HEAT TRANSFER AND QUENCH OIL

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ABSTRACT OF THE DISCLOSURE

An oil composition that has good high temperature stability and that is particularly useful as a heat transfer oil or as an oil for the quenching of metals comprises a major proportion of a hydrocarbon lubricating oil into which has been dispersed a minor proportion of an alkali metal phosphate, silicate or borate with the aid of a minor proportion of a high molecular weight mono-carboxylic acid, dicarboxylic acid or dicarboxylic acid anhydride.

DESCRIPTION OF THE INVENTION

This application is a continuation-in-part of Ser. No. 670,798, filed Sept. 26, 1967, and now abandoned.

This invention concerns an improved oil composition comprising a hydrocarbon lubricating oil into which has been dispersed an inorganic salt of an alkali metal with the aid of a high molecular weight mono-carboxylic acid or dicarboxylic acid or a dicarboxylic acid anhydride. The alkali metal salt is a phosphate, borate, or silicate of sodium, potassium or lithium, and serves primarily as an anti-oxidant for the hydrocarbon oil. The dispersion is particularly useful as a heat-transfer oil and more particularly as a high-speed quenching oil composition that can be used in the heat treatment of metals, particularly ferrous metals such as steel. Thus the invention is especially directed to an improved quench oil and to an improvement in the method of quenching metals using the improved composition of this invention.

Many metal alloys, particularly ferrous alloys and carbon steels, require heat treatment to develop the desired degrees of hardness and strength. The basic heat treatments are generally hardening by quenching and softening by annealing. The hardness of an alloy is mainly dependent upon the formation of a certain physical structure. In the case of steel, for example, it is desirable to form martensite in the steel. The hard martensite structure is particularly suited for such metal parts as gears. To increase the hardness of metal alloys such as steel they are heated to an elevated temperature; for example, above 1600°F. and then plunged into a comparatively cool quenching medium. In some cases the desired structure can be obtained immediately, but in other cases the metals are quenched to maximum hardness and then tempered to achieve the desired hardness and ductility.

In the heat treatment of steel the term quenching covers the process of cooling the steel from the temperature range at which austenite (solid solution of carbon in gamma iron) is formed to a temperature below the critical temperature, which is generally around 1000°F. If the steel is cooled too slowly, the austenite is transformed into the softer pearlite. If the cooling is sufficiently rapid, however, the harder martensite is formed instead. Quenching that is effective in forming martensite is frequently referred to as marquenching.

The quenching problem is basically one of heat transfer. While water can be used for rapid quenching, it is undesirable in most instances, because it tends to cool the metal too quickly and often results in distortion and cracking. Hydrocarbon oils, and particularly mineral oils, are commonly used as quenching liquids, but unmodified straight mineral oils do not usually form satisfactory quenching media, since the initial rate of cooling is too slow. Hence, the development of the quench oil art has been in the direction of modifying hydrocarbon oils by incorporating certain additives therein. See for example U.S. Patents, 3,027,315, 3,113,054, and 3,159,510.

A particularly effective quench oil known to the prior art comprises a major proportion of a hydrocarbon lubricating oil, a minor proportion of an alkali metal hydrocarbon sulfonate or alkaline earth metal hydrocarbon sulfonate and a minor proportion of an alkali metal phosphate, borate or silicate, e.g. trisodium phosphate. The presence of the alkali metal phosphate or alkali metal silicate or borate imparts long oxidation life to the quench oil (see for example U.S. Patent 2,988,506).

The phosphates are particularly effective. Within limits, the oxidation life is directly proportional to the amount of alkali metal phosphate, silicate, or borate in the quench oil. Thus 1.8 wt. percent of trisodium phosphate will give twice the oxidation life afforded by 0.9 wt. percent of trisodium phosphate. When the quench oil contains about 1.2 to 1.3 wt. percent of sodium petroleum sulfonate (2 wt. percent of a 60 to 65 wt. percent concentrate), 0.4 wt. percent of hydrated trisodium phosphate can be dispersed. If the concentration of sodium petroleum sulfonate is increased to about 3 to 3.2 wt. percent (5 wt. percent of the sulfonate concentrate) only 0.9 wt. percent of hydrated trisodium phosphate can be dispersed. It is desirable to enhance the oxidation life of the quenching oil by increasing the trisodium phosphate concentration above 0.9 wt. percent (equals about 0.4 wt. percent of anhydrous Na₃PO₄), but this would require additional sodium petroleum sulfonate. Use of greater proportions of the sulfonate is objectionable because the sulfonate is basically a pro-oxidant.

It has now been surprisingly found that the need for the sulfonate to aid in dispersing the alkali metal inorganic salt in the hydrocarbon lubricating oil can be reduced or eliminated, by employing as the dispersant a high molecular weight monooxylic acid, dicarboxylic acid or carboxylic acid anhydride. The invention is applicable to the dispersion of alkali metal phosphates, alkali metal silicates and alkali metal borates or mixtures of these salts. The carboxylic acids employed in this invention are characterized by having long-chain alkyl or alkenyl hydrocarbon groups with a total molecular weight in the range of about 350 to about 3500, i.e. the total number of carbon atoms in the hydrocarbon groups will be within the range of about 25 to 250.

A monooxylic acid for use in the present invention can be prepared by oxidizing a high molecular weight olefin, e.g. polyisobutylene of about 900 molecular weight, with an oxidizing agent such as nitric acid or oxygen, by preparing an adduct of an aldehyde and an olefin and then oxidizing the adduct, or by halogenating a high molecular weight olefin to form a dihalogen compound and then subjecting the latter to hydrolyzing oxidation. These procedures are taught in British Patent 983,040. A suitable monooxylic acid or derivative thereof can also be obtained by oxidizing an alcohol with potassium permanganate or by reacting a halo- genated high molecular olefin polymer with a ketene. Another convenient method for preparing a monooxylic acid involves the reaction of metallic sodium with an acetooacetic ester or malonic ester of an alkane to form a sodium derivative of the ester and the subsequent reaction of the sodium derivative with a halo-
3,489,619

Monocarboxylic acids can also be prepared from olefin polymers such as a polymer of a C3 to C5 monoolefin, e.g., polypropylene or polyisobutylene by halogenating the polyolefin and then condensing it with an unsaturated monocarboxylic acid. Examples of suitable olefin polymers include polyethylene, polypropylene, or polyisobutylene, having an average molecular weight of about 350 to 3500, preferably about 800 to 1900. Polyisobutylene is preferred, since it has a lessened tendency to gel the product, as compared to some of the other polyolefins such as polyethylene or polypropylene. The polymer is halogenated by contacting it with either bromine or chlorine, preferably by blowing chlorine through the polymer, to provide about one to two atoms of halogen per molecule of polymer. The halogenation step may be conducted in the temperature range of from about 50°C to about 300°C. To aid in the halogenation step, the polymer may be dissolved in a suitable solvent, such as carbon tetrachloride, in order to lower the viscosity of the polymer. However, the use of such a solvent is not necessary.

The time required for halogenation may be varied to some extent by the rate at which the halogen is introduced. Ordinarily from about 2 to about 5 hours is a satisfactory halogenation period. In a representative plant scale operation involving the chlorination of polyisobutylene of 830 molecular weight, a 100-pound batch will be chlorinated with 10 pounds of chlorine introduced into the reactor over a period of 3/2 hours with a chlorination temperature of about 250°F.

The halogenated polymer thus obtained is condensed with an alpha, beta-unsaturated monocarboxylic acid of from about 3 to 8 carbon atoms. Ordinarily, because of their greater availability, acids of this class having 3 or 4 carbon atoms will be used. Such acids include acrylic acid, alpha-methyl-acrylic acid (i.e., 2-methyl propenoic acid) and crotonic or h=localhosteocrotonic acid (beta-methylacrylic acid). Other alpha, beta-unsaturated acids that may be employed include tiglic acid (alpha-methylcrotonic acid), angelic acid (alpha-methylisocrotonic acid), sorbic acid, and cinnamic acid. Esters of such acids, i.e., ethyl methacrylate, may be employed if desired in place of the free acid.

In condensing the halogenated polyolefin with the unsaturated acid, at least one mole of acid is used per mole of halogenated polyolefin. Normally, the acid will be employed in excess and may amount to as much as 1.5 to 2 moles per mole of halogenated polyolefin. The condensation temperature can be in the range of from about 300°C to 500°C and will more preferably be within the range of from about 375°C to 475°C. The condensation may require from about 3 to about 24 hours, but will ordinarily take place in from 6 to 18 hours. After the reaction has been completed, excess acid can be purged from the mixture, for example, by blowing with a stream of nitrogen at a temperature of 400°C to 500°C.

High molecular weight carboxylic olefin acids of the type described above can also be prepared by a so-called one-step process involving the halogenation of the olefin polymer in the presence of the alpha, beta-unsaturated acid. Using proportions of reactants within the ranges discussed above, the starting acid and the olefin polymer are mixed together in the reactor, the temperature being kept below about 150°C until the start of halogen introduction so as to avoid homopolymerization of the alpha, beta-unsaturated acid. Once halogenation has begun, the temperature can be raised to as high as 250°C. After halogen introduction, the temperature can be raised to 300°C to 500°C to effect the condensation reaction. A polycarboxylic acid for use in the invention can be prepared by halogenating a high molecular weight hydrocarbon such as an olein polymer as described hereinabove to produce a polyhalogenated product, converting the polyhalogenated product to a polyonitrile, and then hydrolyzing the polyonitrile. Polycarboxylic acids can be prepared also by oxidation of a high molecular weight polyhydric alcohol with potassium permanganate, nitric acid, or a like oxidizing agent. Another method for preparing such polycarboxylic acids involves the reaction of an olefin or a polar-substituted hydrocarbon such as a chloropropene or a polar-substituted carboxylic acid such as 2-pentene-1,3,5-tricarboxylic acid obtained by dehydration of citric acid.

A particularly useful polycarboxylic acid is a saturated aliphatic-hydrocarbon-substituted succinic acid or anhydride. The hydrocarbon-substituted succinic acid anhydrides may be represented by the formula

R′-CH=OC-CH-CH-CH-O

R and R′ are either hydrocarbon radicals or hydrogen, but at least one of them must be hydrocarbon. The preparation of a hydrocarbon-substituted succinic anhydride is well known in the art and simply involves reacting maleic anhydride with an olefinic hydrocarbon of high molecular weight or with a halogenated high molecular weight hydrocarbon. Typically, about equal molar proportions of maleic anhydride and an olefinic material are merely heated together. See, for example, U.S. Patent 3,172,892, column 2, line 51 to column 3, line 6.

The hydrocarbon radicals in the hydrocarbon succinic anhydrides can be either straight-chain or branched chain and they may be either substituted, as for example, chlorinated or sulfonurized, or they may be unsubstituted, but they will be substantially aliphatic radicals, i.e. at least 7% aliphatic. In most cases R and/or R′ will be long chain alkyl or alkenyl. Preferably, the hydrocarbon groups will have a total molecular weight in the range of about 350 to about 3500, i.e., the total number of carbon atoms in the hydrocarbon groups will be within the range of from about 25 to about 250. More preferably, this total number will be within the range of from about 35 to about 150. Particularly desirable for use, because of low cost and ready availability, are alkenyl groups obtained by reacting maleic anhydride with a polymer of a C3 to C5 monoolefin wherein the polymer has a molecular weight within the range of from about 350 to about 3500. Especially useful products are obtained using polyisobutylene having a molecular weight within the range of from about 500 to about 2100. As specific examples, the alkenyl group may be derived from polypropylene, polyisoprene, or polyisobutylene, e.g., polyisobutylene of 780 molecular weight or of 1200 molecular weight.

Examples of substituted succinic anhydrides in which the hydrocarbon substituents are predominantly, but not completely, aliphatic include a substituted succinic anhydride in which the substituent is derived from a copolymer of styrene and isobutylene, or from a copolymer of a substituted styrene and some other aliphatic olefin. In these cases the copolymer will be substantially aliphatic, that is, the composition of the copolymer will be such that the non-aliphatic portion does not substantially exceed about 30 percent of the whole. Thus, a copolymer of 90 percent of isobutene and 10 percent of styrene or of 80 percent of propylene and 20 percent of alkenyl-styrene is useful to provide the large, substantially aliphatic substituent.

The metal sulfonate that is employed as a dispersant for the alkali metal phosphate, borate or silicate, can be either an alkali metal sulfonate (e.g., sodium or potassium) or an alkaline earth metal sulfonate (e.g., calcium or barium). Preferably, alkali metal sulfonates are used, and most preferably sodium sulfonates. The sulfonates
are preferably salts of petroleum sulfonic acids. The latter are generally produced by the treatment of petroleum fractions, usually of the lubricating oil range, with suitable sulfonating agents such as sulfur trioxide or fuming sulfuric acid. These sulfonic acids normally have molecular weights in the range of about 300 to 1200. Preferably, for the present invention, the metal sulfonates that are used are alkali metal petroleum sulfonates having molecular weights within the range of about 400 to 800, most preferably within the range of about 420 to about 600.

The alkali metal phosphates that can be used in this invention include NaPO₄, KPO₄, LiPO₄, Na₃PO₄, K₂HPO₄, Na₃P₂O₇, Na₂P₂O₇, K₂P₂O₇, NaPO₃, and KPO₃. Trisodium phosphate and disodium phosphate are preferred. The borates include sodium tetraborate, potassium tetraborate, lithium tetraborate, sodium metaborate, and potassium tetraborate. The silicates include orthosilicates disilicates, sesquisilicates, and metasilicates, e.g., Na₂SiO₃, Na₃SiO₄, K₂SiO₃, Na₂SiO₃, K₂SiO₄, Na₂SiO₅, K₂SiO₅, etc.

The lubricating oil base which forms the major component of the quench oil is preferably a refined mineral lubricating oil having a viscosity of about 50 to 2000 SUS at 100°F and preferably about 200 to 1000 SUS at 100°F. Viscosities at 210°F will be in the range of about 40 to 160 SUS. Preferably the oil should have an initial boiling point of at least 600°F.

The quench oils of this invention will be compositions comprising a major proportion of a hydrocarbon lubricating oil and minor proportions of inorganic alkali metal salt, organic carbonyl acid and (when used) metal sulfonate within the following broad and narrow ranges:

<table>
<thead>
<tr>
<th>Alkali metal salt (borate, phosphate or silicate)</th>
<th>0.1-5</th>
<th>0.5-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acid or anhydride</td>
<td>0.1-1</td>
<td>0.5-5</td>
</tr>
<tr>
<td>Metal sulfonate (when used)</td>
<td>0.1-1</td>
<td>0.5-5</td>
</tr>
</tbody>
</table>

To prepare the quench oil of the invention, which in essence amounts to dispersion of the alkali metal phosphate, borate or silicate in oil, wherein the sulfonate and the high molecular weight compound act as dispersing agents, prior art procedures can be used if desired. The most general procedure has consisted in forming an aqueous solution wherein the inorganic salt is dissolved in 10 to 15 times its weight of water, and that solution is then emulsified with the other components and the emulsion is dehydrated until a clear product is obtained. That procedure has the disadvantage of requiring the removal of large quantities of water, but this has been difficult because of the tendency to foam, the formation of foam delaying removal of the water. An alternate and preferred method of preparation, which constitutes an additional feature of this invention, consists of mixing the required amount of dispersing agent with alkali metal phosphate, silicate or borate and a quantity of water that is just sufficient to dissolve the phosphate or other inorganic salt and to form a thick cream with the other components on gentle heating in the range of from about 100 to 200°F. Usually this amount of water will be no greater than 1 to 4 parts by weight, preferably 1 to 2 parts by weight, of water per part of alkali metal salt. This thick emulsion or cream is then heated until the temperature (212 to 530°F) until a clear syrup is obtained, at which stage the syrup can be diluted with the required amount of base oil. In practice it is often preferable to mix a small percentage of the entire amount of oil that is to be used in the finished quench oil composition, e.g. about 10%, into a thick emulsion and then dehydrate this mixture to a clear syrup, after which the remaining oil is added. The dehydration temperature will, of course, be sufficiently high to drive off essentially all of the water, but not so high as to cause degradation of the components of the emulsion.

In a plant operation, heat can be supplied through steam coils that have a temperature of, for example, 300 to 325°F. Dehydration could be assisted by reducing the pressure below atmospheric, but this is normally not necessary. Blowing with air, or preferably with inert gas such as nitrogen also aids water removal. The rate of dehydration should not be so rapid as to cause separation of any of the components, as for example to cause deposition of alkali metal phosphate, silicate or borate on the walls of the vessel. Control of these factors is well within the skill of the plant operator.

The syrup that is obtained as described above is in effect a quench oil concentrate that can be diluted with hydrocarbon oil base stock to obtain the finished quench oil. The syrup, or concentrate, can itself be used as a quench medium, being quite fluid at a temperature of 350°F or so, although it ordinarily be uneconomical to do this. Thus, another aspect of the invention is the providing of a quench oil concentrate. When such concentrate involves the use of metal sulfonate along with the carboxylic acid dispersant it will comprise a major proportion of hydrocarbon oil, from about 1 to about 10 wt. percent of metal sulfonate, from about 5 to 20 wt. percent of high molecular weight monoaicylic acid, diacylic acid or anhydride, and from about 3 to 10 wt. percent of alkali metal inorganic salt. In those formulations where no sulfonate is used it is possible to make a concentrate containing only of the carboxylic acid or anhydride and the alkali metal phosphate, borate or silicate dispersed therein, e.g. 30 to 40 parts of alkali metal salt dispersed in 50 parts of carboxylic acid or anhydride. As a practical matter however, it is preferred to prepare a concentrate comprising a vehicle consisting of 10 to 60 weight percent of high molecular weight carboxylic acid or anhydride and 90 to 40 weight percent hydrocarbon oil, this vehicle containing dispersed therein from 10 to 40 weight percent of alkali metal inorganic salt based on the total composition of concentrate, i.e. vehicle plus inorganic salt. By first dissolving the carboxylic acid or anhydride in oil in the proportions mentioned, before dispersing the inorganic salt, the viscosity of the material is reduced to a level that is more practical for handling.

The following examples include a preferred embodiment.

**EXAMPLE 1**

A mixture was prepared consisting of 2 parts by weight of sodium petroleum sulfonate concentrate, 2 parts by weight of polyisobutylene succinic anhydride, and 1.8 parts by weight of hydrated trisodium phosphate,

\[
\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}
\]

The polyisobutylene succinic anhydride was prepared by reaction of polyisobutylene of about 900 molecular weight with maleic anhydride. The sodium petroleum sulfonate concentrate consisted of 65 wt. percent of sodium petroleum sulfonate of about 460 molecular weight and 35 wt. percent of a mineral lubricating oil.

To the mixture of sodium petroleum sulfonate, polyisobutylene succinic anhydride and trisodium phosphate there were added 5 parts by weight of base oil and 10 parts by weight of base oil. This base oil was a phenol-extracted, Western Canadian distillate lubricating oil of 350 SUS viscosity at 100°F having a viscosity index (V.I.) of 90. The mixture was stirred while heating gently in the range of about 100 to 200°F until a thin cream was produced. Heating and stirring were continued with a bulk temperature of 212 to 220°F until a clear syrup was obtained. Heating was thereafter continued with nitrogen blowing until the temperature of the syrup was about 300°F so as to remove essentially all of the remaining water. The syrup, after dehydration, contained approximately 71 wt. percent oil, 9 wt. percent sulfonate,
14 wt. percent polyisobutylene succinic anhydride, and 6 wt. percent trisodium phosphate (anhydrous basis). To prepare a quench oil, the concentrated syrup was diluted with additional base oil to make a composition containing about 2 wt. percent of polyisobutylene succinic anhydride and about 0.8 to 0.9 wt. percent of anhydrous trisodium phosphate, based on the finished quench oil. A completely clear product was obtained.

**Comparative example**

Using the procedure outlined in Example 1, a prior art quench oil was prepared consisting of 5 parts by weight of the same sodium sulfonate concentrate that was used in Example 1, 0.9 gram of hydrated trisodium phosphate, and a sufficient amount of the base oil described in Example 1 to make up 100 parts by weight of the completed composition. Previous tests had established that 0.9 gram of hydrated trisodium phosphate was all that could be incorporated in the oil using this quantity of the sodium petroleum sulfonate alone as the dispersant.

**EXAMPLE 2 Oxidation test**

The quench oil prepared as described in Example 1 and the prior art quench oil prepared as described in the comparative example were each subjected to an oxidation test. In this test each oil was placed in an enclosed cup. Then a steel ball bearing, supported from above by a vertical shaft, was immersed in the oil about ½ inch below the surface. The bearing was rotated in the oil by means of the shaft during a period of two weeks while the oil temperature was held at 335°F. Since air was not excluded, air tended to be entrained in the oil by rotation of the bearing and its supporting shaft, and was thus present to promote oxidation. At the end of the two-week period, each of the oils was inspected for total acid number, pentane insolubles, and SUS viscosity at 210°F, and the condition of the bearings was noted. The results obtained are given in Table I.

**TABLE I**

<table>
<thead>
<tr>
<th>Percent viscosity increase</th>
<th>Comparative example</th>
<th>Example 1 product</th>
<th>Percent insolubles</th>
<th>Pentane insolubles</th>
<th>Total acid number</th>
<th>Bearing condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28</td>
<td>25</td>
<td>0.9</td>
<td>0.9</td>
<td>2.6</td>
<td>(f)</td>
</tr>
</tbody>
</table>

1 Slight discoloration.
2 No discoloration.

It will be noted that a composition of the present invention as exemplified by Example 1 was much more resistant to oxidation than the prior art composition.

In a second oxidation test, wherein a rapid stream of air was bubbled through each body of oil at 350°F, for 340 hours, the viscosity of the prior art quench oil (comparative example product) increased to 110 SUS at 210°F, whereas the product of Example 1, after a similar period, increased in viscosity to 91 SUS at 210°F. Initial viscosity of both oils was about 70 SUS at 210°F. No sludge was formed in the oil of Example 1 during this test, whereas the oil of the comparative example deposited considerable sludge.

In a third oxidation test a portion of the quench oil composition of Example 1 was diluted with an equal volume of lubricating oil to give a composition containing 0.9 wt. percent of trisodium phosphate on the hydrated basis, which is the same amount of trisodium phosphate that was present in the prior art quench oil of the comparative example. Equal quantities (15 gram samples) of the quench oil of Example 1, of the thus diluted quench oil of Example 1, and of the prior art quench oil of the comparative example were placed in separate glass vessels of equal size and the vessels were placed in an oven at 400° and a steam of air was bubbled through each of the samples at the same rate for 96 hours. At the end of this time the amount of sludge, determined as pentane insolubles, was measured in each oil. The results are given in Table II:

**TABLE II**

<table>
<thead>
<tr>
<th>Percent trisodium phosphate (hydrated basis)</th>
<th>Sludge in grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative example</td>
<td>0.9</td>
</tr>
<tr>
<td>Example 1</td>
<td>1.9</td>
</tr>
<tr>
<td>Diluted Example 1</td>
<td>0.9</td>
</tr>
</tbody>
</table>

It will be noted that not only did the product of Example 1 give less sludge than the prior art quench oil, but that even the diluted sample was considerably superior to the prior art material. This indicates the deleterious effect of the presence of higher concentrations of metal sulfonate in a quench oil and further points up the advantage of employing a hydrocarbon succinic anhydride so that additional alkali metal phosphate can be incorporated without the need of additional metal sulfonate.

**EXAMPLE 3 Effect of presence of water**

The behavior of the oil of Example 1 and that of the oil of the comparative example in the presence of water were compared in the following manner. Ten parts of each oil was shaken with 90 parts of water for five minutes at room temperature. The oil of the comparative example formed an emulsion which did not separate for several hours. The oil of Example 1 did not form an emulsion, and water separation took place within a few seconds.

The ease with which each of the oils could be washed away from the surface of steel was also studied. Separate steel plates, each 1 foot square, were coated with the oil of Example 1, with the oil of the comparative example, and with the base oil that was used in preparing the two compounded oils. Each of the coated steel plates was placed beneath a cone spray nozzle through which water was directed for one minute against the plate with a pressure of 15 pounds per square inch. The data that were obtained are given in the following Table III.

**TABLE III**

<table>
<thead>
<tr>
<th>Percent Water Wash-off</th>
<th>Comparative product</th>
<th>Example 1 product</th>
<th>Base oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80</td>
<td>77</td>
<td>59</td>
</tr>
</tbody>
</table>

It will be noted that the two oils were comparable in their ability to be removed by water spraying and that each was better than the base oil in this respect.

**EXAMPLE 4 Quenching test**

The quenching power of the oils was evaluated using the General Motors Magnetic Quencherometer. This test takes advantage of the fact that some metals lose their magnetism when heated above a critical temperature (Curie point) and regain it when cooled. The metal specimen is heated to incandescent temperature and then quenched within a magnetic field. A special timing device measures the time required for the specimen to cool from the furnace temperature to the Curie point. The laboratory experiments were carried out using % inch diameter nickel balls having a Curie temperature of 670°F. The surface of the nickel was protected from the oxidizing atmosphere with a surface layer of diffused chromium. The balls were supported and insulated in the furnace inside porcelain crucibles. Each test was carried out in duplicate. The arithmetic average was taken as the quenching time.
In conducting these quench tests, each of the oils was used in the state in which it was obtained as described in the examples (Example 1 and the comparative example) and each oil was also evaluated after it had dried by nitrogen blowing for three hours at 350° F. The effect of adding small percentages of water to the dry oils was also studied. The results obtained are given in Table IV which follows:

<table>
<thead>
<tr>
<th>TABLE IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marquench Speed (sec.)</td>
</tr>
<tr>
<td>Comparative product</td>
</tr>
<tr>
<td>As manufactured</td>
</tr>
<tr>
<td>Dry (nitrogen blown for 8 hr. at 350°F)</td>
</tr>
<tr>
<td>Dry plus 0.1 wt. percent water</td>
</tr>
<tr>
<td>Dry plus 0.5 wt. percent water</td>
</tr>
</tbody>
</table>

1 Water content, about 0.06 to 0.1 wt. percent.

It is to be noted from the data of Table IV that a product of present invention (Example 1 product) gave faster quenching speeds than the prior art composition (comparative example product). While traces of water do increase quenching speed to some extent, as a practical matter such traces would disappear from the quench oil during use at 350° F. or so. Suitable means could be devised to replace on a continuous basis the traces of water thus lost, if it were desired to take advantage of this property of the quench oil.

EXAMPLE 5

Quenching of gears

The quench oil of Example 1 is used to quench alloy steel gears designed for the automatic transmission of an automobile. The gears are essentially cylinders about 134 inches in length with a bore of about 1 inch diameter, helical gear teeth being cut on the outside of the cylinders. The gears are heated to 1550° F. in a carburizing furnace having an endothermic atmosphere provided by a mixture of gases including hydrogen, methane and carbon monoxide. The gears are quenched by immersing them in a bath of quench oil positioned at the discharge end of the furnace. The quench oil of Example 1 is used, and its temperature is maintained at 350° F. The quenching operation gives the gears a Rockwell hardness of at least 60. The protective atmosphere used in the furnace is also maintained over the quench bath. This minimizes the degradation of the quench oil so that it can be used over a period of years before it must be replaced in toto and will require only the periodic addition of make-up oil to replace the quantities lost by take-up on the quenched parts or by volatility of the oil.

EXAMPLE 6

Dispersion of disodium phosphate

Using the procedure of Example 1, a quench oil is prepared from 1.5 parts by weight of a sodium petroleum sulfonate concentrate, 2.3 parts by weight of polyisobutylene succinic anhydride, and 2 parts by weight of hydrated disodium phosphate, Na₂HPO₄·12H₂O. The sodium petroleum sulfonate concentrate consists of 60 wt. percent of sodium petroleum sulfonate of about 475 molecular weight and 40 wt. percent of solvent extracted mineral lubricating oil. The polyisobutylene succinic anhydride is derived from 700 molecular weight polyisobutylene.

EXAMPLE 7

In Example 1 the polyisobutylene succinic anhydride had a saponification number of 80 (mg. KOH/gm.). It was found that by using a polyisobutylene succinic anhydride having a saponification number in excess of 100 the trisodium phosphate could be dispersed in oil without the aid of the sodium petroleum sulfonate. The polyisobutylene succinic anhydride of higher saponification number (112) was prepared by chlorinating polyisobutylene of about 950 molecular weight to a 4.5 wt. percent chlorine content and then condensing the chlorinated polyisobutylene with maleic anhydride. The polyisobutylene succinic anhydride was mixed with an equal volume of base oil, this base oil being the same as described in Example 1. To a mixture of 50 parts by weight of the oil and 50 parts by weight of the polyisobutylene succinic anhydride of 112 saponification number there was added 18 parts of hydrated trisodium phosphate dissolved in just sufficient water to make a clear solution. The procedure of Example 1 was then followed, giving a concentrate containing the dispersed trisodium phosphate. To prepare a quench oil, sufficient base oil was added to make a composition that contained 5 wt. percent of the polyisobutylene succinic anhydride and 1.8 wt. percent of trisodium phosphate (on a hydrated basis), the balance being the base oil. This quench oil gave a Marquench speed of 22 seconds in the quenching test described in Example 4. When the quench oil was modified by adding thereto 0.1 wt. percent of water, the quench speed was 16 seconds. In the 400° F. oxidation test described in Example 2, 15 grams of the quench oil produced only 0.2 gram of sludge after 7 days.

EXAMPLE 8

Example 7 was repeated, substituting 18 grams of sodium tetraborate (Na₂B₄O₅·5H₂O) for the trisodium phosphate. The quench oil obtained by diluting the quench oil concentrate to a composition that contained 5 wt. percent of the polyisobutylene succinic anhydride and 1.8 wt. percent of sodium tetraborate (on the hydrated basis) had a quenchemeter rating of 20 seconds as determined by the method of Example 4.

EXAMPLE 9

Following the general procedure of Example 7, 7 parts of hydrated trisodium phosphate was dispersed in a mixture of 50 parts of the base oil of Example 1 and 50 parts by weight of polyisobutylene propionic acid. The polyisobutylene propionic acid was prepared by chlorinating polyisobutylene of 780 molecular weight to 4.3 wt. percent chlorine content, reacting about 11 parts by weight of the chlorinated product with 1 part by weight of acetylenic acid at 425° F. for about 6 hours at 20 p.s.i.g., followed by nitrogen purging to remove unreacted acetylenic acid. The reaction product had a total neutralization number of about 46.2 mg. KOH per gram (ASTM D-664).

In preparing the trisodium phosphate concentrate using the polyisobutylene propionic acid, it may be found that somewhat more care was required during the heating step than in Example 7; nevertheless a satisfactory product was obtained. To prepare a quench oil, the concentrate was diluted with additional base oil as in Example 7.

It is to be noted that, as previously mentioned, while the alkali metal inorganic salt could be dispersed directly in the carboxylic acid or anhydride, such as the polyisobutylene propionic acid or the polyisobutylene succinic anhydride, it is more practical to dilute the acid or anhydride somewhat with hydrocarbon oil, as described, to reduce the viscosity, as this makes for greater ease in handling and also facilitates water removal during the dehydration of the concentrated salt solution. It is also to be noted that while the examples describe preparation of concentrates which are later diluted, it is also possible to make the finished quench oil directly with the aid of the carboxylic acid or anhydride dispersant. Mixtures of such dispersants can be used as well as individual acids or anhydrides.

The acid or acid anhydride serves not only as a dispersant for the inorganic salt dispersed, but it also serves to disperse any sludge that may be formed in spite of the antioxidant properties of the inorganic salt, thus extending the useful life of the quench oil.
Furthermore the quenching properties of the quench oil are enhanced by the presence of the high molecular weight acid or anhydride, as shown by the data presented. The dispersant properties of the high molecular weight acids or anhydrides used in this invention are to be distinguished from those of condensation products of such acids and amines (see for example U.S. Patent 3,272,746). The latter condensation products are not desirable in the present invention because they do not disperse the alkali metal inorganic salts as efficiently as the acids or anhydrides and they tend to give a less stable oil at quenching temperatures, which may be because of thermal decomposition of the amino groups.

Although this invention has been described in its preferred forms with a certain degree of particularity, it is to be understood that numerous modifications and adaptations can be resorted to without departing from the spirit of the invention or from its scope as defined in the appended claims.

What is claimed is:

1. A hydrocarbon oil composition suitable for the quenching of metals which comprises a major proportion of a hydrocarbon lubricating oil having a viscosity of from about 50 to about 2000 SUS at 100°F, from about 0.1 to 10 wt. percent of an alkali metal phosphate, alkali metal borate or alkali metal silicate, or mixtures thereof, and from about 0.1 to 10 wt. percent of a monocarboxylic acid, dicarboxylic acid or carboxylic acid anhydride, or mixtures thereof, wherein said acid or acid anhydride is characterized by having a long chain alkyl or akenyl hydrocarbon group of from 25 to 250 carbon atoms, said alkali metal salt being dispersed in said composition by said carboxylic acid or anhydride, said weight percent being based on the total composition.

2. A hydrocarbon oil composition as defined by claim 1 which additionally contains from 0.1 to 10 wt. percent of a metal salt of a hydrocarbon sulfonic acid of from about 300 to 1200 molecular weight.

3. A hydrocarbon oil composition as defined by claim 1 wherein said alkali metal phosphate is trisodium phosphate.

4. A hydrocarbon oil composition as defined by claim 1 wherein said alkali metal phosphate is disodium phosphate.

5. A hydrocarbon oil composition as defined by claim 1 wherein said alkali metal borate is sodium tetraborate.

6. A hydrocarbon oil composition as defined by claim 1 wherein said carboxylic acid anhydride is a hydrocarbon succinimide derived from polyisobutylene of molecular weight in the range of about 500 to about 2100.

7. A hydrocarbon oil composition as defined by claim 1 wherein said monocarboxylic acid is polyisobutylened proprionic acid prepared from polyisobutylene of about 800 to 1900 molecular weight.

8. A hydrocarbon oil composition as defined by claim 2 wherein said metal sulfonate is an alkali metal salt of petroleum sulfonic acid of about 400 to 800 molecular weight.

9. In a method of quenching that is useful in the treatment of metals wherein a metal to be treated is heated to an elevated temperature and wherein said heated metal is then rapidly quenched in a quenching medium to effect desired metallurgical changes in said metal, the improvement which comprises using as said quenching medium a liquid composition as defined by claim 1.

10. An improved method of quenching as defined by claim 9 wherein said metal is steel and said desired metallurgical change comprises formation of martensite in said steel.

11. A quench oil concentrate comprising a major proportion of a hydrocarbon oil, from about 1 to 20 wt. percent of a metal salt of a hydrocarbon sulfonic acid of from about 300 to 1200 molecular weight, from about 3 to 10 wt. percent of an alkali metal salt selected from the group consisting of alkali metal phosphates, alkali metal borates and alkali metal silicates and mixtures thereof, and from about 5 to 20 wt. percent of a carboxylic acid selected from the group consisting of monocarboxylic acids, dicarboxylic acids and carboxylic acid anhydrides and mixtures thereof, said carboxylic acid being characterized by having a long chain alkyl or akenyl hydrocarbon group of from 25 to 250 carbon atoms, said alkali metal salt being dispersed in said concentrate by said carboxylic acid.

12. A process for preparing a quench oil concentrate as defined by claim 11 which comprises the steps of mixing together the said hydrocarbon oil, carboxylic acid, metal sulfonate, alkali metal salt and a small quantity of water, sufficient to dissolve said salt, gently heating the said mixture with stirring to form a cream or emulsion, and thereafter dehydrating the said cream by means of heat until a clear syrup results.

13. A quench oil concentrate comprising from 10 to 40 weight percent of an alkali metal salt selected from the group consisting of alkali metal phosphates, alkali metal borates and alkali metal silicates and mixtures thereof dispersed in 60 to 90 weight percent of a vehicle, said vehicle comprising from 40 to 90 weight percent of a hydrocarbon oil and from 10 to 60 weight percent of a monocarboxylic acid, dicarboxylic acid or carboxylic acid anhydride, characterized by having a long chain alkyl or akenyl hydrocarbon group of from 25 to 250 carbon atoms, said alkali metal salt being dispersed in said concentrate by said acid or anhydride.

14. A process for preparing a quench oil concentrate as defined by claim 13 which comprises the steps of mixing said vehicle with said alkali metal salt and with a small quantity of water sufficient to dissolve said salt, gently heating the said mixture with stirring to form a cream or emulsion, and thereafter dehydrating the said cream by means of heat until a clear syrup results.

15. A hydrocarbon oil composition as defined by claim 1 wherein said long chain hydrocarbon group is derived from a polymer of a C₂₅ to C₅₅ monoolein.

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