

In accordance with the foregoing principles the dialkyl diphenol sulfide metal salts of the present invention to be successfully employed in slushing oils should have at least 2 alkyl groups on each benzene nucleus and these alkyl groups should contain at least 4 carbon atoms in each chain to provide adequate oil solubility. The metal is preferably of the alkaline earth group such as calcium or barium although I have employed other metal radicals with good success such as potassium, tin, zinc, lead, aluminum, copper, chromium, etc. When polyvalent metals are used complex salts having a number of aryl sulfide groups may be formed, and such complex salts are also included within the scope of the invention.

The dialkyl diphenol sulfide metal salts may be prepared by various methods. We have found that an excellent method is to react the corre-

sponding 2,4-dialkyl phenol with sulfur dichloride in solution in a suitable solvent such as carbon tetrachloride, ethylene chloride, trichlorethylene and the like. The sulfide forms readily with good yield and metal salts can be prepared therefrom by direct action of the metal hydroxide or metal alcoholate in the case of strongly basic metals, or by double decomposition of the alkali metal salt with an alcoholic salt solution of the desired metal. Single metal salts can be prepared or mixed metal salts by using a mixture of the different metal compounds. The barium salt of 2,4-dialkyl phenol sulfide is prepared for example in the following manner:

30 parts of 2,4-diamyl phenol monosulfide is dissolved in a mixture of about 50 parts of absolute alcohol and 50 parts of a petroleum naphtha containing about 70% aromatic hydrocarbons. 17.1 parts of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is added with stirring and the mixture warmed to effect solution and later to evaporate the water along with the solvents. Traces of the solvent are removed by warming in vacuo. The barium salt of the 2,4-diamyl phenol monosulfide is obtained as a viscous product which turns a dark, dull-colored green on exposure to the atmosphere.

The efficiency of our new slushing oils may be demonstrated in an accelerated corrosion test which has been recognized in the art as giving very accurate indications as to the effectiveness of the slushing oil. A small quantity, 0.02% of our dialkyl diphenol sulfide metal salt, is added to a technical white oil and a strip of polished cold-rolled steel is placed therein. After allowing 10 minutes for the dialkyl diphenol sulfide metal salt to plate out on the metal 1% of water is added to the oil and the mixture is stirred continuously throughout the test. In the absence of any inhibitor the polished metal strip will begin to show evidence of corrosion within about 30 minutes whereas with our inhibitors as herein described the polished steel strip may be contacted with the oil and water mixture for periods of a week or more without visible evidence of staining or corrosion.

Because of the great oil solubility of our corrosion inhibitor we may add comparatively large amounts to the oil if desired. In fact, it may be desirable in some cases to sell and ship the inhibitor in the form of a 50% solution in oil. On account of the great effectiveness of 2,4-dialkyl diphenol sulfide metal salts in slushing oils, however, only very small amounts are necessary. Accordingly the range over which our inhibitors may be employed varies widely and may be less than 0.01% of the total weight of the slushing oil to more than 10%. Ordinarily however 0.02-0.5% of the inhibitor will be found adequate for most purposes.

Another advantage of our 2,4-dialkyl diphenol sulfide metal salts is that we are enabled thereby to incorporate in mineral oils certain materials which are known to have good corrosion preventing properties but which cannot normally be used in slushing oils on account of their oil-insolubility. For example, calcium, barium, aluminum, zinc and magnesium stearates, palmitates and naphthenates, etc., are known to be good film-forming materials having anti-rusting properties but are difficultly soluble in petroleum oils. Because of their solubility, however, in our dialkyl diphenol sulfide metal salts and the solubility of the latter class of materials in oils, it is possible to incorporate in slushing oils substantial amounts of these compounds, the pres-

ence of which markedly improves the corrosion resistance of the slushing oil.

Various fatty acids, drying oils, resins, metal oxides, solvents and other materials such, for example, as barium dialkyl dithiophosphates may also be added to our improved slushing oils when it is desired to modify them in other respects.

In our copending application, Serial No. 383,167, filed March 31, 1941, now Patent No. 2,249,626, dated July 15, 1941, we claim a lubricating oil composition containing 2,4-dialkyl phenol sulfide metal salts in which the metal salt is added as a sludge dispersing agent. It will be understood of course that the lubricating oil composition as claimed therein is entirely distinct from the slushing oils of the present invention as set forth in the appended claims; the compositions themselves being not analogous and the dialkyl diphenol sulfide metal salts acting in a different way in the respective compositions. The slushing oils of the present invention are not to be regarded as lubricants since their purpose is not to lubricate but to protect metal surfaces from atmospheric corrosion.

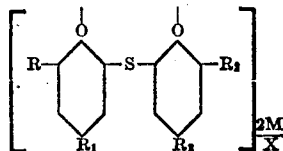
What we claim is:

1. A slushing oil composition containing a major proportion of a mineral oil and 0.01-10% by weight of calcium 2,4-diamyl diphenol monosulfide.

2. A slushing oil composition containing a major proportion of a mineral oil and 0.01-10% by weight of lead 2,4-diamyl diphenol monosulfide.

3. A method of protecting metal surfaces from atmospheric corrosion which comprises applying thereto a slushing oil composition comprising a major proportion of a water-insoluble film-forming mineral oil having dissolved therein 0.1 to 10% of a metal salt of a 2,4-dialkyl diphenol sulfide in which each alkyl group contains at least 4 carbon atoms.

4. A method of protecting metal surfaces from atmospheric corrosion which comprises applying thereto a slushing oil composition comprising a major proportion of a mineral oil and 0.01-10% of a 2,4-dialkyl diphenol sulfide metal salt having the following formula



in which R, R₁, R₂ and R₃ are alkyl radicals having at least 4 carbon atoms, M is a metal and X is the valence of M.

5. A method of protecting metal surfaces from atmospheric corrosion which comprises applying thereto a slushing oil composition containing a major proportion of a mineral oil and 0.01-10% by weight of calcium 2,4-diamyl diphenol monosulfide.

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