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SULFATE PROCESS TALL OIL AS A RUST INHIBITOR FOR FUEL FRACTIONS OF MINERAL OIL

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The present invention relates to the prevention of the formation of rust on metallic surfaces in contact with mineral oil products and more particularly to prevention of a formation of rust on metallic surfaces in contact with mineral oil products such as gasoline, naphthas and burning oils.

The problem of preventing the formation of rust on metallic surfaces in contact with mineral oil products has received considerable attention in the past decade with respect to those fractions of mineral oil which are used for lubricating purposes. However, the prevention of the formation of rust on metallic surfaces in contact with what may be termed "light products"; i. e., gasoline, naphtha and burning oils, has not received so much consideration. While the problem may seem to be the same, nevertheless the problem of preventing the formation of rust on metallic surfaces in contact with gasoline, naphthas and the like presents factors which are not encountered when confronted with the problem of preventing the formation of rust on metallic surfaces in contact with lubricating cuts of mineral oil.

One of the most important limitations upon the use of a rust preventive in gasoline, for example, is the limitation that the color of the product must be the same as that of the unprotected gasoline; i. e., the rust preventive must not cause a color change in the gasoline by reaction with the hydrocarbon constituents of the gasoline, dyes, components of tetraethyl lead fluid, ant-oxidants, etc., normally contained or added to gasolines. Furthermore, the rust inhibitor must be one which has no appreciable effect upon the octane rating or any of the other specifications under which the gasoline is sold.

Another factor which is of relatively no importance when considering the formulation of a lubricating oil is that of the effect of extreme pressures on the separation or other action of the rust preventive. Thus, for example, it is well known that products such as gasoline, naphtha and burning oils are in many instances transferred from the refinery to distributing points via pipe lines. Pressures as high as 1200 p. s. i. may be encountered in such pipe line transportation. Consequently, it is essential that the rust preventive remain with the petroleum cut regardless of the pressure to which the cut is subjected.

Another factor controlling the selection of a rust preventive for mineral oil fractions other than lubricating oil fractions is the tendency of some known rust preventives to cause the formation of emulsions. Rust preventives which tend

to emulsify the water present with the mineral oil fraction are not useful because they tend to hold unusually large amounts of water in the petroleum products.

Indicative of the problem presented in preventing the formation of rust on metallic surfaces in contact with gasoline, naphtha, burning oils and the like is the fact that 110 materials were tested and failed. Of the 110 that failed, failure was due to a color change in the gasoline in 36 instances. Of the remaining 74, 15 failed because of their tendency to form emulsions and the remainder failed to provide the required protection at practical concentrations. Thus, it is manifest that although a large amount of information has been obtained upon the solution of the problem of preventing the formation of rust on metallic surfaces in contact with lubricating fractions of mineral oil, nevertheless the problem of preventing the formation of rust on metallic surfaces in contact with gasoline, naphthas, burning oils and the like still remains to be solved.

An important limitation upon the use of a rust preventive in gasoline is its effect upon gum formation. As a generalization it can be said that rust preventives are non-volatile in nature and increase the amount of gum formed by the amount of rust preventive added. Consequently, a rust preventive useful in gasoline is one which is effective in concentrations not more than about 0.008 weight per cent of non-volatile residue. Accordingly, it is an object of the present invention to provide a gasoline, naphtha or burning oil fraction of mineral oil containing an amount of rust preventive not substantially in excess of about 0.008 weight per cent non-volatile residue.

It has now been discovered that crude "tall oil," deodorized "tall oil," solvent refined "tall oil," polymerized "tall oil" and other available "tall oils" are materials which satisfy all of the requirements of a rust preventive for gasoline, naphthas, burning oils and the like.

"Tall oil" is the name by which a mixture of saturated and unsaturated fatty acids and rosin acids is known to the paper pulp manufacturers. When pulping wood by the sulfate, as distinguished from the sulfite, method the pulping liquor soon becomes contaminated with a soap which can be recovered by acidulating the liquors and skimming the water-insoluble organic material from the liquor. These skimmings of the acidulated liquors are known to the paper pulp manufacturer as tall oil, also spelled talloel, talloil and talloil.

A number of materials are available to in-

dustry all of which are essentially tall oil in the crude, partially refined or refined condition. A few of these are described by one of the purveyors of tall oil as follows:

"Opoil": a high grade crude tall oil having a brown color and an average neutralization number of 173.

"Deoil": a semi-refined tall oil made from "Opoil" by a method whereby most of the mercaptans are removed. This semi-refined tall oil is dark brown and generally has a neutralization number of 173.

"Facoil CB" is a non-crystallizing solvent refined tall oil containing about 40-42 per cent rosin acids and having usually a neutralization number of 164.

"Facoil CS" is a color stabilized solvent refined tall oil usually having a neutralization number of 164.

"Facoil GN" is a tall oil having a neutralization number of 159.

One manufacturer states that tall oils can be made to any desired rosin acid content between 39 and 55 per cent.

Tall oil has been prepared for the purpose of the present invention by acidulating crude sodium soap obtained from a paper manufacturer with sulfuric acid at low temperature. When the crude sodium soap was acidulated at 30° to 50° C. with 98 per cent H₂SO₄ the resulting tall oil had a neutralization number of 140. When a sample of the same crude sodium soap (sometimes called sodium tallate) was acidulated at room temperature with 50 per cent H₂SO₄ the resulting tall oil had a neutralization number of 173. A third sample of tall oil of about the consistency of apple butter which had been in storage for about 15 years had a neutralization number of 155.

In general, and grossly, crude tall oil can be characterized as a mixture of unsaturated fatty acids such as oleic, linoleic and linolenic, rosin acids which have not been completely identified, a small amount of the order of 2 to 3 per cent of saturated fatty acids such as palmitic acid, unsaponifiables, probably phytosterols and malodorous materials probably mercaptans.

At the present time it is difficult to suggest any explanation for the efficacy of the various tall oils since synthetic blends of various fatty acids and rosin acids from sources other than the tall oil were not satisfactory rust inhibitors.

The efficacy of tall oil of various grades and sources was determined by the modified ASTM D665-47 T rust test which has been stated to be more severe in many respects than actual pipe line conditions in that it is run at a higher temperature (80° F.) than is usually encountered in a pipe line, with a much higher relative amount of water present and under conditions such that the test materials are saturated with oxygen at all times. It has been said that test specimens exposed to the severe rusting conditions of this test for two days are rusted to substantially the same degree as those exposed in a products pipe line for 30 to 60 days. The ASTM test was modified to the extent of lowering the test temperature from 140° F. to 80° F. for 48 hours and using distilled water. When a sample of finished gas-line containing normal amounts of dye, tetraethyl lead, antioxidants, etc. and the indicated amounts of "tall oil" was subjected to the afore-said modified ASTM test, the following results were observed:

Tall Oil	Concentration, parts per million	Modified ASTM Rust Test D-665-47T Result	ASTM Glass Dish Gum Mg./100 ml.
Blank		Fail ¹	1.8
		do	1.1
	50	Pass	2.7
	30	do	
10 Facoil CS, N. N. 164	20	Fail ⁴	
	10	do ⁴	
	8	do ⁴	
	50	Pass	3.3
	30	do	
Facoil CB, N. N. 164	20	Fail ⁴	
	10	do ⁴	
	50	Pass	2.5
15 Facoil GN, N. N. 159	30	do	
	20	Fail ⁴	
	10	do ⁴	
	50	Pass	
Deoil, N. N. 173	30	Fail ⁴	
	10	do ⁴	
	50	Pass	
20 Crude Tall Oil (after 15 years storage), N. N. 155	30	do	
	10	do	
	50	Pass	
Tall Oil (from soap with 98% H ₂ SO ₄)	30	do	
	10	do	
	50	do	
25 Tall Oil (from soap with 50% H ₂ SO ₄)	30	Fail	
	10	do	

Pass: indicates no rust.

¹ Heavy rust.

² Light to medium rust.

³ More than 20 pin point rust spots.

⁴ 10 to 20 pin point rust spots.

⁵ Less than 10 pin point rust spots.

It is to be noted that when tall oil denominated Facoil CS was added to solvent refined turbine oil in amounts sufficient to provide 600 p. p. m. and tested at 140° F. it failed to provide rust protection. The specimen after testing had 75 to 100 pin point rust spots.

A typical analysis of a commercially available tall oil is the following:

Facoil CB

Specific gravity @ 25° C.	0.9763.
Viscosity, Saybolyt Univ. @ 210° F. sec.	118.5.
Viscosity, Gardner-Holt	V-Z.
Flash point	395° F.
Fire point	40° F.
Color, Lovibond 1 in. 70 yellow	18.8 red.
Color, Hellige scale	10-12.
Moisture	0.24%.
50 Ash	0.003%.
Acid number	166.3.
Saponification value	174.2.
Rosin acid number	84.4.
Rosin acids	47.8%.
55 Fatty acids	45.4%.
Sterols	6.6%.
Iodine number (Wijs)	142.5.

Facoil CS is a solvent refined product made from Facoil CB. Deoil has the same chemical specifications as "Opoil" crude. Opoil has the following chemical specifications:

Moisture and volatile matter --per cent--	0.9
Ash	do
65 Unsaponifiable fat	6.5
Free fatty acids (oleic)	85.95
Saponification value	173.9
Acid number	171.9
Fatty acids	per cent-- 49.52
70 Rosin acids	do-- 42.21
Iodine value (Wijs)	159.1

Accordingly, sulfate tall oil obtained in the sulfate pulping of wood is useful as a rust inhibitor in liquid non-lubricating fractions of min-

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eral oil such as gasoline, naphthas, burning oils and the like.

We claim:

1. A liquid fuel fraction of mineral oil containing from about 0.00003 per cent to about 0.008 weight per cent of sulfate process tall oil.
2. A liquid fuel fraction of mineral oil containing an amount not exceeding about 0.008 weight per cent of sulfate process tall oil effective to prevent rusting.
3. Gasoline containing an amount not exceeding 0.006 per cent of sulfate process tall oil effective to prevent rusting.
4. Kerosine containing an amount not exceeding 0.006 per cent of sulfate process tall oil effective to prevent rusting.
5. Diesel fuel containing an amount not exceeding 0.006 per cent of sulfate process tall oil effective to prevent rusting.

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6. Fuel oil containing an amount not exceeding 0.006 per cent of sulfate process tall oil effective to prevent rusting.

7. Naphtha containing an amount not exceeding 0.006 per cent of sulfate process tall oil effective to prevent rusting.

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