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CORROSION INHIBITOR

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This invention relates particularly to corrosion inhibitors and more especially to the use of a material which under various environments has been found to be particularly effective for the purpose of inhibiting corrosion of metallic surfaces such, for example, as iron.

It is a principal object of this invention to provide a corrosion inhibitor which is effective under a wide variety of conditions for metallic surfaces generally, and which is particularly effective with iron or ferrous surfaces. Other objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however of but a few of the various ways in which the principle of the invention may be employed.

Broadly stated, this invention comprises the use as a corrosion inhibitor of benzyl thio cyanate.

The corrosion inhibiting properties of benzyl thio cyanate may be utilized in a variety of environments such as, for example, in the production of decorative or preservative coatings for metallic surfaces, and in particularly in the field of lubrication.

When employed as a corrosion inhibitor in surface protective materials, the benzyl thio cyanate is included as a constituent of the paint, varnish, or lacquer which comprises the primary protective material. When thus used, the base of the covering material may be any such as are conventionally employed and which are compatible with benzyl thio cyanate. Protective films of a non-drying character applied to a metallic surface may also advantageously contain this corrosion inhibitor. Thus the oily film which is applied to metallic articles for the purpose of preserving the same against corrosion during or subsequent to fabrication will advantageously contain small amounts of this inhibitor.

It will thus be seen that this inhibitor is effective whether used in a drying oil base such as in paints, varnishes and lacquers, or in a non-drying oil base such as mineral oil. The principal field of usefulness of benzyl thio cyanate as a corrosion inhibitor is in the field of lubricants in which an oily body is employed as the lubricant, but which may contain accidental or intentional inclusions of materials which will chemically react with metallic surfaces with which the lubricant comes in contact, and which have a tendency to cause corrosion of such surfaces.

In commercial lubricants this inclusion of materials, the corrosiveness of which is inhibited by benzyl thio cyanate, may be inadvertent or unavoidable as by the accidental remainder in the composition of materials employed in refining processes or by the presence in the oil base of materials which occur naturally therein, and which it is either inexpedient or for other reasons not desirable to remove.

Examples of such inclusions are the traces of solvents and the like employed in the refining of mineral oil and the inclusions in mineral oil of naturally occurring materials in minor amounts which have a tendency to be corrosive to metallic surfaces such as iron.

Still a further and perhaps the most valuable use of benzyl thio cyanate as a corrosion inhibitor is in lubricating compositions to which are intentionally added, for various purposes, materials which have either as their primary or purely collateral property the ability to react with the metallic surfaces with which the lubricant comes in contact. As examples of addition agents to lubricating compositions generally, having the ability to react with metallic surfaces as one of the desired properties thereof, the generally employed extreme pressure addition agents may be mentioned. An extreme pressure agent in general relies for its effectiveness upon its ability to react with the metallic surfaces being lubricated in such a way as to either retain a thin film of oil between such surfaces under conditions of extreme pressures, or to provide an anti-fluxing film between such surfaces which is effective to prevent actual metal to metal contact and consequent seizure and scoring under conditions of extreme pressures. Compounds of chlorine or sulfur or both as well as the intentional inclusion in the composition of elemental sulfur in solution are examples of extreme pressure addition agents which function by virtue of their being able to react with the metallic surfaces with which they come in contact, particularly under conditions of extreme stress as imposed by high unit bearing pressures.

Benzyl thiocyanate is an effective corrosion inhibitor in such extreme pressure lubricating compositions to materially inhibit the reaction of the composition with metals, particularly iron, without, however, materially interfering with the reaction of such lubricants with the metallic bearing surfaces for the purpose of imparting

extreme pressure characteristics in the manner above defined. By the employment of this inhibitor, it is therefore possible to utilize active extreme pressure addition agents which are desirable on account of the high film strength which they impart to the composition; the inhibitor serving to protect the metallic surfaces of containers and other parts of the apparatus being lubricated from corrosion by these active addition agents.

A further class of lubricating composition addition agents with which this inhibitor is particularly useful is that class of materials which is added to lubricating compositions for purposes other than to impart extreme pressure characteristics, but which are of such a nature that they do react with metals such as iron. Examples of this class of addition agents are pour point depressors, inhibitors of sludge, and addition agents which lend oiliness to the composition.

The materials which impart improved oiliness to lubricating compositions are generally oxygen-bearing organic compounds. These, when employed in conjunction with extreme pressure addition agents of the character previously defined, in many cases have an auxiliary effect of activating the extreme pressure addition agents. Benzyl thio cyanate is, therefore, particularly suited for use as a corrosion inhibitor in lubricating compositions which include a material capable of reacting with the metallic surfaces being lubricated and an organic oxygen compound, especially when the latter is of the type which, as indicated, will activate the former.

Halogenated or more specifically chlorinated aliphatic compounds are generally less stable and more reactive with metal surfaces than are the halogenated or more specifically chlorinated ring compounds. While this invention contemplates the use of benzyl thio cyanate with both types of halogen compounds, its greater field of usefulness will be found when employed in conjunction with the aliphatic halogen compounds. The ring type halogen compounds with which this inhibitor may be employed in combination are those, for example, disclosed in United States Patent No. 1,986,651. Inasmuch as the presence of oxygen, either in separate compound or in the same molecule with the halogen, in general has an activating influence on the halogen, the present inhibitor may be used to advantage in combination with extreme pressure addition agents of the type disclosed in United States Patent No. 2,137,-782 to which patent reference may be had for a list of specific examples of such compounds.

Halogen bearing aliphatic esters, acids and salts are examples of the more reactive type of halogen bearing addition agents with which this inhibitor may be used with great advantage.

In certain instances the particular extreme pressure addition agent is produced from a naturally occurring material since these are usually more generally available and thus can be produced at a lower cost than pure compounds. The naturally occurring materials such as sulfur containing or sulfurized petroleum fractions, or more particularly halogenated or chlorinated petroleum fractions such as mineral oil, foot's oil, kerosene, paraffin wax are examples of materials of this character. Benzyl thio cyanate has been found to be particularly effective as a corrosion inhibitor when employed in combination with the latter class of materials in lubricating compositions generally.

Examples of sulfur bearing extreme pressure addition agents in addition to elemental sulfur as above defined, are the organic sulphides, polysulphides, mercaptans, thio acids, thio esters, etc., used either as the only extreme pressure addition agent or in combination with another extreme pressure addition agent such as an organic halogen compound. This combination is particularly effective since it has been demonstrated that these two classes of extreme pressure addition agents have a cooperative effect.

Lubricating compositions made in accordance with the present invention may include as the only addition agents, those named, or more generally may also include materials previously identified as oiliness agents such as, for example, those which may be produced by the oxidation of petroleum fractions. The oxidized petroleum fractions are generally found useful as the oiliness material employed in a composition of the character to which this invention relates, since the nature of their source makes them particularly compatible with and effective in compositions in which the base is mineral oil.

The concentrations in which benzyl thio cyanate is employed as an inhibitor will depend, of course, upon the type of composition in which it is incorporated and the use for which such composition is designed. For all of the above uses, however, and especially where an oil vehicle is employed whether of the drying or non-drying type, but particularly when the base of the composition is a non-drying oil, the inhibitor will be employed in amounts of from about .005% to .5%. For use in lubricating compositions of the character above referred to generally satisfactory results will be secured by the employment of the inhibitor in amounts of from about .01% to about .2%.

It is understood, of course, that when reference is had herein to a compounded lubricating composition including benzyl thio cyanate as a corrosion inhibitor, the base of such composition may be any suitable lubricating oil which in most instances will be a refined mineral oil—refined to the extent necessary to suit the oil base to the particular service for which it is designed. Similarly the addition agents should be oil soluble at least to the extent to which they are required to be present and sufficiently non-volatile so that they will not be driven off from the compositions at the temperatures encountered in service. In general this requirement is met by addition agents which have a vapor pressure less than atmospheric at a temperature of 140° C. or preferably at a temperature of 170° C. Compositions of this character generally comprise a major proportion of mineral lubricating oil and minor amounts of the addition agents named along with the inhibitor in the proportions above specified. When a concentrate is made to be blended with mineral oils, then, of course, the percentages, within which the various addition agents including the inhibitor may be present, will be correspondingly greater depending upon the extent to which the concentrate is to be diluted in the manufacture of the finished product.

Benzyl thio cyanate is particularly effective as a corrosion inhibitor in the presence of moisture and especially so in instances where the corrosive effect of the primary corrosive constituent is either augmented or produced entirely by the presence of moisture.

For the above reasons benzyl thio cyanate has particular usefulness in lubricating compositions

which contain water as a part of the normal environment or with which water may accidentally come in contact. Examples of the former are lubricants such as are used in reciprocating steam engines, steam turbines, boiler pumps and the like; and examples of the latter are lubricants used in gear boxes and gear cases such as differentials and transmissions of automobiles. The following is a specific example of a lubricating composition which would be useful for the latter purpose:

Gear lubricant

	Per cent
Chlorinated paraffin wax (40% Cl)	8
Dibenzyl disulphide	2.5
Benzyl thio cyanate	0.1

The remainder being substantially all S. A. E. 90 mineral gear oil, viscosity about 85 sec. S. U. S. at 210° F., which may also contain such other addition agents as are sometimes employed in this type of composition.

The following is a specific example of a lubricating composition which may be advantageously employed in the presence of large quantities of water at high temperatures such as in steam turbines and the like:

Turbine lubricant

	Per cent
An extreme pressure addition agent such as hexachlor diphenyl oxide	1
An oxidation inhibitor such as tri(methyl cyclohexyl) phosphite	.05
Benzyl thio cyanate	.1

and the remainder being substantially all a highly refined S. A. E. 20 mineral lubricating oil having a viscosity of about 300 S. U. S. at 100° F., which may also contain such other addition agents as are sometimes employed in this type of composition.

Another example of a lubricating composition useful in the presence of moisture, i. e., for example, as a turbine lubricant, is the following:

	Per cent
Ortho-dichlor benzene	0.3
Hexachlor diphenyl oxide	0.3
Tri(methyl-cyclohexy) phosphite	0.06
Benzyl thio cyanate	0.05

and the remainder being substantially all a highly refined S. A. E. 20 mineral lubricating oil having a viscosity of about 300 S. U. S at 100° F., which may also contain such other addition agents as are sometimes employed in this type of composition.

Another class of compositions in which benzyl thio cyanate may be employed to advantage as a corrosion inhibitor is the class of hydraulic oils since a certain amount of moisture is usually present in these. The "turbine lubricant" described above would also be suitable for use as a hydraulic oil. In addition, the following specific composition is useful for this purpose:

Hydraulic oil

	Per cent
Ortho-dichlor benzene	0.4
Hexachlor diphenyl oxide	0.4
Methyl stearate	0.4
Benzyl thio cyanate	0.1

the remainder being substantially all a highly refined mineral oil having a viscosity of from 200 to 500 S. U. S. at 100° F., and preferably having a viscosity index (Dean and Davis) of about 100 or higher, and a viscosity of about 300 S. U. S. at 100° F.

Motor oils for use in the crankcases of internal combustion engines are also subject to contamination with moisture and may therefore be benefited by including small amounts of benzyl thio cyanate as a corrosion inhibitor. An example of a motor oil for this purpose is as follows:

Crankcase lubricant

	Per cent
Methyl chlorsalicylate	0.2
Benzyl thio cyanate	0.05

the remainder being substantially all a highly refined S. A. E. 20 mineral lubricating oil having a viscosity of about 300 S. U. S. at 100° F., which may also contain such other addition agents as are sometimes employed in this type of composition.

As previously indicated, benzyl thio cyanate is particularly effective as a corrosion inhibitor where the metallic surfaces are iron, accounting for the great utility of this material in the class of compositions above referred to.

As an example of the corrosion inhibiting effect of benzyl thio cyanate, reference may be had to the following laboratory tests by which its effectiveness as a corrosion inhibitor may be rather accurately determined.

The test procedure is as follows:

A 1 x 2 in. strip of 24 gauge low carbon steel (S. A. E. 1015–1020) polished with emery cloth, is drilled in the center with a #19 drill, and the diagonally opposite corners bent at an angle of about 15° along a line extending from one corner to the center of the opposite long side. The strip is accurately weighed on an analytical balance. This test piece is then attached to the lower end of a $\frac{3}{8}$'' steel (drill rod) shaft. The end of the shaft is threaded to take an 8–32 nut, and the test piece is held between two nuts (machine steel). 5 cc. of distilled water is added to 300 cc. of the oil, placed in a 400 cc. beaker. The beaker is heated by means of a water bath at a temperature of 200° F. and agitated by rotating the steel shaft at 500 to 750 R. P. M., with the shaft held in position centered with the beaker and so that the steel strip is about 1'' above the bottom of the beaker. The test is continued for 24 hours. The steel strip is then removed, washed with benzol, and wiped clean with a dry cloth. The loss in weight of the steel strip is determined and its appearance observed.

The following results were obtained with this procedure:

Number	Composition	Percent BTC	Test piece	
			Grams loss in weight	Appearance
1	Commercial hypoid gear lubricant.	0	.001	Rusty.
2	Same as No. 1	.05	.001	No rust.
3	Experimental hypoid gear lubricant.	0	.015	Rusty.
4	Same as No. 3	.10	.004	No rust.
5	Experimental hypoid gear lubricant.	0	.020	Rusty.
6	Same as No. 5	.10	.001	No rust.
7	Experimental hypoid gear lubricant.	0	.025	Rusty.
8	Same as No. 7	.10	.000	No rust.

Benzyl thio cyanate in small amounts is also useful to inhibit the corrosion of bearing alloys of the type used for crankshaft and connecting rod bearings of internal combustion engines, for example lead-bronze.

The following laboratory test method has been used to indicate the degree of such corrosion:

A piece of lead-bronze metal, one cm. square and about 1 mm.±.1 thick is suspended from a glass hook in a 100 cc. Griffin low form beaker containing between 70 and 80 cc. of the oil in question. The beaker is placed in an oven maintained at a temperature of 150° C.±1° C. for 192 hours. The test piece is removed from the oil, washed in benzene, then washed in naphtha and weighed, and the percentage loss in weight determined.

The following results were obtained with this procedure:

No.	Composition	Percent BTC	Percent loss in weight of test piece
1	S. A. E. 40 Pennsylvania motor oil containing .5% of the mono dichlor-stearate of ethylene glycol	0	.68
2	Same as No. 1	.05	.30
3	S. A. E. 10 Pennsylvania motor oil containing .25% methyl chlorsalicylate	0	.38
4	Same as No. 3	.05	.29
5	S. A. E. 10 Pennsylvania motor oil containing .75% of a mixture of methyl and ethyl dichlor stearates	0	.85
6	Same as No. 5	.05	.35

Benzyl thio cyanate may be prepared by any of the well-known methods for preparing alkyl or aryl thio cyanates, for example the following:

Equal molecular amounts of NaCNS and benzyl chloride were placed in a reaction vessel equipped with reflux condenser and a mechanical agitator. The reaction vessel was heated by a bath maintained at a temperature of 175° C. The time of heating was one hour. During this time, the temperature must not exceed 180° C. After heating for 1 hour at 175° C. the reactants were cooled at 150° C. and 5%, by weight, of solid anhydrous Na_2CO_3 were added. The reactants and Na_2CO_3 were agitated for 1 hour; no heat was applied during this time.

After agitating with Na_2CO_3, a vacuum was applied to the reaction vessel and the products distilled at an absolute pressure of 12 mm. of Hg. All materials distilling below 125° C. were discarded. All materials distilling between the temperatures of 125 and 135° C. were collected as benzyl thiocyanate.

Instead of benzyl chloride, benzyl sulfate may be used and potassium thiocyanate substituted for sodium. Care should be exercised in carrying out the reaction and purification of the product to prevent the product from being exposed to high temperatures, say 180° C. or more, since the thiocyanates are easily converted to isothiocyanates at such elevated temperatures.

The characteristics of typical preparations follow:

Melting point	° C.	34–36
Boiling point	° C./760 mm.	231–233
Sulfur	percent	20.5

The term "benzyl thiocyanate" as used herein is intended to apply to the product obtained as indicated above or by any satisfactory commercial process as well as to the chemically pure compound.

Other modes of applying the principles of our invention may be employed, change being made as regards the details described provided the features stated in any of the following claims, or the equivalent of such, be employed.

We therefore particularly point out and distinctly claim as our invention:

1. A lubricating composition comprising a major proportion of lubricting oil and a minor amount of benzyl thio cyanate.

2. A lubricating composition comprising a major proportion of lubricating oil and from about .005% to about .5% of benzyl thio cyanate.

3. The method of improving the characteristics of a lubricating oil composition to materially reduce its tendency to be corrosive to metallic surfaces which comprises admixing therewith a small amount of benzyl thio cyanate.

4. The method of improving the characteristics of a refined mineral oil offecting its use as an extreme pressure lubricant which comprises admixing therewith small amounts of both an addition agent capable of reacting with the metallic surfaces being lubricated, and benzyl thio cyanate.

5. The method of improving the characteristics of a refined mineral oil affecting its use as a lubricant which comprises admixing therewith a minor amount of an oil soluble halogen bearing organic compound, having a vapor pressure less than atmospheric at 140° C., and a minor amount of benzyl thio cyanate.

6. The method of improving the characteristics of a refined mineral oil affecting its use as a lubricant which comprises admixing therewith a minor amount of an oil soluble halogen bearing organic compound, having a vapor pressure less than atmospheric at 140° C., a minor amount of an oil soluble, organic oxygen compound, and a minor amount of benzyl thio cyanate.

7. A lubricating composition comprising a base of refined mineral lubricating oil containing a minor amount of benzyl thio cyanate.

8. A lubricating composition comprising a major proportion of lubricating oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein from about .005% to about .5% of benzyl thio cyanate.

9. An extreme pressure lubricating composition comprising a major proportion of lubricating oil with the properties of such composition affecting its use as an extreme pressure lubricant improved by incorporating therein minor amounts, based on the amount of lubricating oil, of an addition agent capable of reacting with the metallic surfaces being lubricated, and benzyl thio cyanate.

10. An extreme pressure lubricating composition comprising a major proportion of lubricating oil with the properties of such composition affecting its use as an extreme pressure lubricant improved by incorporating therein minor amounts, based on the amount of lubricating oil, of an addition agent having a vapor pressure less than atmospheric at 140° C., and capable of reacting with the metallic surfaces being lubricated, and from about .005% to about .5% of benzyl thio cyanate.

11. A lubricating composition comprising a major proportion of mineral oil and minor proportions of a halogenated organic ring compound, and benzyl thio cyanate.

12. A lubricating composition comprising a major proportion of mineral oil and minor proportions of a halogenated aliphatic compound, and benzyl thio cyanate.

13. A lubricating composition comprising a major proportion of mineral lubricating oil, and minor proportions of a halogenated organic com-

pound, oil soluble, organic oxygen compound, and benzyl thio cyanate.

14. A lubricating composition comprising a major proportion of mineral oil and minor proportions of a halogenated petroleum fraction and benzyl thio cyanate.

15. A lubricating composition comprising a major proportion of mineral oil and minor proportions of a halogenated petroleum fraction, an organic sulphur compound and benzyl thio cyanate.

16. The method of inhibiting corrosion of a metal surface otherwise subject to chemical action which comprises treating such surface with benzyl thiocyanate.

17. The method of inhibiting corrosion of an iron surface otherwise subject to chemical action which comprises treating such surface with benzyl thiocyanate.

18. The method of inhibiting corrosion of a metal surface otherwise subject to chemical action which comprises treating such surface with a minor amount of benzyl thiocyanate in an organic solvent.

19. The method of inhibiting corrosion of an iron surface otherwise subject to chemical action which comprises treating such surface with a minor amount of benzyl thiocyanate in a mineral oil.

20. As a new composition of matter a concentrate for use in lubricating compositions comprising in combination an addition agent capable of reacting with metallic surfaces, and benzyl thiocyanate.

21. As a new composition of matter a concentrate for use in lubricating compositions comprising in combination an extreme pressure addition agent having a vapor pressure less than atmospheric at 140° C. and capable of chemical reaction with an iron surface, and benzyl thiocyanate.

22. An extreme pressure lubricating composition comprising a major proportion of lubricating oil with the properties of such composition affecting its use as an extreme pressure lubricant improved by incorporating therein minor amounts based on the amount of lubricating oil of an addition agent capable of reacting with an iron surface, and benzyl thiocyanate.

23. As a new composition of matter, a concentrate for use in lubricating compositions comprising in combination a major proportion of an organic addition agent capable of reacting with metallic surfaces, such addition agent containing sulphur and a halogen, and a minor amount of benzyl thiocyanate.

24. As a new composition of matter, a concentrate for use in lubricating compositions comprising in combination a major proportion of an organic addition agent capable of reacting with metallic surfaces, such addition agent comprising an organic halogen compound, and a minor amount of benzyl thiocyanate.

25. As a new composition of matter, a concentrate for use in lubricating compositions comprising in combination a major proportion of an organic addition agent capable of reacting with metallic surfaces, such addition agent comprising an organic halogen compound and an organic sulphur compound, and a minor amount of benzyl thiocyanate.

26. As a new composition of matter, a concentrate for use in lubricating compositions comprising in combination a major proportion of an organic addition agent capable of reacting with metallic surfaces, such addition agent comprising an organic halogen compound and an organic polysulphide, and a minor amount of benzyl thiocyanate.

27. As a new composition of matter, a concentrate for use in lubricating compositions comprising in combination a major proportion of an organic addition agent capable of reacting with metallic surfaces, such addition agent comprising an organic halogen compound and an aromatic disulphide, and a minor amount of benzyl thiocyanate.

28. As a new composition of matter, a concentrate for use in lubricating compositions comprising in combination a major proportion of an organic addition agent capable of reacting with metallic surfaces, such addition agent comprising chlorinated paraffin wax and an aromatic disulphide, and a minor amount of benzyl thiocyanate.

29. As a new composition of matter, a concentrate for use in lubricating compositions comprising in combination a major proportion of an organic addition agent capable of reacting with metallic surfaces, such addition agent comprising chlorinated paraffin wax and a benzyl disulphide, and a minor amount of benzyl thiocyanate.

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