Oct. 18, 1966 L. E. ST. PIERRE ETAL 3,280,027

LUBRICANTS AND LUBRICATED STRUCTURES

Filed Dec. 29, 1965

Fig. 1.

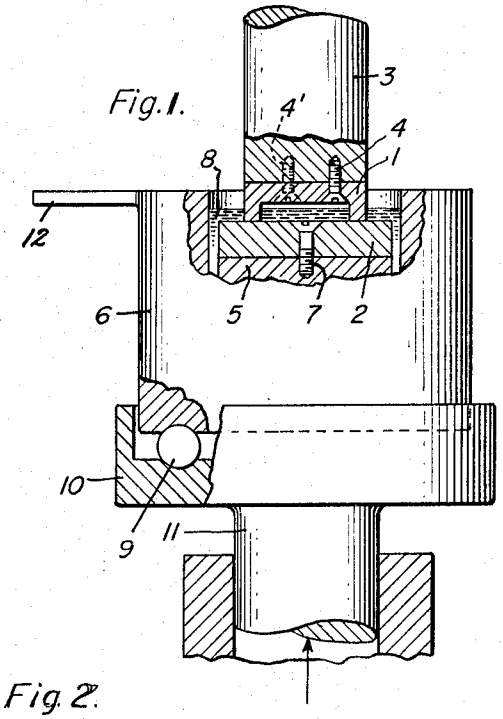


Fig. 2.

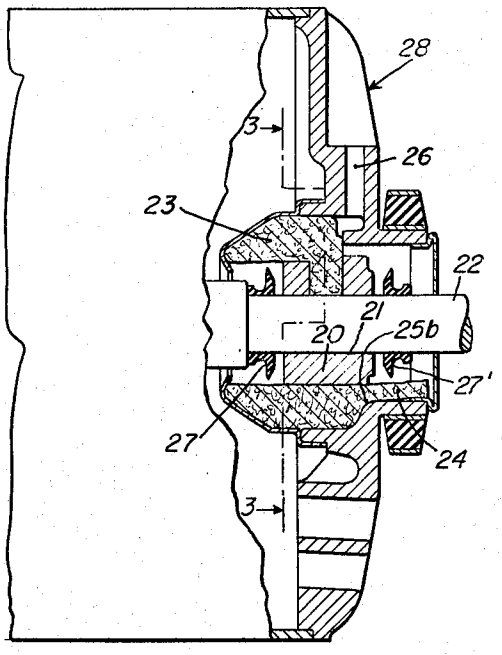
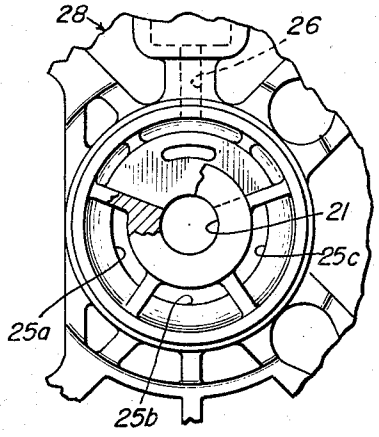


Fig. 3.



Inventors:
Leon E. St. Pierre;
Robert S. Owens
by James W. Underwood
Their Agent.

United States Patent Office 3,280,027
Patented Oct. 18, 1966

3,280,027

LUBRICANTS AND LUBRICATED STRUCTURES

Leon E. St. Pierre, St. Lambert, Quebec, Canada, and Robert S. Owens, Latham, N.Y., assignors to General Electric Company, a corporation of New York

Filed Dec. 29, 1965, Ser. No. 522,014
30 Claims. (Cl. 252—45)

This application is a continuation-in-part of our copending application Serial No. 180,884, filed March 19, 1962, as a continuation-in-part of our application Serial No. 101,917, filed April 10, 1961, now abandoned, both of which are assigned to the assignee of the present application.

The present invention relates to improved lubricants and uses of these materials as lubricants for various contacting metallic surfaces, particularly aluminum surfaces. More particularly, the invention relates to a new class of lubricants which are monoolefinic compounds containing a polar group and a long chain saturated aliphatic group. These lubricants have been found to be especially useful in those cases where new metal surfaces are being created or where high wear is a problem particularly in cases of boundary lubrication. These lubricants may be used either alone, or as emulsions, suspensions, for example, in aqueous media. They likewise may be used as additives in combination with other well known lubricating materials having the desired lubricating viscosity such as mineral oils, silicone oils, diester lubricants, etc., in the form of solutions, emulsions, suspensions, etc.

Attempts have been made in the past to effect lubrication of aluminum surfaces. Thus, it has been desired to effect lubrication of relatively moving surfaces in which one of the surfaces is a metal composition containing at least 50% by weight aluminum, for instance, pure aluminum, alloys of aluminum, etc. The lubrication of such aluminum surfaces is especially difficult in cases where extreme pressure conditions exist requiring lubrication under boundary conditions, i.e., actual solid-to-solid contact, for instance, as may be found in a bearing before a hydrodynamic film of lubricant is created or where new solid surfaces are being generated, for example, in shaping by drawing through a die, in cutting, for example, in a lathe or punch-press, in shaping, for example, by stamping, drawing, extrusion, spinning, cold-rolling, in polishing, for example by lapping, burnishing, etc. For convenience, this type of lubrication is hereinafter referred to as boundary lubrication. Under such conditions, it has been found that aluminum compositions are lubricated with great difficulty due to the fact that under extreme pressure conditions of boundary lubrication, the aluminum surface tends to score, gall or seize, even when great care is exercised. To the best of our knowledge, no previous lubricant has been known which completely satisfies the requirements of boundary lubrication of aluminum metal compositions containing at least 50% by weight aluminum.

Unexpectedly, we have found that monoolefinic compounds in the unpolymerized, that is, the monomeric state, having a polar group or no more than 4 carbon atoms removed from the olefinic groups, can be used as lubricants between two solid surfaces which move relative to each other, even under high pressure conditions, or may be used as additives to other well known lubricants to

impart improved boundary lubricating characteristics to such lubricants, as, for instance, those mentioned above, examples of which are mineral oils of lubricating viscosity, lubricating greases, silicone lubricating oils, diester lubricating oils, polyester lubricants, silicate ester lubricants, etc. When these monoolefinic compounds are employed in lubricating the aluminum surface or surfaces, it is found that the coefficient of friction is greatly reduced, and the tendency to gall or seize, particularly under boundary lubrication conditions, is materially reduced and in many instances is completely eliminated. Furthermore, it is found that in addition to the improved lubricating characteristics of these monoolefinic compounds, the act of one surface moving across another surface in the presence of these monoolefinic compounds imparts a high polish to the aluminum surface in many applications, thereby still further increasing the ease with which our lubricating compositions can contribute to the lubricating act.

In addition to our lubricating compositions being especially adaptable for lubricating relatively moving surfaces at least one surface of which is an aluminum surface, we have also found unexpectedly that these lubricating compositions are also useful in effecting improved lubrication of other solid surfaces moving relative to each other, especially when one of these surfaces is a metal used for fabricating structural shapes, for example, iron, molybdenum, silver, copper, beryllium, tungsten, magnesium, titanium, zirconium, chromium, nickel, cobalt, aluminum, tin, etc., and various metal compositions, for example, alloys of the aforesaid metals, of which typical examples are steels, brasses, the various alloys of magnesium, cobalt, zinc, zirconium, beryllium, iron (e.g., stainless steel), etc. The other surface may be the same or different metal, or it may be another solid material for example, wood, molded synthetic resins, laminates, etc., or a special compounded composition, such as, porous metal, graphite, graphite-impregnated metal, soft bearing alloys, e.g., babbitts, etc., or very hard compositions, for example, metal carbides, nitrides, etc.

The fact that our monoolefinic compounds may be used as lubricants for these various classes of materials and are particularly useful as lubricants under a wide variety of conditions for two solid surfaces moving relative to each other where at least one of the surfaces is either aluminum or an alloy of aluminum, was entirely unexpected and in no way could have ben predicted, because the prior art has been of the impression that the usual lubricants and the usual lubricating materials and techniques were not effective lubricants under many conditions for relatively moving surfaces in which one of the surfaces was aluminum or one of its many alloys. This was due to the fact that aluminum and many of its alloys are relatively soft and when the usual lubricants, even extreme pressure lubricants containing additives to increase the load bearing characteristics of the lubricant, are used for lubricating such materials, undesirable wear, galling, and ultimate seizure of the relatively moving parts occurs. This is particularly borne out by a recent article by R. D. Guminski and J. Willis entitled "Development of Cold-Rolling Lubricants for Aluminum Alloys," in Journal of the Institute of Metals, 88, pages 481–492 (1960), where the authors point out the undesirability

of having unsaturated additives as lubricants in the cold-rolling of aluminum alloys.

Our invention may be better understood from the following description taken in conjunction with the appended drawings, in which:

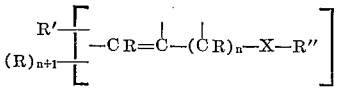
FIG. 1 shows, partly in section, the portion of a standard four-ball wear tester which has been modified to evaluate lubricating compositions using metals in various shapes other than balls;

FIG. 2 shows the bell housing, partly in section, of one end of an electric motor cut away to show an aluminum sleeve bearing integrally cast as part of the bell housing; and

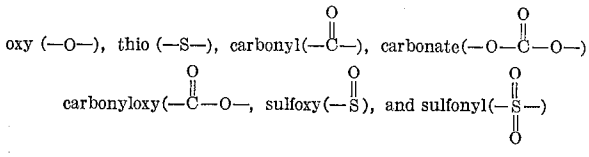
FIG. 3 showns an end view of a portion of the bell housing of FIG. 2 along line **3–3**.

These new lubricants are monomeric compounds (hereinafter so designated) having the general formula

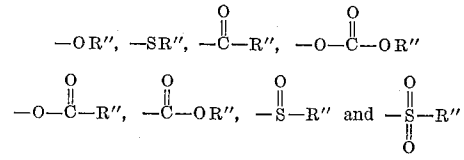
(I)



where n is one of the integers 0, 1, R is a monovalent radical selected from the group consisting of hydrogen and fluorine, R′ is a monovalent radical selected from the group consisting of hydrogen, fluorine, methyl, monofluoromethyl, difluoromethyl, and trifluoromethyl, X is a divalent radical selected from the group consisting of

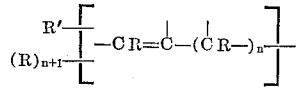


and R″ is a monovalent radical selected from the group consisting of linear alkyl radicals with from 11 to 60 carbon atoms, and linear fluoroalkyl radicals with from 11 to 60 carbon atoms. X and R″ together represent the monovalent group —XR″ which encompasses the radicals



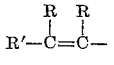
where R″ is as previously defined.

In the foregoing general formula, the radical represented by

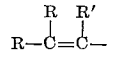


is the representative of the following more specific formulae when n is 0, it represents the two radicals

(a)

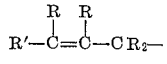


(b)

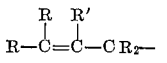


and when n is 1, it is representative of the following three formulae:

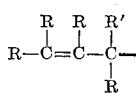
(c)



(d)



(e)



It will be recognized that when R′ is either hydrogen or fluorine, Formulae *a* and *b* represent the same radicals, and Formulae *c*, *d* and *e* also represent the same radicals. However, when R′ is methyl, or one of the three fluoromethyl radicals, all four formulae represent different radicals.

Typical of the radicals represented by Formulae *a* and *b* are, for example vinyl, propenyl, 1-methylvinyl and the fluorine-substituted derivatives of these three hydrocarbon radicals, for exaxmple,

1-fluorovinyl,
2-fluorovinyl,
1,2-difluorovinyl,
2,2-difluorovinyl,
1,2,2-trifluorovinyl,
1-fluoropropenyl,
2-fluoropropenyl,
3-fluoropropenyl,
3,3-difluoropropenyl,
3,3,3-trifluoropropenyl,
1-(fluoromethyl)vinyl,
1-methyl-2-fluorovinyl,
1-(difluoromethyl)vinyl,
1-(trifluoromethyl)vinyl,
1-(trifluoromethyl-2,2-difluorovinyl), etc.

Typical of the radicals covered by Formulae *c*, *d* and *e* are, for example allyl, crotonyl, (2-butenyl), isocrotonyl, (2-isobutenyl), 1-methylallyl, 2-methylallyl and the fluorine-substituted derivatives of these five hydrocarbon radicals, for example,

1-fluoroallyl,
2-fluoroallyl,
2,3-difluoroallyl,
1-fluorocrotonyl,
2-fluoroisocrotonyl,
3,4-difluorocrotonyl,
4,4-difluorocrotonyl,
1-methyl-3-fluoroallyl,
2-methyl-3-fluoroallyl,
2-(fluoromethyl)allyl,
2-(fluoromethyl)-3-fluoroallyl,
1-(trifluoromethyl)alkyl,
2-(trifluoromethyl)-3,3-difluoroallyl, etc.

Typical examples of radicals represented R″ are the linear alkyl radicals, e.g., undecyl, dodecyl, tridecyl, tetradecyl, hexadecyl, octadecyl, nonadecyl, eicosyl, dicosyl, tricosyl, heptacosyl, triacontyl, dotriacontyl, tetracontyl, pentacontyl, hexacontyl, and the fluorosubstituted derivatives of these hydrocarbons, in which one or more, up to all, of the hydrogen atoms have been substituted by a fluorine atom. Typical of the linear fluoroalkyl radicals are, by way of example, the mono-, di-, tri-, tetra-, penta-, hexa-, up to pentacosylfluorododecyl, the mono-, di-, tri-, tetra-, penta-, etc., up to hentetracontylfluoroeicosyl, etc., radicals.

The compounds are monoolefinic alkyl ethers when X is oxygen; monoolefinic alkyl sulfides sometimes also known as thioethers, when X is sulfur; monoolefinic alkyl ketones when X is carbonyl; monoolefinic alkyl carbonates when X is carbonate; monoolefinic alkyl sulfoxides when X is sulfoxy; monoolefinic alkyl sulfones when X is sulfonyl; and may be either the monoolefinic alcohol ester of an alkyl carboxylic acid, or an alkyl alcohol ester of a monoolefinic unsaturated carboxylic acid when X is carbonyloxy.

Typical examples of the various compounds falling within this general formula are as follows:

Vinyl undecyl ether, vinyl undecyl sulfide, vinyl undecyl ketone, vinyl undecyl carbonate, vinyl undecyl sulfoxide, vinyl undecyl sulfone, undecyl acrylate, vinyl laurate, vinyl tetradecyl ether, vinyl hexadecyl ether, vinyl octadecyl ether, vinyl eicosyl ether, vinyl tricosyl ether, vinyl hexacosyl ether, vinyl octacosyl ether, vinyl tri-

acontyl ether, vinyl dotriacontyl ether, vinyl tetracontyl ether, vinyl pentacontyl ether, vinyl hexacontyl ether, 1-methylvinyl dodecyl ether, allyl dodecyl ether, 2-methylallyl dodecyl ether, isocrotenyl dodecyl ether, crotenyl dodecyl ether, allyl dodecyl sulfide, 2-methylallyl tetradecyl ketone, crotonyl hexadecyl carbonate, isocrotonyl octadecyl sulfoxide, 2 - methylallyl eicosyl sulfone, hexadecyl acrylate, dodecyl methacrylate, octadecyl vinylacetate, eicosyl crotonate, tetradecyl isocrotonate, dodecyl angelate, tricontyl tiglate, vinyl searate, vinyl palmitate, allyl stearate, methylallyl palmitate, crotonyl behanate, isocrotonyl cerotate, vinyl myristate, dodecyl vinylacetate, 1-methylvinyl octadecyl sulfide, 1-methylallyl docosyl ketone, allyl hexadecyl sulfone, 2-methylallyl octadecyl sulfoxide, crotonyl nonadecyl carbonate, etc., including the fluorine substituted derivative of these compounds wherein one or more hydrogen atoms are substituted for the fluorine atom, for example, fluorovinyl dodecyl ether, 2-fluoroallyl octadecyl sulfide, fluorocrotonyl tricosyl carbonate, 2-fluoromethylallyl eicosyl ketone, fluorovinyl tetrafluorotricosyl sulfone, 2-fluoroallyl hexafluorotriacontyl sulfoxide, hexadecyl trifluoroacrylate, tetradecyl fluoromethacrylate, 2-fluoroallyl myristate, etc.

Because of the ready availability of raw materials and ease of synthesis, and the suitability and outstanding properties as lubricants and as additives to other well known lubricants, we prefer to use the vinyl, allyl and crotonyl esters of the saturated fatty acids (linear allyl carboxylic acids) having from 11 to 24 carbon atoms in the alkyl groups of the carboxylic acid, or crotonic acid esters of linear alkyl alcohols having from 11 to 24 carbon atoms.

All of the above materials may be used alone, mixed with each other, or mixed with other well known lubricants, for example, mineral oils of lubricating viscosity, greases made from such lubricating oils, silicone lubricating oils, diester lubricating oils, etc.

When one solid surface moves relative to another surface with a lubricant between the two surfaces, there may be a complete film of lubricant separating the two surfaces or there may be varying degrees of solid to solid contact. The former condition exists under ideal hydrodynamic lubrication while the latter condition is characteristic of boundary lubrication. Complete hydrodynamic lubrication may be obtained under certain ideal conditions found in bearings but is influenced by such factors as design of the two solid surfaces, load on the surfaces, and the relative speed of the one part to the other. However, even under these conditions, boundary lubricating problems are encountered during stopping and starting operations and, from a practical standpoint perfect hydrodynamic lubrication is approached rather than attained. Therefore, the ability to improve boundary lubrication is to be greatly desired.

Our compositions improve the lubrication of two solid surfaces moving relative to each other especially when one of these surfaces is a metal used for fabricating structural shapes, e.g., iron, molybdenum, silver, copper, beryllium, tungsten, magnesium, titanium, zirconium, chromium, nickel, cobalt, aluminum, tin, etc., and various metal compositions, for example alloys, of which typical examples are steels, brasses, the various alloys of magnesium, cobalt, zinc, zirconium, beryllium, aluminum, iron (e.g., stainless steels), etc. The other surface may be the same or a different metal or it may be another solid material, e.g., wood, molded synthetic resins, laminates, etc., or a special compounded composition such as porous metal, graphite, graphite impregnated metal, soft bearing alloys, e.g., babbitts, etc., or very hard compositions, e.g., metal carbides, nitrides, etc.

Normally, in the design of equipment where one solid surface moves relative to another, both solid surfaces are the same material if the wear is to be equal on both parts or one is made of a material softer than the other when the wear is to be essentially all on the softer part. This is usually done when one part is easier to replace than the other or the one part is being cut or shaped by the other.

A concentration of as little as 0.1% by weight of our compositions in another lubricant improves the boundary lubricating properties of these materials, but we have found that for a solid surface of aluminum or a metal composition containing at least 50% aluminum, such as an alloy of aluminum (hereinafter all these aluminum materials being referred to as "aluminum composition"), moving relative to another solid surface of an aluminum composition, or another metal, the coefficient of friction suddenly decreases by a considerable amount when the amount of our monomeric compound is at least 10% by weight of the total lubricant. This discovery permits the use of a wide variety of aluminum compositions for the first time in the fabrication of bearings and like surfaces, since, as far as we are aware, prior to our invention, no way was known to prevent galling and seizing of bearings made of many of these materials. Although specific alloys of aluminum were made for bearings, the use of such compositions required concessions to be made as to bearing clearances, life, etc., in order to provide adequate performance.

For other lubricating applications, especially where metals harder than soft aluminum are used, concentrations of less than 10% by weight of our monomeric, olefinic compounds have been found to be useful. For example, in the lubrication of a steel journal in a die cast aluminum bearing or a stainless steel journal in a babbitt bearings, mineral lubricating oils containing concentrations of 2–7% by weight of the monomeric, olefinic compounds have been found to be very effective lubricants, whereas the same mineral lubricants without our additives were not a satisfacory lubricant for these applications.

Likewise, our monomeric compounds, or mixtures thereof, permit aluminum compositions to be shaped, for example, by drawing, spinning, extrusion, and the like, with a very smooth finish. When our materials are used as the lubricant without dilution for extrusion or drawing, the aluminum composition is formed with a very smooth, mirror-like finish which is impossible to obtain by the use of any previously known lubricant. Typical examples of the various aluminum compositions that may be lubricated by our monomeric compounds are those disclosed on pages 851–853 and 865–958 of Metals Handbook, volume 1, Properties and Selection of Metals, American Society for Metals, Novelty, Ohio, eighth edition, 1961, for example, the high purity aluminum alloys which are greater than 99% aluminum, e.g., EC alloy, 1060 alloy, 1100 alloy, etc., and alloys of aluminum with other metals, for example, copper, silicon, magnesium, tin, zinc, etc., as are more fully described on pages 955–958 of the above reference.

Typical of the mineral or hydrocarbon oils of lubricating viscosity are the hydrocarbon lubricants obtained from petroleum. These products normally have viscosities in the range of 25 to 10,000 Saybold Universal Seconds (S.U.S.), and may be a single mixture of hydrocarbons.

Typical of the silicone lubricating oils are those disclosed in, for example, U.S. 2,410,346—Hyde; 2,456,496—Ford et al.; 2,469,888—Patnode; 2,469,890—Patnode; 2,970,162—Brown; etc.

Typical of the diester and polyester lubricants are those disclosed in U.S. 2,450,221—Ashburn et al.; 2,450,222—Ashburn et al.; U.S. 2,977,301—Bergen et al.; and on pages 16–24 of Technical Publication No. 77, published by American Society for Testing Materials, Philadelphia, entitled "Symposium on Synthetic Lubricants." Other lubricating materials, as well as suitable mixtures of these; lubricating materials, may be used in the practice of our invention without departing from the scope of the invention.

The compositions of our invention covered by the above general formula vary from liquid to solid materials. The solids when dissolved in lubricating oils are capable of

producing fluids and greases having lubricating properties depending on the composition and concentration. In low concentrations the effect is to lower the viscosity of some of the oils.

To aid in obtaining the grease-like consistency desired for lubricating grease, non-abrasive fillers such as silica gel, carbon black, diatomaceous earth, molybdenum sulfide, tin sulfide, graphite, etc., may be added or soaps or other materials may be incorporated to produce a gel structure. Particularly useful soaps are the metallic soaps such as the alkaline or alkaline earth soaps of the fatty acids, but other soaps may also be used, for example, zinc, tin, lead, copper, etc., soaps of the fatty acids. A particularly desirable grease composition may be made from lithium stearate and lithium hydroxy stearate. These grease compositions may be made by any of the well known methods, for example, as disclosed in U.S. Patent 2,450,221—Ashburn et al.; 2,450,222—Ashburn et al.; and 2,260,625—Kistler.

We have also prepared satisfactory greases by merely mixing the monomeric compounds, a lubricating oil and a soap at room temperature. In addition, pour depressants, stabilizers, inhibitors, and the like, may be added to our compositions if desired.

The ability of our monomeric olefinic compounds to function as lubricants either alone or as additives to other lubricants is due to their being present in the monomeric or unpolymerized state. Our compounds in which the olefinic moiety is allyl or crotyl do not polymerize under the conditions encountered in use as lubricants. However, any compounds in which the olefinic moiety is vinyl (including acrylates and methacrylates) are susceptible to polymerization if exposed to elevated temperatures for extended periods of time. For those lubricants containing compounds which can be polymerized, it is necessary that the latter remain essentially unpolymerized. This presents no problem for many applications since at the normal ambient temperatures encountered in their use as lubricants, there is little if any tendency for our compositions to polymerize. In general, bearings are designed so that the temperature of the bearing does not exceed 200° F. and preferably 160–180° F. If polymerization does occur, there is a marked increase in the viscosity of the lubricant. In carrying out the specific examples illustrating our invention, we never detected any viscosity increase of the lubricant.

For those lubricants in which polymerization might occur, especially where the lubricant may be subjected to elevated temperatures, it is desirable to have a material dissolved in the lubricant which will inhibit polymerization. A host of materials are well known in the art which will inhibit or retard polymerization. These are generally compounds which contain one or more of the following groups: nitro, nitroso, quinoid, phenolic hydroxyl, amino, etc. Sulfur and sulfur-containing compounds also can be used. Typical specific examples are: picric acid, trinitrobenzene, 2,5 - dihydroxy-1,4-benzoquinone, 1,4-naphthoquinone, 1,4-benzoquinone, chloranil, 9,10-phenanthroquinone, tert-butylcatechol, 4-amino-1-naphthol, hydroquinone, phenyl-β-naphthylamine, triphenyl phosphite, nitrodimethylaniline, hydroxydimethylaniline, nitrosodimethylaniline, sulfur, paraformaldehyde, phenylacetylene, the condensation products of aliphatic aldehydes with aromatic amines, etc.

The choice and amount used is dependent on the particular desires of the user and the properties desired in the lubricant. In general, it should be one that is soluble in the lubricant, is compatible with other ingredients and will not deleteriously affect the lubricant or the lubricated parts. Generally, a small but effective amount, sufficient to stabilize the composition against polymerization during use, should be used. Such an amount is known as a stabilizing amount.

The ability of inhibitors and retarders to prevent polymerization varies between the particular compounds. In general, those compounds known as inhibitors are more effective in preventing polymerization than retarders, but the latter are effective if used in amounts larger than normally used with inhibitors. Some compounds, for example the quinones, act as both inhibitors and retarders. These properties of inhibitors and retarders are well known and are discussed in detail in many books on polymerization. When either an inhibitor or retarder are used in amounts to essentially prevent polymerization, they are called stabilizers or polymerization stabilizers. Generally, amounts from 0.01 to 5% by weight of the polymerizable material are effective amounts to stabilize the compositions against polymerization.

In preparing a lubricant in which one or more of the monomeric, olefinic compounds is dissolved in an oil of lubricating viscosity, it may not be necessary to add a polymerization stabilizer even though the monomeric, olefinic compound is one that can be polymerized and the lubricant is to be used for extended periods of time at elevated temperatures. Such a case would arise if the oil of lubricating viscosity already had a material dissolved in it that had been added either as an oxidation inhibitor or other additive, but which also is a polymerization stabilizer. Such additives are generally used in concentrations from 0.1 to 1% by weight of the oil. Therefore, such an amount would be sufficient to stabilize the monomeric, olefinic compound against polymerization when it was dissolved in such an oil.

In order that those skilled in the art may better understand how our invention may be practiced, the following examples are given by way of illustartion, and not by way of limitation. In all of the examples, the olefinic compounds were unpolymerized, i.e., they were monomeric in form and retained the olefinic group, and the percentages are by weight.

Example 1.—A billet of commercially pure aluminum (1100 alloy) 1 inch in diameter by 3 inches long was heated to 200° F. and forward extruded through a 5/16 inch die heated to 260° F. using an extrusion force of 66,000 lbs./square inch. Vinyl stearate was melted onto the surface of the billet before being placed in the extruder to act as a lubricant. The aluminum extruded smoothly producing a rod with a smooth, highly polished mirror finish. When this example was repeated but using an oil composition made by dissolving 25% by weight vinyl stearate, 25% by weight α-hexadecylene and 50% by weight of a mineral lubricating oil having a viscosity of 600 S.U.S. (Saybolt Universal Seconds), the aluminum also extruded readily to produce an aluminum rod having a smooth matte finish.

When the example was repeated using a commercially available lubricant recommended for extrusion of aluminum, galling of the surface of the rod was encountered during the extrusion which caused the surface to be striated with relatively wide, deep scratches.

Example 2.—A round bar of commercially pure aluminum (1100 alloy) 1¾ inches in diameter was placed in an engine lathe equipped to measure the cutting force exerted on the tool tip, the radial force exerted on the cutting tool, and the feed force necessary to feed the cutting tool along the surface of the aluminum. The tool was set to feed at the rate of 10 mils per revolution, the depth of cut was 100 mils, and the speed of rotation of the test piece was such as to give a surface speed of 10 feet per minute. The aluminum had a Brinell hardness of 27.2. Three test cuts were made, one using no lubricant, the second using a commercially available aluminum cutting fluid, and the third using a 20% by weight solution of vinyl stearate in a mineral lubricating oil of nominal 300 S.U.S. The solution had a nominal viscosity of 150 S.U.S. Table I presents the results of the three forces using the three test conditions as well

as the surface finish of the cut surface as measured in microinches on a center-line average:

TABLE I

[Force (lbs.) to machine aluminum]

	No Lubricant	Commercial Cutting Fluid	20% Vinyl Stearate in 300 S.U.S. Oil
Cutting	450	230	115
Feed	125	55	15
Radial	110	65	17
Finish	78	59	45

These results show that the vinyl stearate-lubricating oil solution not only gives a lubricant which requires much less cutting force, but also produces a smoother finish.

Example 3.—Aluminum strip 0.075 inch thick by 3 inches wide was heated to 350–400° C. and rolled to give a reduction in thickness to 0.013 inch. When a water based, rolling lubricant is use, the aluminum welds to the hardened steel rolls in spots, resulting in poor rolling and requires frequent stops to clean the roll. However, when vinyl stearate was melted and painted onto the cold rolls as lubricant, the aluminum strip was satisfactorily sheeted to produce an aluminum strip with a smooth finish.

Example 4.—In order to determine the ability of our monomeric compounds to satisfactorily lubricate two surfaces, one moving relative to the other, the following tests were carried out, using a modified 4-ball wear test machine described, for example, in an article by R. G. Larson, entitled "Study of Lubrication Using Four-Ball Type Machine," Lubrication Engineering 1, page 35, August 1945. This machine was modified by replacing the four balls and their holder with a cup and washer as shown in FIG. 1. Rider **1**, made of one of the metals to be investigated, is cup-shaped and is rotated at preselected speeds against stationary test washer **2** made of the same or different metal to be tested, by means of motor driven shaft **3** to which rider **1** is attached by machine bolts **4** and **4'**. Washer **2** is rigidly fastened by means of machine bolt **7** to a base member **5** which is restrained from rotation with respect to chamber **6**. A reservoir of lubricant **8** under test is maintained around the test pieces. A heater (not shown) is provided in the base of chamber **6** to permit operation at various temperatures. Chamber **6** rides on a series of ball bearings, one of which is shown as **9**, which ride upon member **10**, which forms the uppermost portion of plunger **11**, which is connected to a hydraulic system (not shown) to permit various loadings to be established between the two test samples **1** and **2**. When rider **1** is rotated against test washer **2** by means of clock-wise rotation of shaft **3**, chamber **6** will rotate upon member **10** due to the frictional force existing between members **1** and **2**. The force required to prevent such rotation is measured by a strain gauge attached to arm **12**. This modification permits the coefficient of friction to be calculated and examination of riders **1** and **2** permits evaluation of the amount and type of wear produced. It is desirable to have the lower surface of rider **1** in parallel contact with the upper surface of washer **2**. This can be obtained either by machining the rider and washer to close tolerances, or more conveniently by inserting a resilient pad (not shown) between the base member **5** and the top surface of the heater in the base of chamber **6**. Since this pad must be resistant to oil and heat, it is conveniently made of silicone rubber. This pad not only permits the washer **2** and base member **5** to self adjust so that the top surface of washer **2** will be in parallel contact with the lower surface of rider **1** but also prevents base member **5** from rotating on the face of the heater without fastening.

Using this apparatus, the following measurements were made. The rider with a flat annular area of 0.393 square inch was rotated under a 10 kilogram load at 0.88 r.p.m. (surface speed of 0.0461 inch per second) against the test washer. These conditions represent operation in the bondary friction region, the most difficult condition of bearing operation from a lubrication standpoint. The composition of the test pieces, the lubricant, and the results obtained are given in Table II. All percentages are by weight, and the tests were run at room temperature unless otherwise noted.

TABLE II

Lubricant	Rider	Washer	Average Coefficient of Friction	Wear Surface
Phenyl vinyl ether	1100 aluminum	1100 aluminum	>0.5	Galled after few seconds of forced running.
N-allyl aniline	do	do	>0.5	Do.
Diallyl azelate	do	do	>0.5	Do.
Allyl stearate	do	do	0.12	Very little wear after 1 hr.
Hexadecyl crotonate	do	do	0.10	No visible wear after 1 hr.
Vinyl stearate	do	do	0.10	Very little wear after 1 hr.
20% vinyl stearate, 80% SAE–10 spindle oil (150 S.U.S. lubricating oil).	do	do	0.12	Do.
20% methyl stearate, 80% SAE–10 spindle oil.	do	do	0.22	Badly galled surface after 1 hr.
Vinyl stearate (tested at 110° F.)	Hardened steel, 60–62 Rockwell.	Aluminum alloy 43 (5% Si).	0.12	Highly polished 1–2 micro inch finish, wear track 20–30 micro inch deep after 3 hrs.
Do	1100 aluminum	1100 aluminum	0.1	Slight wear track after 3 hrs.
47% vinyl stearate, 53% SAE–10 spindle oil.	Hardened steel, 60–62 Rockwell.	Aluminum alloy 43	0.17	Highly polished 1–2 micro inch finish, wear track 20–30 micro inch deep after 3 hrs.
Do	Cold rolled steel, 10–12 Rockwell.	do	0.12	Polished wear track in 3 hrs.
Do	do	1100 aluminum	0.12	Do.
Do	1100 aluminum	do	0.12	Slight wear track in 3 hrs.
SAE–10 spindle oil	Cold rolled steel 60–62 Rockwell.	Aluminum alloy 43	0.29	Wear track grooved; galled areas during 3 hr. test.
Do	do	1100 aluminum	0.29	Do.
Do	do	Cold rolled steel 10–12 Rockwell.	0.18	Slight wear track in 1 hr.
20% vinyl stearate, 80% SAE–10 spindle oil.	do	do	0.12	Do.
SAE–10 spindle oil	do	Magnesium	0.24	Deep wear track in 1 hr.
20% vinyl stearate, 80% SAE–10 spindle oil.	do	do	0.20	Slight wear track in 1 hr.
SAE–10 spindle oil	Copper	Copper	0.40	Galled badly in 1 hr. run.
20% vinyl stearate, 80% SAE–10 spindle oil.	do	do	0.21	Slight wear track.
SAE–10 spindle oil	Titanium	Titanium	[1] 0.56–>0.68	Badly galled and grooved during 1 hr. run.
20% vinyl stearate, 80% SAE–10 spindle oil.	do	do	0.31	Slight wear track.

See footnotes at end of table.

TABLE II—Continued

Lubricant	Rider	Washer	Average Coefficient of Friction	Wear Surface
SAE-10 spindle oil	Phenolic laminate	Aluminum alloy 43	[2] 0.25	Polished track.
25% SAE-10 spindle oil, 75% vinyl stearate	do	do	0.1	Do.
Octyl acrylate	1100 aluminum	1100 aluminum	0.30	Galled in 30 minutes.
Decyl acrylate	do	do	0.20	Grooved wear track in 30 minutes.
Dodecyl acrylate	do	do	0.10	Polished wear track in 30 minutes; slight grooves in 60 minutes.
Octadecyl acrylate (run at 95° F.)	do	do	0.10	Slight wear in 30 minutes.
Phenyl ethyl acrylate	do	do	>0.68	Seized in 5 minutes, badly galled.
2-butoxy ethyl acrylate	do	do	>0.68	Seized in 2 minutes, badly galled.
Decyl methacrylate	do	do	>0.68	Badly galled during 30 minute test.
Dodecyl methacrylate	do	do	0.17	Slight groove after 30 minutes.
Allyl benzoate	do	do	>0.68	Seized in 2 minutes; badly galled.
Allyl pelargonate	do	do	[1] 0.32->0.68	Badly galled during 30 minute test.
Allyl palmitate	do	do	0.16	Slight wear after 30 minutes.
Silicone lubricating oil [3]	do	do	[1] 0.2->0.68	Galled during 1 hr. test.
20% vinyl stearate, 80% silicone lubricating oil.[3]	do	do	0.13	Polished track after 1 hr.
12.94% vinyl stearate, 51.76% mineral lubricating oil (300 S.U.S.), 35.30% lithium hydroxy stearate.	do	do	0.10	Very slight wear after 1 hr.
26% vinyl stearate, 39% mineral lubricating oil (300 S.U.S.), 35% lithium hydroxy stearate.	do	do	0.08	Slight wear after 1 hr.
10% vinyl stearate, 10% dodecyl acrylate, 80% mineral lubricating oil (150 S.U.S.).	do	do	0.13	Do.
13% vinyl stearate, 52% mineral lubricating oil (300 S.U.S.), 35% lithium stearate.	do	do	0.07	Polished track; no wear evident after 1 hr.
5% vinyl stearate, 95% SAE-10 oil	Machine steel	Die cast aluminum	0.14	Polished track; slight wear after 3 hrs. 20 kg. load.
26% vinyl stearate, 39% mineral lubricating oil (300 S.U.S.), 35% lithium stearate.	1100 aluminum	1100 aluminum	0.08	Polished track; no wear evident after 1 hr.

[1] Very erratic during entire run.
[2] Erratic.
[3] Commercially available methyl phenylpolysiloxane fluid containing 50 mole percent silicon-bonded phenyl groups and 50 mole percent silicon bonded methyl groups.

Example 5.—The apparatus described in Example 4 was used to measure the coefficient of friction of various percentage compositions of vinyl stearate in SAE–10 spindle oil. The rider and test washed were both made from aluminum. The results are shown in Table III.

TABLE III

	Average coefficient of friction
0 (erratic)	0.40
10	0.21
15	0.20
20	0.13
30	0.13
50	0.12

Example 6.—Standard production ⅓ H.P. motors having a normal speed of 1,725 r.p.m. were made with the only modification being as illustrated in FIGURES 2 and 3. Generally, the bearing 20 is made by machining shaft hole 21 to a size which permits a steel babbitted bearing to be pressed into place. This bearing is machined to fit shaft 22 with the necessary clearance. Cylindrical oil felt 23 has three fingers 24, one of which is shown in FIG. 2, which protrude from slots 25*a*, 25*b* and 25*c*. Oil is added to oil hole 26 and is fed through felt 23 to shaft 22. Any oil creeping along the shaft is thrown off by slinger rings 27 and 27′. A similar bearing is at the opposite end of the motor. One motor was made in the usual way with a babbitted bearing at each end of the motor. Four other motors were made; in each case, the bell housing 28 was cast in one piece with the diameter of hole 21 as cast being slightly smaller than the diameter of shaft 22 to permit machining and finishing of the bearing surface with nominal bearing clearance. The bell housing was cast from aluminum alloy 43 containing 95% aluminum, 5% silicon. The motor with the babbitted bearings and one motor with the machined aluminum bearing were lubricated with the mineral hydrocarbon oil having a nominal viscosity of 150 S.U.S. recommended by the manufacturer for lubrication of the standard motor. The other three motors were lubricated with the same type of hydrocarbon oil but containing 20% by weight vinyl stearate. Although vinyl stearate is a solid material at room temperature, it lowers the viscosity of a hydrocarbon oil when it is dissolved. In order to eliminate any effects of viscosity, the vinyl stearate was dissolved in a hydrocarbon oil having a nominal viscosity of 300 S.U.S., which gave the resulting solution a nominal viscosity of 150 S.U.S., the same viscosity as the oil without vinyl stearate used to lubricate the other two motors. A weight was suspended through a ball bearing on the end of the shaft of the motor with the babbitted bearings and one of the motors containing the machined aluminum bearings lubricated with the vinyl stearate-hydrocarbon oil lubricant composition to give a bearing pressure in each motor of 147 lbs./square inch. The other three motors had a bearing pressure of 5 lbs./square inch. The two motors with the high bearing pressure and one of the other motors lubricated with the vinyl stearate hydrocarbon oil composition were placed on cyclic operation where they ran for 30 minutes and were off for 10 minutes. The other two motors were placed on continuous operation. After 2 minutes of operation, the motor with the machined aluminum bearings lubricated with a straight hydrocarbon oil failed due to seizure of the bearings which was so severe that it has been impossible to free the shaft to permit it to rotate. The other four motors have been running for over 13,750 hours with no sign of failure with the three motors on cyclic operation having made over 20,625 starts and stops.

When two other motors, one with babbitted bearings lubricated with straight hydrocarbon oil and the second motor containing the machined aluminum bearings lubricated with the 20% vinyl stearate in hydrocarbon oil, were measured for starting friction, it was found that the motor with babbitted bearings had a starting friction of 8 oz.-ft. when there is a belt pull of 50 lbs. on the shaft, and a starting friction of 28 oz.-ft. when there is a belt pull of 75 lbs. on the shaft. These corresponding values for the machined aluminum bearings lubricated with the vinyl stearate hydrocarbon oil composition were 3 and 6-oz.-ft., respectively, illustrating the effectiveness of our materials in reducing the starting friction as well as their ability to lubricate a bearing made from a regular aluminum casting alloy.

Example 7.—A standard production locomotive axle, made of low carbon steel, was mounted in an engine lathe and rotated against an M–2 steel finishing roller using a 50% by weight solution of vinyl stearate in kerosene.

These techniques produced a 3-microinch finish on the rolled surface.

Example 8.—Using the same technique and equipment as in Example 4, an aluminum washer and rider, both made of 1100 alloy (commercially pure aluminum) were used with the lubricants and results shown in Table IV. Each run was for one hour.

TABLE IV

Lubricant	Average coefficient of Friction	Wear Surface
Cetane	0.21–0.4, very erratic during entire run.	Galled during 1 hr. test.
Corn oil (a vegetable oil containing a major proportion of glyceryl esters of unsaturated fatty acids).	0.27–0.38, very erratic	Badly galled during 1 hr. test.
20% butyl stearate, 80% cetane.	0.14 at start after 20 minutes became erratic and in 30 minutes was 0.32. At end of period lubricant replaced by following lubricant.	Galled during 1 hr. test.
20% hexadecyl crotonate, 80% cetane.	In two minutes coefficient declined from 0.32 to 0.13 and ran at this low value for balance of test.	Polished wear track over original galled area.
Do	0.12	Polished wear track
20% vinyl stearate, 80% cetane.	0.12	Do.

In Examples 4, 5 and 8, where the average coefficient of friction is noted as erratic, it is meant that the various readings were quite widely spread showing a tendency to grab and break loose, which is indicative of very poor lubrication. It is to be noted that our lubricants did not display this characteristic. Furthermore, Example 8 demonstrates the ability of our lubricants to repair the damage caused by a poor lubricant and to then lubricate the damaged surface with almost the same ability as a smooth surface.

Example 9.—Vinyl stearate was used as a lubricant on two wire drawing dies, and approximately 5000 feet of aluminum wire (EC aluminum) was drawn down from 0.061 to 0.57 and then to 0.051 inch by these dies. Very smooth, shiny wire was obtained with no evidence of galling, formation of slivers, or striations.

Example 10.—About 100 aluminum slugs (1100 alloy) 1½" x 2½" x ¼" with ends on the 1½" dimension coated with vinyl stearate and backward extruded to form cans 1½" x 2½" x 5" x 0.023" wall. The cans had a 3-microinch surface finish which was very bright without buffing. The vinyl stearate was easily removed with a trichloroethylene vapor degreaser. When similar cans were made using lanolin and zinc stearate as the lubricant, the surface finishes were 15 and 8 microinches, respectively.

Example 11.—When the apparatus of Example 4 was used but using a load of 5 kilograms, a rider made of 10–12 Rockwell cold rolled steel and a washer of aluminum alloy 48, and a lubricant of 10% vinyl stearate and 90% SAE–10 spindle oil, the average coefficient of friction was 0.24 for a 16-hour test period with only a narrow spread in data. At the end of the test there was only a slight wear track.

When the test was repeated for 2 hours using a 10 kg. load, the coefficient of friction was 0.14 and the washer had a shiny wear track and no evidence of grooving or galling. When the vinyl stearate concentration was reduced to 5% and the load was 10 kg. and also 20 kg., the coefficient of friction was 0.15 and the washer had a shiny wear track with no evidence of galling and grooving in both cases in a 2 hour test. When the test was repeated using a 20% concentration of vinyl stearate and a 10 kg. load, the coefficient of friction was 0.12 and the washer had a shiny wear track with no evidence of galling or grooving in 4½ hours.

Example 12.—An emulsion was made by heating to 95° C., 15 grams of vinyl stearate, 1.5 grams of triethanol amine and 2.6 grams stearic acid. After a homogeneous melt was obtained, 100 grams of water, heated to 100° C. were slowly added with vigorous stirring which was continued until the emulsion had cooled to room temperature. This emulsion was stable and did not separate on standing. This emulsion was tested in the apparatus described in Example 4 using an aluminum cup and washer. The coefficient of friction was 0.3 at the start and decreased to 0.08 in approximately 3 minutes where it remained constant over several hours of running. Only very slight grooving was observed on examination of the washer after the run, which probably occurred in the initial few minutes of the test before the pieces became coated with the vinyl stearate.

Example 13.—Both aluminum and stainless steel strip 1 inch wide x 10 feet long and 55 mils thick were roll formed into decorative trim strip having a U-shaped cross-section ⅝ inch on the bottom with ¼ inch side walls which were then bent into a square 30 inches on edge with 1 inch radius corners. Using commercially available lubricants, it was necessary to form the U-shaped cross-section using a soluble oil which was then washed from the piece, the piece dipped in bees' wax, dried in an oven, and then bent into the square finished piece. Attempts to use a soluble oil for both the forming and bending resulted in distortion at the corners. When a solution of 30% vinyl stearate in 70% light petroleum distillant known as naphtha or Stoddard solvent was substituted for the above lubricants, both the roll forming to the U-shaped cross-section and bending to the square final shape could be accomplished with only the one lubricant without the intermediate steps.

Example 14.—A die was made for drawing 43 mil thick stainless steel strip into a 4⅜ inch long tube having a 4.5 inch I.D. and a ¼ inch wide flange at the top, stepwise reduced to a 3.5 inch I.D. at the center and a further step reduction to a 3¼ inch I.D. ½ inch from the bottom with a ⅛ inch flange at the bottom. None of the commercially available drawing lubricants would permit this part to be fabricated from the die. When a solution of 40% vinyl stearate in one of the above commercial hydrocarbon drawing oils was used as the lubricant, the parts were readily formed.

Example 15.—When attempts were made to substitute a galvanized sheet steel 90 mils thick for regular steel of the same thickness, in the making of a motor shell for use under high humidity conditions where resistance to rusting was necessary, it was found that the commercial hydrocarbon drawing oil which was satisfactory for the regular steel was incapable of producing parts from the galvanized steel because they would fracture in the final drawing operation. This motor shell was in the shape of a cup approximately 6¼ inches I.D. with a ⅝ inch rim at the top, 3¼ inches deep with a back draw in the center of the bottom 1.5 inches in diameter and 1 inch deep. When a solution of 40% vinyl stearate was made in the same hydrocarbon drawing oil, the motor shell could be readily drawn from the galvanized steel without fracture occurring. The dies were then washed with solvent and attempts made to use the straight oil again. Fracturing occurred as before, but was eliminated when the vinyl stearate solution in the oil was substituted.

Example 16.—SAE 430 stainless steel 31 mils thick was drawn to produce a cup-shaped part having a 3¼ inch diameter x ⅝ inch deep. In this simple part it was found that using a one draw operation, the lower edge would tear with a commercial hydrocarbon drawing oil, but by using a 25% solution of vinyl sterate in the same drawing oil, the drawing could be made and less pressure was required.

Example 17.—In the making of a flywheel from SAE 430 stainless steel, cone-shaped dimples 1 inch in diam-

eter x ½ inch deep were drawn using a commercially available hydrocarbon drawing oil. It was found that it required 7 drawing operations and 3 anneals to complete the formation of the dimple. When a solution of 30% vinyl stearate in the hydrocarbon drawing oil was substituted, the number of drawing operations could be reduced to 2 with no anneals between the draws.

Example 18.—A die cast piece of aluminum was polished on a belt sander. In one case a high viscosity hydrocarbon oil was used as a lubricant and in the other case 100% vinyl stearate was used. The high viscosity hydrocarbon oil produced a 4 microinch finish, whereas the vinyl stearate produced a 1 microinch finish.

Example 19.—Polyvinyl stearate has a melting point of 47–48° C., but it so viscous in the molten state that it cannot be used as a lubricant in the same way as vinyl stearate which is a very fluid liquid above its melting point.

In an attempt to reduce the viscosity, a 20% solution of the polyvinyl stearate was made in SAE 10 hydrocarbon lubricating oil using an elevated temperature to hasten the solution. When the material was cooled to room temperature, the entire mixture turned to a solid block of waxy yellow material, as contrasted to the liquid solution obtained with vinyl stearate. Even a 10% solution formed a thick grease at room temperature. However, a run was made to measure the coefficient of friction at 150° F. using the 10% solution, the apparatus described in Example 4 and an aluminum cup and washer. The coefficient of friction was 0.16 and after 4 hours, examination of the washer showed that it was badly grooved, with greater than 2 mils of wear. A 10% solution of vinyl stearate in the same lubricating oil is liquid at room temperature. In order to make a comparative test, a grease of substantially equivalent consistency to that of the 10% polyvinyl stearate in the oil was made from 10% vinyl stearate, 55% SAE 20 hydrocarbon lubricating oil and 35% lithium stearate. This grease, when tested in the same way as the polyvinyl stearate grease, had a coefficient of friction of 0.07. After four hours, the aluminum washer had only a slightly polished wear track with no evidence of grooving or galling. The results of these tests indicate that polyvinyl stearate is definitely not the equivalent of the monomeric vinyl stearate as a lubricant.

feed rate of 0.25 g.p.m. A thermocouple was imbedded near the trailing edge of the babbitt pad.

Various loads could be applied to the babbitted test pad by means of a clevis-mounted hydraulic cylinder working through a hardened steel ball in a spherical seat in the back of the test pad. To stimulate the action caused by a solid wear particle in the lubricant, a solid ¼ inch diameter, mild steel cylindrical pin with a small taper on the leading and trailing edge of the face of the pin contacting the rotor, was inserted through a hole in the center of the test pad. After the test rotor was brought up to speed, this pin was forced against the rotor by means of an Allen-head screw with a 70° tapered end acting on a 20° angle on the base of the pin. The pin was forced against the rotor by taking a quarter turn of the screw which provided a pin advance of approximately 4 mils to produce wear particles of the pin. If failure of the test pad or journal did not occur after five minutes, another quarter turn was taken on the screw. This was continued until failure did occur or the maximum insertion possible of approximately 16 mils was attained. Prior to the test, each pin and screw was calibrated so that the actual amount of travel of the pin for each quarter turn of the screw was known.

The rotor was brought up to speed using the timed sequence shown in Table V.

TABLE V

Time Period, minutes	Speed	Load on Test Pad, p.s.i.	Pin Insertion Increment
0–5	1,300	0	----------
5–15	1,300	39	----------
15–25	1,800	78	----------
25–35	2,400	117	----------
35–45	3,000	156	----------
45–55	3,600	195	----------
55–60	3,600	195	1st
60–65	3,600	195	2nd
65–70	3,600	195	3rd
70–75	3,600	195	Final

Tests were conducted using a standard 150 S.U.S. (measured at 100° F.) hydrocarbon lubricating oil generally used for lubrication of turbines. This oil was tested with and without several additives at 5% by weight concentration. The results are shown in Table VI.

TABLE VI

Additive	Probe Insertion Maximum, mils	Failure	Maximum Depth of Journal Scoring, microinches	Maximum Babbitt Temperature, ° F.	
				Before Pin Insert.	During Pin Insert.
None	10	Yes	>400	218	270
Zinc dialkyl thiophosphate	10	Yes	>400	187	190
Tricresyl phosphate	3	Yes	>400	226	262
Vinyl stearate	18	No	40	188	210

Example 20.—The following test unit was used to evaluate the ability of our lubricants to lubricate a stainless steel journal and babbitt bearing. A 10 inch diameter test rotor of high chrome steel (0.20%, 11% Cr, 1% Mo, 1% W, 0.25% V), ground to a 16 microinch finish, was supported in oil lubricated spherical roller bearing pillow blocks. It was belt driven to operate at speeds up to 3600 r.p.m. A babbitted test specimen consisting of a 5/16 inch layer of tin babbitt (84% Sn, 8% Sb, 8% Cu) was centrifugally cased onto a steel pad 1 inch wide by 2 inches circumferential length. The inside diameter of the babbitted pad was 25 mils greater than the rotor diameter to stimulate the clearance between a bearing and journal. An oil-distributing groove cut in the leading edge of the test pad provided an inlet for the test lubricant which was supplied at 100° F. from a 3-gallon capacity circulating system using a gear pump to provide a

Example 21.—Samples of vinyl stearate, vinyl stearate containing 0.5% hydroquinone as a polymerization inhibitor and vinyl stearate containing 0.5% hydroquinone as a polymerization inhibitor and 0.5% phenyl-α-naphthylamine as an oxidation inhibitor were prepared. Samples of each were heated for 90 minutes at temperatures of 100°, 150° and 200° C. At the end of this time the samples of vinyl stearate with no additive which had been heated at 150° and 200° C. were viscous liquids, whereas the other samples were still very fluid. After cooling to room temperature, the melting point of each was determined and found to be 34° C., the melting point of the monomeric vinyl stearate, except for the samples of vinyl stearate with no additive which had been heated to 150° and 200° C. They had melting points of 44° C. showing that both had polymerized, but the other samples had not. In other words, vinyl stearate can be

used as a lubricant with no stabilizer, at temperatures up to 100° C. with no polymerization occurring over a 90 minute period or at much higher temperatures, if stabilized with a polymerization inhibitor or retarder.

Example 22.—Vinyl stearate containing 0.5% hydroquinone and 0.5% phenyl-α-naphthylamine was tested at 115° F. in the apparatus of Example 4 using an aluminum washer and rider. Over a period of 7 hours, the average coefficient of friction was very steady at 0.12. The wear track was very shiny with only one slightly grooved spot.

This test was repeated except that the temperature was raised from 100° to 350° F. over a period of 110 minutes. The initial average coefficient of friction was 0.15 and decreased only slightly until a temperature of 350° F. was reached when it quite rapidly decreased to 0.04 over a period of ten minutes. After an additional ten minutes at 350° F., the temperature was raised to 400° F. but this caused the average coefficient of friction to increase, apparently because of incipient failure of the lubricating film under the severe conditions of boundary lubrication and high temperature. The temperature was decreased to 350° F. and held for 80 minutes. At the end of this time, the average coefficient of friction was 0.057 and the lubricant showed no increase in viscosity nor evidence of polymerization.

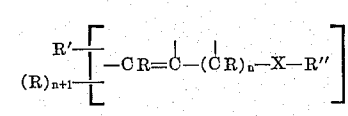
Example 23.—A 10% solution of vinyl stearate and 0.5% hydroquinone in SAE 10 mineral lubricating oil was tested at 300° F. in the apparatus of Example 4 for 4 hours using an aluminum washer and rider. During the test the average coefficient was 0.10. Because of the high temperature at which this test was run, some volatile components of the lubricant distilled from the apparatus and the lubricant became noticeably darker in color. Infrared analysis of the lubricant before and after testing showed no evidence of polymer formation, thus showing the effectiveness of the addition of a polymerization stabilizer to the lubricant to prevent polymerization of the vinyl stearate. Similar results were obtained when 0.5% sulfur was used in place of hydroquinone.

In the appended claims, we use the term "solid" as an adjective in its broad sense to differentiate between solids, liquids, and gases. The term "solid part" includes within its meaning those solid bodies which are hollow, honeycombed, porous, etc., bodies which have a solid surface.

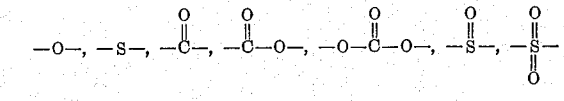
The above examples have illustrated many of our compositions which may be utilized as lubricants. Equally good results will be obtained by the utilization of other compositions falling within the broad general formula. The examples have also illustrated many of the ways that our compositions may be mixed with other materials to provide outstanding lubricants. Other modifications and variations will be readily apparent to those skilled in the art and are included within the meaning of the appended claims.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A lubricant comprising an oil of lubricating viscosity containing dissolved therein at least 0.1 percent by weight of a monoethylenically unsaturated compound having the formula



where *n* is one of the integers 0, 1, R is a monovalent radical selected from the group consisting of hydrogen and fluorine, R′ is a monovalent radical selected from the group consisting of hydrogen, fluorine, methyl, monofluoromethyl, difluoromethyl, and trifluoromethyl, X is a divalent radical selected from the group consisting of



and R″ is a monovalent radical selected from the group consisting of linear alkyls having from 11–60 carbon atoms, and linear fluoroalkyls having from 11–60 carbon atoms, and a polymerization stabilizer selected from the group consisting of inhibitors and retarders in an amount effective to inhibit polymerization of said monoethylenically unsaturated compound.

2. The lubricant of claim **1** wherein the oil of lubricating viscosity is selected from the group consisting of mineral, silicone and diester lubricating oils and the monoethylenically unsaturated compound is present in a concentration of at least 2% by weight of the oil.

3. The lubricant of claim **2** wherein the oil is a mineral lubricating oil and the unsaturated compound is an alkyl ester of acrylic acid wherein the alkyl group is a monovalent, linear alkyl radical having from 11–24 carbon atoms.

4. The lubricant of claim **2** wherein the oil is a mineral lubricating oil and the unsaturated compound is a vinyl ester of an alkyl monocarboxylic acid wherein the alkyl group is a monovalent, linear alkyl radical having from 11–24 carbon atoms.

5. The lubricant of claim **2** wherein the oil is a mineral lubricating oil and the monoethylenically unsaturated compound is vinyl stearate.

6. The lubricant of claim **2** wherein the oil is a mineral lubricating oil and the monoethylenically unsaturated compound is hexadecyl crotonate.

7. The lubricant of claim **2** wherein the oil is a mineral lubricating oil and the monoethylenically unsaturated compound is allyl stearate.

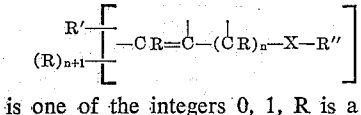
8. The lubricant of claim **2** wherein the oil is a mineral lubricating oil and the monoethylenically unsaturated compound is allyl palmitate.

9. The lubricant of claim **2** wherein the oil is a mineral lubricating oil and the monoethylenically unsaturated compound is dodecyl acrylate.

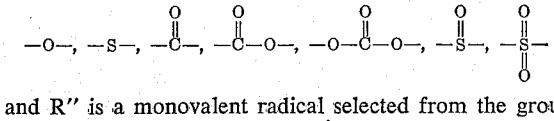
10. The lubricant of claim **2** wherein the oil is a mineral lubricating oil and the monoethylenically unsaturated compound is dodecyl methacrylate.

11. The lubricant of claim **2** wherein the oil is a mineral lubricating oil and the monoethylenically unsaturated compound is octadecyl acrylate.

12. A grease comprising an oil selected from the group consisting of mineral, silicone and diester lubricating oils containing a thickener and a monoethylenically unsaturated compound having the formula



where *n* is one of the integers 0, 1, R is a monovalent radical selected from the group consisting of hydrogen and fluorine, R′ is a monovalent radical selected from the group consisting of hydrogen, fluorine, methyl, monofluoromethyl, difluoromethyl, and trifluoromethyl, X is a divalent radical selected from the group consisting of



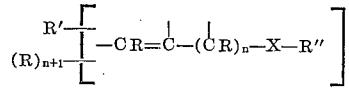
and R″ is a monovalent radical selected from the group consisting of linear alkyls having from 11–60 carbon atoms, and linear fluoroalkyls having from 11–60 carbon atoms.

13. The grease of claim **12** wherein the oil is a mineral oil, the thickener is lithium stearate, and the unsaturated compound is an alkyl ester of acrylic acid wherein the alkyl group is a monovalent, alkyl radical having from 11–24 carbon atoms.

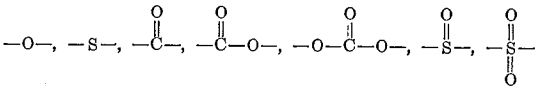
14. The lubricating grease in claim **12** wherein the oil is a mineral oil, the thickener is lithium stearate, and the unsaturated compound is vinyl ester of an alkyl monocarboxylic acid wherein the alkyl group is a mono-

valent linear alkyl radical having from 11–24 carbon atoms.

15. The method of lubricating two solid surfaces between which there is relative motion, at least one of said surfaces being a metal, which comprises effecting relative motion between the two solid surfaces and maintaining between the two surfaces while they are moving relative to each other, a monoethylenically unsaturated compound having the formula



where n is one of the integers 0, 1, R is a monovalent radical selected from the group consisting of hydrogen and fluorine, R′ is a monovalent radical selected from the group consisting of hydrogen, fluorine, methyl, monofluoromethyl, difluoromethyl, and trifluoromethyl, X is a divalent radical selected from the group consisting of



and R″ is a monovalent radical selected from the group consisting of linear alkyls having from 11–60 carbon atoms, and linear fluoroalkyls having from 11–60 carbon atoms.

16. The method of claim **15** wherein the lubricant is an aqueous emulsion containing at least 10% by weight of the monoethylenically unsaturated compound.

17. The method of claim **15** wherein one of the said solid surfaces is a metal composition containing at least 50% by weight aluminum.

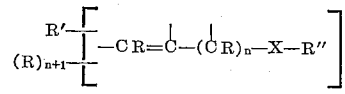
18. The method of claim **15** wherein one of the said solid surfaces is stainless steel and the other said solid surface is babbitt.

19. The method of claim **15** wherein one of the said solid surfaces is steel and the other said solid surfaces is cast aluminum.

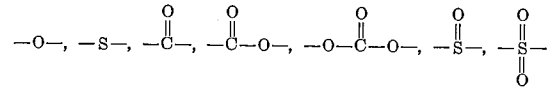
20. The method of claim **15** wherein the unsaturated compound is an alkyl ester of acrylic acid wherein the alkyl group is a monovalent, linear alkyl radical having from 11–24 carbon atoms.

21. The method of claim **15** wherein the unsaturated compound is a vinyl ester of an alkyl monocarboxylic acid wherein the alkyl group is a monovalent, linear alkyl radical having from 11–24 carbon atoms.

22. The process of shaping a metal composition containing at least 50% by weight aluminum which comprises maintaining a film of lubricant between the metal composition and a shaping member and, at the same time subjecting the metal composition to sufficient force to create relative motion between said composition and said forming member and to cause displacement of some of said metal composition with respect to the remainder, said lubricant comprising a monoethylenically unsaturated compound having the formula



where n is one of the integers, 0, 1, R is a monovalent radical selected from the group consisting of hydrogen and fluorine, R′ is a monovalent radical selected from the group consisting of hydrogen, fluorine, methyl, monofluoromethyl, difluoromethyl, and trifluoromethyl, X is a divalent radical selected from the group consisting of



and R″ is a monovalent radical selected from the group consisting of linear alkyls having from 11–60 carbon, atoms, and linear fluoroalkyls having from 11–60 carbon atoms.

23. The process of claim **22** wherein the lubricant is an aqueous emulsion containing at least 10% by weight of the monoethylenically unsaturated compound.

24. The process of claim **22** wherein the unsaturated compound is an alkyl ester of an acrylic acid wherein the alkyl group is a monovalent, linear alkyl radical having from 11–24 carbon atoms.

25. The process of claim **22** wherein the unsaturated compound is a vinyl ester of an alkyl monocarboxylic acid wherein the alkyl group is a monovalent, linear alkyl radical having from 11–24 carbon atoms.

26. The process of claim **22** wherein the shaping member is an extrusion die.

27. The process of claim **22** wherein the shaping member is a wire drawing die.

28. The process of claim **22** wherein the shaping member is the set of rolls of a rolling mill.

29. The process of claim **22** wherein the shaping member is a metal cutting tool.

30. The process of claim **29** wherein the cutting tool is the tool bit in an engine lathe.

References Cited by the Examiner

UNITED STATES PATENTS

2,020,714	11/1935	Wulff et al.	252—56
2,204,597	6/1940	Humphreys et al.	252—56
2,257,969	10/1941	Loane et al.	252—48.2
2,788,326	4/1957	Bondi et al.	252—56

DANIEL E. WYMAN, *Primary Examiner.*

L. G. XIARHOS, *Assistant Examiner.*