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SOLVENT RESISTANT LOW TEMPERATURE LUBRICANT

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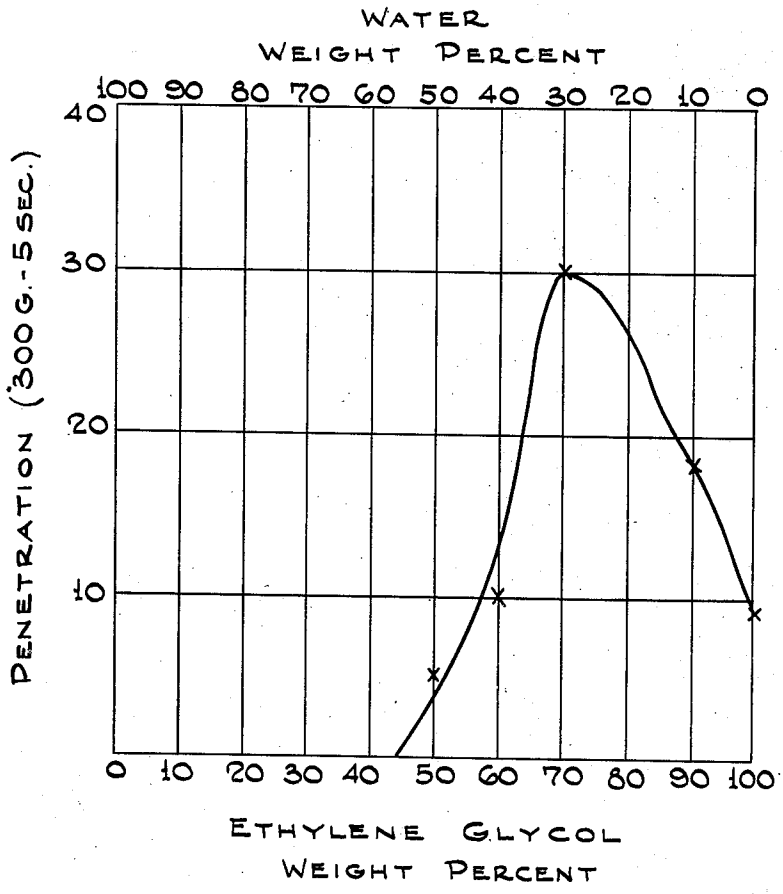

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SOLVENT RESISTANT LOW TEMPERATURE LUBRICANT

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This invention relates to solvent resistant lubricants and particularly to extremely low temperature lubricants which are highly resistant to hydrocarbon solvents and related compositions.

In the lubrication of machinery or equipment used in the presence of certain solvents at very low temperatures, considerable difficulty has been encountered in securing a composition which has the necessary low temperature lubricating characteristics and at the same time is not soluble in hydrocarbons and other solvents of oils, greases, and the like.

It has long been known in the prior art that certain polyhydric alcohols, such as glycerin and the various glycols have certain lubricating characteristics and also that they may be used at moderately low temperatures under some conditions. These materials have been used for lubricating refrigerating machinery and the like with limited success but have not been at all satisfactory for use at very low temperatures, e. g. below about —100° F., since they solidify. These same materials are also subject to the limitation that they are too low in viscosity at normal or slightly elevated temperatures.

It is an object of the present invention to modify lubricants of the oil insoluble type, especially polyhydric alcohol type lubricants, in such a way as to make them useful as lubricants in the presence of hydrocarbon and other organic solvents. It is a further object to prepare a lubricating composition based on the use of lubricating properties of polyhydric alcohols which will be useful at various temperatures, especially for lubrication of machinery and equipment in the presence of liquid hydrocarbons.

It is well known in the prior art that lubricating oils of the mineral oil type may be thickened to produce lubricating grease compositions by the use of various metal salts of fatty acids. It is also known that the polyhydric alcohols, such as glycerin and the glycols are relatively insoluble in hydrocarbons and are generally incompatible with soaps of the character just described. Efforts have been made in the prior art, without complete success, to use some of the alkali metal soaps in combination with glycerin for lubricating purposes. It has now been discovered, however, that certain soaps, i. e., metal salts of fatty acids, which are not ordinarily compatible with polyhydric alcohols, may be combined with such alcohols, and preferably with a definite amount of water, as pointed out hereinafter, to form satisfactory lubricating compositions for use at very low temperatures. We have discovered also that

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where the polyhydric alcohol does not satisfactorily wet the soap which is used, the lubricating properties and the mechanical stability of such compositions are materially improved by the use of a small amount of a suitable wetting agent or surface active material. The present invention is particularly characterized by the use of an optimum amount of water with the polyhydric alcohol to lower its effective solidification temperature. It also involves preferably the use of a surface active material, specifically a wetting agent, to secure an intimate mixture of soap with the lubricant to impart extremely low temperature characteristics to lubricants of the polyhydric alcohol and soap type.

For the lubrication of machinery which must operate in the presence of liquid hydrocarbons, soaps alone have been used to a limited extent but the soaps, when used alone, are quite unsatisfactory because they do not provide good lubricating films and the films provided are not stable. Such lubricants do not remain effective to reduce friction over extended periods of time. It has also been suggested in the prior art that certain soaps, such as the sodium soaps, might be emulsified with glycerin and oil to provide lubricants for use in the presence of hydrocarbons or at moderately low temperatures. These are usable at temperatures of the order of 0° C. or a few degrees below, but they are not satisfactory for extremely low temperature use. The present invention is based on the discovery that a much superior lubricant is produced by the use of a suitable metal soap, preferably a water-insoluble soap such as zinc stearate, or other metal soaps of stearic acid. Other soaps of saturated or unsaturated aliphatic acids, such as the palmitates, oleates, and the like, and mixtures thereof, may be combined in finely divided form with a polyhydric alcohol, and a small amount of water to form a good low temperature lubricant. If the soap is not wetted by the polyhydric alcohol, a small quantity of wetting agent should be employed to obtain a stable composition. Other known bodying agents for grease may be used instead of soaps for some purposes. Examples are carbon black or bentonite which may be used singly or in combination and with or without soaps, but the preferred thickening agents are the metal soaps of the fatty acids which are solid at ordinary temperatures and which are not water soluble. The soaps should be very finely divided to obtain a fine grained stable composition.

As the principal liquid lubricating ingredients of greases made according to the present inven-

tion, the common aliphatic polyhydric alcohols of moderately low molecular weight and related materials, which are liquid at ordinary temperatures and at fairly low temperatures, are preferred. These include glycerin, ethylene glycol, propylene glycol, diethylene glycol, and the like, as well as the monoalkyl ethers thereof, and mixtures of such materials. Some of these materials, by themselves, solidify at temperatures only a few degrees below the freezing point of water, but those which are useful in the present invention have the peculiar property of remaining plastic or soft and grease-like in texture at temperatures far below their normal freezing points and even as low as —150° F., or lower, when combined with optimum quantities of water. Certain of the so-called "carbitols," i. e. monoalkyl ethers of diethylene glycol, have fairly low freezing points per se, but the important criterion is not the freezing point of the alcohol as such but rather the hardening point or the point below which the lubricant ceases to function effectively as a lubricant. The "carbitols" are mentioned in Morgan Patent No. 2,383,915 as possible low temperature lubricants, for example temperatures that are subzero but above —40° F., but they are not suitable per se for use at extremely low temperatures such as —100° F. or below.

Thus the use of an optimum amount of water with the polyhydric alcohol, or derivative, so as to retain a degree of mobility at very low temperatures is a distinct and important feature of the invention, although in some compositions and for some purposes it is not absolutely essential. The optimum amount of water varies somewhat with the polyhydric alcohol or ether employed but in general it appears to lie between 15 and 50% by weight and usually between 25 and 35% based on the composition of the alcohol (or ether) plus water. In the case of ethylene glycol, for example, the optimum composition of the glycol and water is about 70% glycol and 30% water by weight. With glycerin the optimum water content appears to be about the same.

The use of a wetting agent has been mentioned as a desirable feature of the invention. When a soap is used which is not soluble in the polyhydric alcohol, the wetting agent renders the soap compatible with the polyhydric alcohol, or the alcohol-water mixture. The water-insoluble soaps are normally preferred and hence the use of a wetting agent ordinarily is essential. With some compositions, and for some purposes, however, it may be omitted.

The sulfonates are satisfactory wetting agents, as are also the oleates, etc., of polyhydric alcohols, such as pentaerythritol, and the like. The wetting agent employed may be selected from a wide variety of known agents, so long as it is effective to promote the formation of an intimate mixture of the metal soap and the polyhydric alcohol or equivalent liquid lubricating material. Ordinarily the quantity of wetting agent required is very small, for example of the order of 0.1 to 0.5%, based on the liquid lubricant (i. e. without soap). A broader range of 0.01 to 5.0%, based on the entire grease composition appears to have utility, but in general a quantity of the general order of 0.1 to 2.0% appears quite satisfactory. The wetting agent may be omitted only if the soap is adequately wetted by the polyhydric alcohol per se.

Example 1

A liquid lubricant composition without water was first prepared, consisting of a mixture of 29% by weight of finely divided zinc stearate and about 71% of glycerin with a very small amount, about 0.1%, based on the glycerin, of a wetting agent. The particular wetting agent used in this example was a dioctyl sodium sulfosuccinate having the formula

The composition of Example 1 was a grease like material having the finely divided soap well dispersed in the glycerin. It was tested by the use of a standard ASTM penetrometer at various temperatures and was found to have a penetration at —11° F. of 250. At —108° F. the penetration was only 36 and at —142° F. it was 0. The latter indicates that the grease was solid at —142° F. but it still had a slippery feel, doubtless due to surface melting and could provide some lubrication even at that low temperature. Such a grease would provide satisfactory lubrication down to about —108° F.

Example 2

Another example of a grease prepared without the use of water, was a composition consisting of about 50% by weight of zinc stearate, 50% by weight of a glycol (ethylene glycol) and 0.1% by weight of the wetting agent referred to in Example 1. This material was found to have a grease-like consistency at quite low temperatures, as also was the case in Example 1, the penetration being 250 at —11° F. and 10 at —142° F. Thus the composition of Example 2 was somewhat softer at the extremely low temperature than that of Example 1, indicating that ethylene glycol grease is somewhat better than glycerin base lubricant for extremely low temperature lubrication. It was still objectionably hard at the very low temperature of —142° F. but would lubricate satisfactorily down to about —120° F.

Example 3

Another example of a grease including water, according to the present invention, was prepared in the form of a composition having the following formula:

	Per cent by weight
Zinc stearate	47.4
Ethylene glycol	36.8
Water	7.9
Sodium sulfonate solution [1]	7.9

[1] The sodium sulfonate solution is a commercial cleaning solvent composed of about 25% by weight of the sulfonate with 50% isopropyl alcohol and 25% water. The sodium sulfonate itself is a salt obtained by neutralizing with NaOH the oil-soluble sulfonic acid produced by treating petroleum residuums or heavy oil fractions with strong sulfuric acid.

The composition of Example 3 was tested for penetration in the same manner as Examples 1 and 2 and was found to have a penetration of 250 (25 mm.) at —11° F. and 30 (3.0 mm.), at —142° F. This indicates that ethylene glycol, with a relatively small amount of water, mixed with a suitable thickener such as zinc stearate, has a softer consistency at very low temperatures than the non-aqueous compositions of Examples 1 and 2. In general, the glycols are somewhat softer than glycerin at very low temperatures and they are therefore useful at somewhat lower temperatures. The use of the wetting agent, sodium sulfonate in this instance, served to maintain physical stability of the lubricant, preventing separation of the finely divided soap from the glycol and water.

The lubricant composition of Example 3 was used over an extended period in a butyl rubber reactor operating at low temperatures most of the time. The reactor varied over a temperature range from −150° F. during normal production of polymer up to +160° F. during times when the reactor was being cleaned. Under all conditions, the lubricant of Example 3 was found to give satisfactory performance. The composition of this example, though not a true grease in the sense of having a micelle structure, was grease-like in appearance and maintained good plasticity and moderate torque resistance even at the extremely low temperatures indicated.

From the foregoing data it is evident that lubricants of the glycerin or glycol type may be thickened to a grease-like consistency by the employment of suitable soaps, such as zinc stearate, for example, or any of the oil-insoluble soaps, where the grease is to be unaffected by hydrocarbons, in various proportions. Proportions preferred are from 20 to 50% of zinc stearate or equivalent soap, based on the total composition. Amounts as low as about 10% up to as high as 60% or more of the soap may be employed, depending somewhat upon the intended operating temperature. When the soap is not wetted by the polyhydric alcohol, as is the case with zinc stearate, a wetting agent is employed.

The wetting agent must be soluble at least to a moderate degree in the polyhydric alcohol and preferably should have a greater affinity for the metal to be lubricated than has the hydrocarbon liquid or other solvent which is present at the point of lubrication. When such wetting agents are used, they appear to help to establish on the metallic surface to be protected a more stable lubricating film which is not readily removed by the hydrocarbons.

Various wetting agents, preferably of the sulfonate type, may be employed in suitable concentrations, usually within the limits of .01 up to 5%, based on the total composition. The secondary alcohol sulfonates are among those especially preferred. These may be conventionally prepared by reacting an appropriate secondary alcohol with maleic anhydride followed by addition of sodium bisulfite. Alternatively, an appropriate petroleum fraction may be sulfonated and the sodium or other alkali or alkaline earth metal sulfonate obtained and used in small proportions, for example 0.01 to a maximum of about 5.0%, based on the weight of the total composition. The composition of Example 3, of about 47% zinc stearate, about 37% glycol, about 8% water, and about 8% of the 25% alcohol solution of wetting agent is quite satisfactory.

While the sulfonate type wetting agents are preferred, by which is meant the conventional petroleum sulfonates, the salts of sulfonated alcohols and of the sulfonated aliphatic esters such as dioctyl sodium sulfo-succinate described above, and their obvious equivalents, it will be understood that other surface active agents, such as some of the esters, may be employed. Certain of the aliphatic alcohols, for example, isopropyl alcohol, have some wetting properties but these alcohols are not satisfactory for use, for example in lubricants for low temperature operation as in butyl rubber reactor machinery, because the solvents present, such as methyl chloride, would dissolve and extract the monohydric alcohols out of the lubricant. In all cases, it is desirable, as noted above, that the wetting agent should have a greater affinity for the metal to be lubricated than has the solvent to be resisted.

In the accompanying drawing, there is shown graphically the effect of water on the penetration characteristics of a grease type lubricant consisting of water, ethylene glycol and zinc stearate at a very low temperature of −142° F. The composition of this figure had a solid-liquid ratio of 52.6% liquid and 47.4% solid. The glycol and water, of course, varied. Otherwise, the composition was essentially that of Example 3. The figure shows the striking effect of the use of water at the very low temperature of −142° F. and it will be noted that ethylene glycol is softened or plasticized to the maximum extent by a water content of approximately 30% by weight, based on the total composition of water plus polyhydric alcohol. The same is true to a large degree of other polyhydric alcohols although the glycerin base lubricant, as noted above, is not nearly as soft, penetrable, or grease-like at this temperature as ethylene glycol, the latter being much superior for such very low temperature. The low penetration number of glycerin lubricant, Example 1, indicates considerable resistance to rotation or somewhat inferior lubrication at very low temperature.

The formulation given above in Example 3 retains mobility at much lower temperatures than prior art compositions such, for example, as those typified by the Morgan Patent No. 2,383,915 mentioned above. The difference appears to be attributable mainly to the presence of water, although the superior physical properties due to the use of a wetting agent also contribute. For example, ethylene glycol alone shows a penetration of 50 at −142° F. whereas a 70:30 mixture of glycol and water, under similar conditions, shows a penetration of 250. Mixed with zinc searate, ethylene glycol alone shows substantially no penetration at −142° F.

As indicated above, various glycols and derivatives thereof such as the monoalkyl ethers of ethylene glycol and the like may be employed. As suggested above the freezing point of the glycol per se is not particularly significant as long as the lubricating properties are preserved at operating temperatures by the effects of the water and to some extent, of the wetting agent. By use of the latter, the mobile properties of the grease are improved, apparently, because of the unusually intimate mixture of soap and liquid lubricant which results.

In some of the cases referred to specifically above (Examples 1 and 2) normal octyl alcohol was reacted with maleic anhydride and sodium bisulfite to produce the particular wetting agent, but it will be understood that various other wetting agents may be used, as suggested above. While the proportions may be varied somewhat, they usually will not exceed about 2%.

The following table shows further data obtained by comparison of compositions of glycerin or glycol (ethylene glycol) with or without water, using various thickeners and, in some cases, a wetting agent. In general, the soap type thickeners are better for very low temperatures. The superior mobility at −142° F. of a glycerin soap composition containing water over those which do not contain it is apparent from a comparison of Examples 4 and 6. The composition of Example 6 is relatively stiffer because it contains more soap. The data were obtained in the usual manner in conventional grease penetrometers by the ASTM procedure, where readings are pene-

tration depths of the standard penetrometer in tenths of a millimeter.

Table I

Example No.	Composition	Penetration
4	Zinc stearate, 29.00% Glycerin, 70.94% Wetting agent,[1] 0.06%	At −108° F., 29 At −142° F., 0
5	Zinc stearate, 49.95% Ethylene glycol, 49.95% Wetting agent,[1] 0.10%	At −11° F., 250+ At −142° F., 10
6	30% H_2O to 70% glycerin, 65.03% Zinc stearate, 34.80% Wetting agent,[1] 0.17%	At −108° F., 9 At −142° F., 5
7	30% H_2O to 70% diethylene glycol, 33.00% Bentonite clay, 67.00%	At −142° F., 0
8	30% H_2O to 70% diethylene glycol, 71.40% Bentonite clay, 14.30% Zinc stearate, 14.30%	At −142° F., 0

[1] This wetting agent was a commercial product, known as "Aerosol OT" consisting of dioctyl sodium sulfosuccinate in 10% aqueous solution. Analogous esters of sulfonated dibasic or bicarboxylic acid, such as succinic acid and its homologues may be used.

It will be noted from the foregoing that bentonite, which is wetted naturally by polyhydric alcohols of the glycerine-glycol type may be used in lieu of soap as a thickener. The same is true of carbon black. The latter behaves very much like zinc stearate whereas bentonite has a greater stiffening effect, as indicated in Example 7. The bentonite grease retains mobility down to about −108° F.

The solid ingredients are needed to prevent loss of the lubricant when the temperature is raised. At very low temperatures the polyhydric alcohol and water mixture sets to a soft gel of grease-like consistency, but as soon as the temperature is raised, for example to −50° F., it becomes quite fluid and loses most of its lubricating value. Hence the preferred composition contains enough thickener to prevent complete liquefaction upon foreseeable temperature rises. The amount of finely divided solid thickener may very widely but usually it will be not less than about 10% by weight and it may be as much as about 60% of the total composition.

Although the optimum quantity of water is preferred, it will be noted from the foregoing data that in some special cases water can be omitted. It may be used with polyhydric alcohols in proportions up to a 50–50 mixture. Preferably at least 15% of the liquid constituent should be water, the range of 25 to 35% and especially about 30% being particularly preferred. Hence the over-all composition may comprise 10 to 60%, preferably 20 to 50%, of a hydrocarbon insoluble thickener such as zinc stearate, other soaps, or other grease thickening finely divided solids, and 40 to 90% of liquid constituent, essentially hydrocarbon insoluble polyhydric alcohol preferably containing enough water to materially increase its fluidity at very low temperatures, e. g. at −100° F. or lower. Preferably, also, the composition contains a small amount of wetting agent unless the solid thickener is directly wetted by the alcohol as explained above.

The preferred polyhydric alcohol compounds are the aliphatic alcohols having 2 to 4 carbon atoms, glycol, glycerol, and glycol ether (diethylene glycol) being specifically preferred. Others of similar characteristics as regards low temperature gelation, especially with water, may be employed.

We claim:

1. A lubricating composition resistant to hydrocarbon solvents consisting essentially of 40 to 90% by weight of a polyhydric alcohol having lubricating properties, said alcohol being selected from the group which consists of glycerine, C_1 to C_4 glycols and the lower monoalkyl ethers thereof which have freezing points below 0° C., combined with enough water to substantially increase fluidity of said alcohol below a temperature of about −100° F., 10 to 60% of zinc stearate, and 0.01 to 5% of a sulfonate type wetting agent which has a greater affinity for the surfaces being lubricated than said solvents to maintain dispersion of said stearate in said alcohol and water.

2. A composition according to claim 1 wherein said polyhydric alcohol is glycerin.

3. A composition according to claim 1 wherein said polyhydric alcohol is a glycol.

4. A composition according to claim 1 wherein said polyhydric alcohol comprises ethylene glycol.

5. A composition according to claim 2 wherein said wetting agent is a sulfonated maleic acid ester of a secondary alcohol.

6. A composition according to claim 2 wherein said wetting agent is a dioctyl sodium sulfosuccinate.

7. A lubricating composition having approximately the following formula

	Per cent
Zinc stearate	47.4
Ethylene glycol	36.8
Water	9.3
Isopropyl alcohol	4.0
Oil-soluble sodium petroleum sulfonate	2.0

8. A lubricating composition resistant to hydrocarbon solvents consisting essentially of 40 to 90% by weight of a polyhydric alcohol having lubricating properties, combined with enough water to substantially increase mobility of said alcohol below a temperature of about −100° F., 10 to 60% of zinc stearate, and 0.01 to 5% of dioctyl sodium sulfo-succinate.

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