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SLUSHING COMPOSITION

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This invention relates to improvements in rust preventive compounds, otherwise known as slushing compounds, and more particularly to petroleum rust preventives or slushing compounds.

Metal surfaces whenever possible are protected from corrosion by a coating of some kind. In general, two types of protective coatings have been employed, namely permanent and temporary coatings. Under the first class are included oxide coatings, phosphate coatings, heat bluiings, coatings of metals such as zinc, cadmium, chromium, etc. and paints, varnishes, enamels and other non-metallic materials which form dry hard films. In the second class of protective coatings, which are of the type which must at some time be readily removed from the surfaces they are protecting, are those products prepared from petroleum oil and/or petroleum products such as lubricating oils, paraffin oils, petroleum naphthas, cylinder stocks, black oils, petrolatums, greases, asphalts, waxes, etc. While practically all such petroleum products give satisfactory protection under certain conditions, many such petroleum products have added thereto rust and/or corrosion inhibitors for added protection. For example, soaps of preferentially oil-soluble sulfonic acids derived from the sulfuric acid treatment of petroleum oils have been added to slushing compounds, as exemplified by United States Patents Nos. 1,630,101 and 1,795,993, which disclose broadly the use of soaps of oil-soluble sulfonic acids derived from petroleum oils in slushing compounds and in slushing greases respectively.

While the soaps of preferentially oil-soluble sulfonic acids derived from the sulfuric acid treatment of petroleum oil are generally effective in inhibiting corrosion and the formation of rust, it has been observed that the surfaces of metals coated with such slushing compounds are frequently badly tarnished or discolored. Although this problem of discoloration and tarnishing of metals coated with slushing compounds containing soaps of preferentially oil-soluble sulfonic acids derived from petroleum oils has been investigated for a number of years it has not been solved prior to the present invention.

It is an object of the present invention to provide a slushing compound containing as a constituent thereof a soap of a preferentially oil-soluble sulfonic acid, derived from a petroleum oil, which will not cause tarnishing or discoloration of the metal to which it is applied.

It is another object of the present invention to provide a slushing compound containing a non-

tarnishing soap of an oil-soluble sulfonic acid derived from petroleum oils.

Other objects and advantages of the invention will become apparent as the description thereof proceeds.

Heretofore, it had been the general belief that the soaps of preferentially oil-soluble sulfonic acids obtained by the treatment of petroleum oils with sulfuric acid were of the same type, and therefore were equally effective as inhibitors for the prevention of corrosion and/or the formation of rust. We have now discovered that contrary to the general belief, there is a marked difference in the corrosion inhibiting properties of soaps of preferentially oil-soluble sulfonic acids obtained from oils under various treating conditions. We have discovered that the formation and/or development of tarnish and discoloration upon metal surfaces treated with slushing compounds can be eliminated by employing the soaps of preferentially oil-soluble sulfonic acids derived from a particular sulfuric acid treatment of petroleum oil distillates; namely the soaps of the preferentially oil-soluble sulfonic acids derived by treating distillates of from about 70 seconds to about 500 seconds or higher, and preferably from about 200 seconds to about 400 seconds Saybolt Universal viscosity at 100° F. with from about 6 to about 9 pounds, and preferably from about 7 to about 8 pounds of concentrated sulfuric acid, preferably fuming sulfuric acid, per gallon of oil.

The method of obtaining these desirable soaps of preferentially oil-soluble sulfonic acids derived from petroleum oils is illustrated by the following example:

The petroleum oil distillate having Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 400 seconds is treated with from about 7 to about 8 pounds of fuming sulfuric acid per gallon of oil in one-half pound increments or "dumps." After the acid sludge from each one-half pound acid "dump" is settled and withdrawn, the next one-half pound of fuming sulfuric acid is added to the oil. The temperature of the oil before the fuming acid is added thereto is maintained at a temperature below about 60° F. but due to the heat of reaction upon the addition of the sulfuric acid, the temperature of the oil may rise to from about 90° F. to about 100° F. After the required total amount of fuming sulfuric acid has been added to the oil and the oil freed of acid sludge, the acid treated oil containing oil-soluble sulfonic acids dissolved therein, is neutralized with a solution of sodium hydroxide. The aqueous alkali solution is then sepa-

rated from the oil solution containing dissolved therein sodium soap of sulfonic acids and the latter then separated from the oil by extraction with alcohol of about 60% strength. The alcohol layer containing dissolved sodium sulfonates is then separated from the oil and subsequently distilled to recover the alcohol and water. The sulfonic soap obtained in this manner contains from about 30% to about 60% sodium sulfonate, from about 30% to about 60% oil, from about 1% to about 10% water, and up to 10% of inorganic salts which may be removed by the procedure hereinafter described.

The above procedure may be modified after the acid sludge is removed from the acid treated oil. The oil containing dissolved sulfonic acids is extracted with about 60% alcohol to remove the sulfonic acids which may then be neutralized with sodium hydroxide and subsequently freed of the alcohol by distillation.

The crude soaps of these preferentially oil-soluble sulfonic acids obtained by the procedure described above may be freed of inorganic salts by purification. This purification is preferably accomplished by dilution of the crude soap with from about 1/2 to about 10 parts, preferably 1 to 2 parts of 50% or higher strength alcohol, preferably alcohol of 60 to 70% strength, and allowing the salts to settle while maintaining the mixture within the temperature range of 130 to 175° F., preferably 155 to 165° F. When the salts have settled the supernatant alcohol-soap layer is separated and the alcohol is recovered by conventional distillation procedure.

The soaps of these preferentially oil-soluble sulfonic acids obtained in the manner above described differ from other oil-soluble soaps of sulfonic acids from other fractions such as for example, those obtained by treating petroleum distillates of from about 60 seconds to about 130 seconds Saybolt Universal viscosity at 100° F. with from about 3 pounds to about 4 pounds of fuming sulfuric acid per gallon of oil, and the petroleum sulfonates obtained by treating distillates of from about 80 seconds to about 130 seconds Saybolt Universal viscosity at 100° F. with about 5 pounds of fuming sulfuric acid per gallon of oil. In addition to inhibiting the formation of tarnish and/or discoloration, which other sulfonates do not, the petroleum sulfonates of the present invention differ from other petroleum sulfonates in that the former are substantially less soluble in water than are the latter, although they do show some hygroscopic tendencies.

The effectiveness of the particular petroleum sulfonates used in the present invention in preventing discoloration and/or tarnish of metal surfaces on which it is applied is demonstrated by accelerated tests carried out in a humidity cabinet wherein intermittent periods of heating and cooling are employed while maintaining saturated air conditions within the cabinet. The humidity cabinet which is provided with heating units and thermal regulators for automatic temperature control is maintained on a cycle of 24 hours cooling at 40-45° F. and four hours heating at 100 to 105° F. A water level of 2-3 inches is maintained in the bottom of the cabinet to give approximately saturated conditions at all times. Cold-rolled open hearth steel strips of approximately 1 x 4 inches are coated with the rust preventive material and suspended by glass hooks to a glass rod running across the top of the humidity cabinet. To insure that only moisture of condensation comes in contact with the

strips, stainless steel shields are placed above the strips in such a position that no moisture from the shields could drip on the strips. The following petroleum sulfonates were tested under the foregoing conditions:

"Sulfonate I" obtained from distillates of 200-400 seconds Saybolt Universal viscosity at 100° F. treated with from about 7 to about 8 pounds of fuming sulfuric acid per gallon of distillate, and neutralized with sodium hydroxide. The sulfonate so obtained is that employed in accordance with the present invention.

"Sulfonate II" sulfonates obtained from distillates of from about 60 to about 130 seconds Saybolt Universal viscosity at 100° F. by treating with from 3 to 3 1/2 pounds of fuming sulfuric acid per gallon of distillate, and neutralizing with sodium hydroxide.

"Sulfonate III" sulfonates obtained from distillates of about 80 seconds to about 130 seconds Saybolt Universal viscosity at 100° F. by treating with 5 pounds of fuming sulfuric acid per gallon of distillate, and neutralizing with sodium hydroxide.

Sulfonates II and III are the type of sulfonates heretofore used in slushing compounds. These were found to cause tarnish and discoloration of metal surfaces.

The results obtained in the humidity cabinet tests on naphtha solutions of the foregoing type of petroleum sulfonates are shown in the following table.

TABLE I

Humidity cabinet tests of petroleum sodium sulfonates in naphtha solution

Petroleum sodium sulfonate	Analysis of sodium sulfonate				Soap used	Duration of test	Condition of strips
	Soap	Oil	Salt	H ₂ O			
	Per-cent	Per-cent	Per-cent	Per-cent	Per-cent	Days	
I.....	34.2	58.8	4.6	6.0	10 20 30 30	2 3 5 3	No tarnish. Do. Do. Do.
II.....	46.9	46.2	1.8	1.6	10 20 30 30	2 2 2 3	Severe rust. Tarnish. Severe rust. Tarnish. Severe rust. Tarnish. Severe rust. Tarnish.
III.....	45.7	48.6	1.34	1.4	30	2	Tarnish. Severe rust.

The foregoing data clearly demonstrate the tarnish forming tendencies of sodium sulfonates II and III and the absence of any tendency of sulfonate I to form tarnish.

Depending upon the severity of the conditions under which the various grades of slushing compounds are to be employed from about 1% to about 40% of the petroleum sulfonates of the present invention are employed in the slushing compounds. While we prefer to employ the sodium soap of such sulfonic acids, other soaps of metals of groups I, II, IV, VI, and VIII of the periodic table may be employed. Thus, for example, we may employ the potassium, calcium, barium, tin, lead, aluminum, chromium, cobalt, and nickel soaps of the sulfonic acids obtained by treating petroleum distillates of from about 70 to about 500 seconds or higher, and preferably of from about 200 seconds to about 400 seconds

Saybolt Universal viscosity at 100° F. with from about 6 to about 9 pounds, and preferably from about 7 to about 8 pounds of fuming sulfuric acid per gallon of distillate. In addition to the sulfonate the slushing compounds employed may contain mineral oils, petroleum naphthas, waxes, petrolatums, fatty materials such as degreas, oxidized paraffin wax or esters thereof, or mixtures thereof.

The consistency of the slushing compounds employed can be varied to suit the need, oils of various viscosities being used to obtain compositions of the desired fluidity. For indoor protection we have found that mixes of the petroleum sulfonate of the type hereindescribed and oils having Saybolt Universal viscosities of from about

wax we may use to advantage is the refined grade of very high melting point "tacky" petroleum wax having a melting point of from about 140° F. to about 150° F. or higher. We may also employ blends of high melting point petrolatum waxes and beeswax. As constituents we may use petrolatums of about 110° F. to about 130° F. melting point and/or petrolatum base stocks of about 135° F. to about 150° F. melting point or mixtures of each or both of these.

The following table gives, in percentages by weight, the compositions of various grades of slushing compounds. These compositions are given by way of illustration only and are not intended to limit the scope of the present invention thereto.

TABLE II
Composition of slushing compounds

	Example							
	1	2	3	4	5	6	7	8
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Sodium sulfonate ¹ (oil free).....	11	20	35	20.0	10.0	10	18	20
Petrolatum (118-128° F. M. P.).....			20	40				
Petrolatum (112-120° F. M. P.).....					50.0			
Petrolatum base (135-145° F. M. P.).....								
Paraffin wax (165° F. M. P.).....						55	22	49
Mineral oil (80-85 seconds ² at 100° F.).....	89	26	45	40	40	35	40	
Mineral oil (160-165 seconds ² at 210° F.).....		54					20	
Diluent (petroleum naphtha).....								
Mineral wax ³								33
								8

¹ Obtained by treating distillates of from about 200 seconds to about 400 seconds Saybolt Universal viscosity at 100° F. with 7-8 pounds of fuming sulfuric acid, and neutralizing with sodium hydroxide.

² Saybolt Universal viscosity.

³ In place of the mineral wax we can employ a blend of about 2% petrolatum wax of about 165° F. melting point and about 6% crude beeswax.

60 seconds at 100° F. to about 200 seconds or more at 210° F. are effective in providing adequate protection to the metal surfaces to which they are applied. If necessary, slushing compounds of the proper viscosity may be obtained by mixing oils of high viscosity with oils of low viscosity. Light liquid slushing compounds are particularly well suited for protecting highly finished metal articles such as fishing reels, razor blades, cutlery and the like. They are also effective in protecting the interior surfaces of gun barrels.

Under certain conditions it is desirable to employ slushing compounds which are semi-solid or solid since under very severe conditions of exposure, such as exposure to heavy rains, hot suns, dirt and dust liquid slushing compounds are not as effective as the semi-solid or solid compositions. When slushing oils are used under these severe conditions they may be washed off by rain, leaving the surface exposed to rusting. Exposure to the hot sun, tends to evaporate the more volatile slushing oils containing a relatively volatile diluent such as petroleum naphthas as the diluent, and dirt and dust falling upon the surfaces absorb the oil and make it ineffective as a protective film. For these reasons the use of semi-solid or solid slushing compounds are to be preferred to the liquid compositions for protection under severe conditions.

Suitable solid or semi-solid slushing compounds may be prepared with waxes, such as paraffin wax, montan wax, carnauba wax, etc., and/or petrolatums and/or petrolatum bases in combination with petroleum sulfonates of the type hereindescribed and oil to obtain the desired consistency. As the paraffin wax constituent we prefer to use a refined grade of wax, for example, one having a melting point of at least about 125° F. Another

The compositions of the slushing compounds given in Table II, cover slushing compounds ranging from light liquids to solid products at room temperatures. The slushing compounds which are solid at room temperatures are usually melted to facilitate application, the melted product being applied either by dipping, swabbing, or by spraying. To facilitate the application of the solid slushing compounds without heating, the same may be thinned with a solvent, preferably a petroleum naphtha having an initial boiling point of about 300° F. and a maximum distillation temperature of about 430° F. The inspections of typical petroleum naphthas we may employ are as follows:

	Naphtha A	Naphtha B
Initial boiling point.....° F.	307	302
Maximum boiling point.....° F.	400	418
5% distillation point.....° F.	337	342
Gravity, °A. P. I.....	49.6	49
Flash.....° F.	102	103

Petroleum solvents falling within the above specifications are oleum spirits and Stanisol.

While we have described our invention in connection with certain specific embodiments thereof it is to be understood that these are by way of illustration only and not by way of limitation. It is to be understood that a particular composition described may be modified without departing from the scope of our invention as defined by the appended claims.

We claim:

1. A slushing composition containing a metal soap of preferentially oil-soluble sulfonic acids obtained by treating a petroleum distillate having

a Saybolt Universal viscosity at 100° F. above about 70 seconds with about 6 pounds to about 9 pounds of concentrated sulfuric acid per gallon of distillate.

2. A slushing composition as described in claim 1 containing from about 1% to about 40% of the metal soap of the preferentially oil-soluble sulfonic acids.

3. A slushing composition containing a metal soap of preferentially oil-soluble sulfonic acids obtained by treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 70 seconds to about 500 seconds with about 6 pounds to about 9 pounds of concentrated sulfuric acid per gallon of distillate.

4. A slushing composition as described in claim 3 in which the metal soap is sodium soap.

5. A slushing composition as described in claim 3 in which the metal soap is a calcium soap.

6. A slushing composition as described in claim 3 in which the metal soap is an aluminum soap.

7. A slushing composition as described in claim 3 containing from about 1% to about 40% of the metal soap of the preferentially oil-soluble sulfonic acids.

8. A slushing composition containing a metal soap of preferentially oil-soluble sulfonic acids obtained by treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 400 seconds with about 7 pounds to about 8 pounds of fuming sulfuric acid per gallon of distillate.

9. A slushing composition as described in claim 8 in which the metal soap is a calcium soap.

10. A slushing composition as described in claim 8 in which the metal soap is an aluminum soap.

11. A slushing composition as described in claim 8 in which the metal soap is a sodium soap.

12. A slushing composition containing from about 1% to about 40% of a metal soap of preferentially oil-soluble sulfonic acids obtained by treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 400 seconds with about 7 pounds to about 8 pounds of fuming sulfuric acid per gallon of distillate.

13. A slushing composition containing a mineral oil and from about 1% to about 40% of a metal soap of preferentially oil-soluble sulfonic acids obtained by treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 400 seconds with about 7 to about 8 pounds of fuming sulfuric acid per gallon of distillate.

14. A slushing composition containing mineral

oil, wax and a metal soap of preferentially oil-soluble sulfonic acids obtained by treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 400 seconds with about 7 to about 8 pounds of fuming sulfuric acid per gallon of distillate.

15. A slushing composition containing mineral oil, a fatty material and a metal soap of preferentially oil-soluble sulfonic acids obtained by treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 400 seconds with about 7 to about 8 pounds of fuming sulfuric acid per gallon of distillate.

16. A slushing composition as described in claim 15 in which the fatty material is degrass.

17. A slushing composition containing a mineral oil, oxidized paraffin wax and a metal soap of preferentially oil-soluble sulfonic acids obtained by treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 400 seconds with about 7 to about 8 pounds of fuming sulfuric acid per gallon of distillate.

18. A slushing composition containing mineral oil, wax, a metal soap of preferentially oil-soluble sulfonic acids obtained by treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 400 seconds with from about 7 pounds to about 8 pounds of fuming sulfuric acid per gallon of distillate and a sufficient amount of a petroleum solvent to render the composition fluid at ordinary room temperatures.

19. A slushing composition as described in claim 18 in which the petroleum solvent is a petroleum naphtha having an initial boiling point of about 300° F. and a maximum boiling point of about 430° F.

20. A slushing composition containing mineral oil, petrolatum wax, beeswax and a metal soap of preferentially oil-soluble sulfonic acids obtained by treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 400 seconds with about 7 to about 8 pounds of fuming sulfuric acid per gallon of distillate.

21. A slushing composition containing a metal soap of preferentially oil-soluble purified sulfonic acids obtained by treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 70 seconds to about 500 seconds with about 6 pounds to about 9 pounds of concentrated sulfuric acid per gallon of distillate.

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