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RUST PREVENTATIVE COMPOSITIONS

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Our invention relates to rust preventative compositions, of the slushing oil type, which have particular value for protecting metal surfaces in acid atmospheres.

Various organic acids have been proposed for use in oil compositions for preventing rusting of metal surfaces in acid atmospheres. Although aromatic acids have considerable effectiveness, their practical effectiveness is substantially reduced by their relative insolubility in hydrocarbon oils. Efforts have been made to solubilize such materials to an extent permitting practical utilization without interfering with or reducing their rust inhibiting capacities. This, however, has proved difficult to accomplish and, accordingly, it is an object of our invention to provide a rust preventative composition of improved properties for use in acid atmospheres.

We have found that the combination of a higher aliphatic primary amine with an aromatic acid, e. g., benzoic acid, when used in conjunction with zinc naphthenate in mineral oil provides an unusually effective corrosion and rust inhibiting composition. The ingredients have sufficient solubility in light hydrocarbon oils for use in sufficient concentration for practical applications. The amine of choice is a branched chain C_{18} to C_{24} primary amine in which the hydrocarbon chain is derived from propylene tetramer or a light isobutylene polymer. Such amines are available commercially, for example, Primene J. M. R. amine of Rohm & Haas. Other high aliphatic primary amines, however, may be used as long as the resultant product is soluble in oil. Thus, primary amines containing long, usually branched, chains of C_{12} to C_{40} in length have value.

Benzoic acid is particularly valuable as the aromatic acid component in the invention, but other aromatic acids possess useful rust inhibiting properties, e. g. salicyclic, phthalic, toluic and cinnamic acids. The amine-aromatic acid combination may be preformed as the amine salt of the acid and dissolved in the hydrocarbon oil base for the rust preventative composition, or the amine and aromatic acid components can be added separately to the base oil so that the product is formed in situ. In either case, we have found that the desired proportion of the amine-aromatic acid product is suitably in the range of about 8 to about 12% by weight.

The zinc naphthenates employed are zinc soaps of naphthenic acid, i. e., the C_5 to C_6 cyclic acids averaging about 150 to 250 in molecular weight which are recovered from naphthenic type crudes by caustic washing. The products commercially available are variable in zinc content and usually contain about 8 to 14% zinc. About 14 to about 28% by weight of zinc naphthenate, based on a concentration of zinc of about 8% by weight, may be used in formulating the compositions of the invention.

The base oil may comprise a light lubricating oil distillate, e. g. a neutral oil, with advantage. Heavier lubricating oil fractions, however, may be used and kerosene or various light hydrocarbon solvents may be used to cut the finished compositions back to the desired viscosity for convenient application by dipping, spraying

or brushing. A particularly well balanced formulation may contain about 8 to 12% of the amine-benzoate product, about 20 to 28% of zinc naphthenate (8% Zn), about 50 to 80% of a lubricating oil of 60 to 100 SSU at 100° F., and about 12 to 20% of a solvent naphtha such as Stoddard's solvent.

In evaluating the compositions of the invention, representative samples were formulated and tested by means of a specially devised corrosion test for rating performance of rust inhibitors in strongly acid atmospheres. The procedure was conducted as follows: Three steel ball bearings were placed in a gooch crucible 1" high by 1⅜" diameter at the bottom. The crucible and ball bearings were slushed for one minute in hot naphtha to remove foreign material. The crucible and ball bearings were set on an absorbent paper for about ½ hour to allow cooling to room temperature and evaporation of the solvent. These were then slushed for one minute in the rust preventive compound and allowed to drain for two hours on a fresh piece of absorbent paper. The speciments were then placed in a dessicator which was prepared in the following manner . One hundred ml. of 5% acetic acid solution was placed in a 100 ml. beaker which in turn was placed in a crystallization dish 2" high by 4" diameter . The dish was filled with water and the assembly placed in the bottom of the dessicator. The porcelain table was supported on its edges with corks in the dessicator to raise it above the beaker containing the acid. The crucible and balls were set on this porcelain table and the cover to the dessicator put in place. The test was run at room temperature, and the ball bearings were checked daily for presence of rust.

In the following examples, the amine used was Primene J. M. R. which is a mixture of tertiary alkyl primary amines predominating in $C_{18}H_{37}NH_2$ but ranging up to $C_{24}H_{49}NH_2$. Physical tests on the amine included: 5–70% over at 262 to 315° C., specific gravity at 25° C. of 0.845, refractive index at 25° C. of 1.460 and flash point of 260° F.

In one method of preparation, the amine and benzoic acid were separately incorporated in the base oil, and the mixture was stirred at 150° F. until no crystals remained in solution. In a second method of preparation, the amine-benzoate product was formed by combining one mole of the amine with two moles of acid. The materials were stirred and heated at 150° F. for a few minutes at which point the addition of benzoic acid to the amine was complete. The resultant product was a honey-like material in consistency and odor. In preparing the additive product, temperatures of about 200° F. or more are to be avoided since at that temperature, water is eliminated and the amide is formed.

The data of Table I below indicate by comparison the superiority of compositions of the invention containing the amine-benzoate additive when used in conjunction with greater than about 12–16% by weight of zinc naphthenate. It will be noted that zinc naphthenate alone is ineffective in inhibiting rusting of steel in acid atmospheres. Although the formulation made without use of an amine showed activity, the sample had to be applied carefully as a suspension. The additives in the test did not remain in solution, and such formulations lack practical utility. Use of the amine-benzoic acid combination, however, whether preformed or produced in situ in the base oil, eliminates the problem of solubility encountered with the use of the acid alone while providing a significantly superior rust preventative composition. When low percentages of the amine-acid combination are used, the inhibiting effectiveness of the composition is markedly reduced. See, for example, sample 6. At least about 8% of the additive product should be used for satisfactory results.

Table I[1]

	1a	1	2	3	4	5	6	7	8	9
Zn Naphthenate (14.5% Zn)	26.3	0	0	0	0	24	0	0	0	0
Zn Naphthenate (Nuodex 8% Zn)	0	4	12	16	24	0	24	24	24	24
Pale Oil, 80 SSU at 100° F	0	70	62	54	50	50	55	55.3	60	50
White Oil	50	0	0	0	0	0	0	0	0	0
Solvent Naphtha	16.5	16	16	16	16	16	16	16	16	16
Sodium Sulfonate	2.5	0	0	0	0	0	0	0	0	0
Primene J. M. R	0	5.25	5.25	5.25	5.25	5.25	2.62	0	0	0
Benzoic Acid	4.7	4.75	4.75	4.75	4.75	4.75	2.38	4.7	0	0
Primene-Benzoic Acid Product	0	0	0	0	0	0	0	0	0	10
Appearance	Precipitate	clear	clear	clear	clear	clear	clear	Precipitate	clear	clear
Days to rust in Acid Atmospheres	14	7	7	14	21	18	3	14	3	15+

[1] All proportions are percent by weight of the total composition.

We claim:

1. A rust preventative composition of the slushing oil type characterized by capacity for protecting metal surfaces in acid atmospheres consisting essentially of a hydrocarbon oil as base and containing dissolved therein about 8 to about 12% in combination of a higher aliphatic primary amine containing about 18 to 24 carbon atoms and an aromatic acid, and about 14 to about 28% of zinc naphthenate.

2. The composition of claim 1 in which the amine is a C_{18} to C_{24} aliphatic branched chain primary amine.

3. The composition of claim 1 in which the acid is benzoic acid.

4. A rust preventative composition of the slushing oil type characterized by capacity for protecting metal surfaces in acid atmospheres consisting essentially of a lubricating oil distillate as base and containing dissolved therein about 8 to about 12% in combination of a C_{18} to C_{24} aliphatic branched chain primary amine and benzoic acid, about 14 to about 28% of zinc naphthenate and about 12 to about 20% of a solvent naphtha.

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