

UNITED STATES PATENT OFFICE

2,451,895

SYNTHETIC GREASE

Ellis Ross White, Berkeley, and Denham Harman, Albany, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application June 8, 1946, Serial No. 675,332

16 Claims. (Cl. 252-42.1)

1

This invention relates to lubricants and to processes of preparing them, and refers more particularly to stable grease compositions comprising certain thioether derivatives and a lithium soap.

It is known in the art to prepare various lubricating grease compositions adapted for particular uses. The uses to which the various grease compositions are employed present a wide variety of conditions, and generally a grease prepared with a given set of conditions in mind is not suitable for use in a different environment. Conversely, all sets of conditions met in the great variety of lubricating systems encountered today cannot be satisfied by mineral oil base greases, for example.

To illustrate further: not only are high temperature conditions frequently met, but low temperature lubrication is becoming increasingly important. Airplanes are controlled in flight by special mechanisms such as rudders, elevators, and ailerons which are adapted to the main portions of the airplane such as fuselage and wings by specially designed hinges. These hinges have metal to metal contact bearing surfaces which offer a very difficult lubrication problem. Airplanes are operated under the most severe changes in climatic conditions and since the failure of even one part of the mechanism might well result in a catastrophe, it is imperative that all parts should be free and well lubricated at all times. It is not uncommon for a plane during a single trip to be subjected to extremely high ground temperatures, as well as subzero temperatures in the upper atmosphere, in addition to conditions of high humidity such as rain, snow or ice. Any lubricant used upon the control mechanisms of the plane must therefore be capable of withstanding these conditions without disintegration.

High temperature greases such as sodium greases are known to the art. However, they are quite water-soluble and readily disintegrate under humid conditions. Water-insoluble greases such as calcium soap greases, are also known, but these compositions will not withstand high temperatures. Aluminum soap greases are also water insoluble, but have a relatively low transition point where they become fluid and run out of the bearing. Barium soap greases are only slowly affected by the presence of water and effectively withstand elevated temperatures, but have the disadvantages of losing their grease structure on standing at lower temperatures and of be-

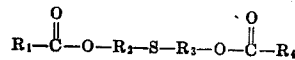
2

coming quite stiff and heavy at elevated temperatures.

The common mineral oil and vegetable oil bases have shortcomings which limit their complete utility as grease bases. The viscosity indices of such bases, for example, are unsatisfactory where extreme conditions, both high and low temperatures and pressures, are to be met. Various synthetic bases, such as chlorinated diphenyl, have been investigated, but have not proved satisfactory for general use, especially because of their generally low thermal decomposition temperature characteristics.

It is an object of this invention to produce a grease composition which will provide adequate lubrication at both high and low temperatures and will not decompose in the presence of excessive moisture or at relatively high temperatures. Another object of this invention is to provide grease compositions which are not unduly subject to thermal cracking such as is encountered with mineral and vegetable oil greases. A further object is to provide greases of uniform consistency and texture, and which vary from extreme hardness to extreme softness, in accordance with the nature and proportions of the ingredients.

Now, in accordance with this invention, it has been found that superior greases are obtained by the use of compositions predominating in an ester of a dihydroxy thioether, such as those having the general formula



in which R_1 and R_4 are hydrocarbon radicals, and R_2 and R_3 are aliphatic radicals, and, in addition thereto, from about 4% to about 40% of a lithium soap. Lubricating greases having the above composition possess important features which render them highly desirable, such as substantial non-inflammability, thermal stability, etc. Also, in accordance with this invention, it has been found that such greases, although comparatively stable in regard to oxidation, are further improved in stability by the incorporation therein of an inhibitor. Still in accordance with this invention these greases may be toughened by the addition thereto of a minor amount of polymers of an esterified methacrylic acid.

The several constituents of the grease will now be discussed.

The soap

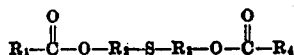
The particular type of soap employed comprises predominantly a lithium soap, although minor

amounts of fatty acid salts of other metals, particularly sodium, potassium, calcium, barium, zinc, aluminum, etc., may also be present. The fatty acids which may be used in forming the lithium soaps useful in the invention comprise the lower fatty acid series as well as the higher members. These include acetic, propionic, butyric and caproic acids, among others. Preferably, however, the fatty acid should contain twelve or more carbon atoms, such as in lauric, myristic, palmitic, margaric, stearic, nondecyclic, carnaubic, cerotic, montanic, oleic, behenic, linoleic and linolenic acids. Likewise, mixtures of acids obtained from various natural products form suitable lithium soaps useful in the present invention. Such natural products are tallow, lard, various seed oils, wool fat, naphthenic acids such as may be derived from petroleum oils; rosin, tall oil, oxidized paraffin, fish oils, olive oil, palm oil, etc.

Not only are the acids having twelve or more carbon atoms preferred for use in preparing lithium soaps, but those acids are most preferred which are saturated or contain no more than about one unsaturated linkage in the molecule, including saturated fatty acids, mono-olefinic fatty acids and mono-acetylenic fatty acids, all having twelve or more carbon atoms.

The grease base

The bases for the greases which comprise this invention are thioether derivatives having the general structural formula



in which R_1 to R_4 are hydrocarbon radicals. Preferably, R_1 and R_4 are non-aromatic, but instead are aliphatic or alicyclic. The most useful grease bases of this class are those in which R_1 and R_4 are saturated aliphatic radicals, and of this group those having from 4 to 11 carbon atoms are preferred.

Together with the $-\text{COO}-$ group to which they are attached, R_1 and R_4 form ester groups such as the valeric acid radicals, including normal valeric, isovaleric, tertiary valeric or trimethyl acetic, (which is the preferred acid radical) and d-l valeric (or methylethylacetic) acid radicals. The saturated 5-carbon atom radicals, together with the $-\text{COO}-$ group to which they are attached, comprise the caproic (or hexoic) acid radicals, including butyl-acetic, iso-caproic (or secondary butylacetic), pseudocaproic (or tertiary-butylacetic), secondary-caproic (or diethylacetic), secondary active-caproic (or methylpropylacetic) or tertiary-caproic (dimethylethyl acetic) acid radicals. The 6-carbon saturated aliphatic radicals, together with the adjacent $-\text{COO}-$ group, form radicals of the heptoleic acid series, including enanthic, isoenanthic, methyl-diethylacetic, ethylpropylacetic, methyl-butylacetic, etc. acid radicals. The 7-carbon atom saturated aliphatic radicals and the adjacent $-\text{COO}-$ group form the octoleic acid radicals such as n-octoleic, dipropylacetic, methylethylisopropyl acetic, 2-methylheptoleic, 2-ethylhexoleic, 3-propylvaleric, etc., acid radicals. Of this latter group the 2-ethylhexoleic radical is preferred.

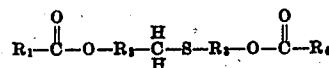
The R_1 and R_4 radicals having 8 to 11 carbon atoms form, with the adjacent $-\text{COO}-$ radicals, the various isomers of the acid radicals



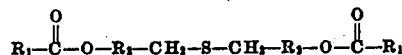
including pelargonic, capric, undecylic and lauric

acid radicals, as well those of 2,3-diethylvaleric acid, 3-propylcaproic acid, 4-isobutylheptoleic acid, etc. The higher molecular weight radicals, both saturated and unsaturated, likewise form suitable ester groups in combination with the two $-\text{COO}-$ groups in the thioether molecule. The mono-olefinic acids and the naphthenic acids are the preferred classes within this group. The naphthenic acid derivatives are conveniently prepared from the naphthenic acids found in certain petroleum fractions. These acids, which are usually a mixture of various naphthenic acid homologues or alkylated derivatives thereof, are referred to hereinafter as petroleum naphthenic acids or simply as naphthenic acid. The thioether derivatives containing petroleum naphthenic acid radicals make especially suitable grease bases for lithium soaps.

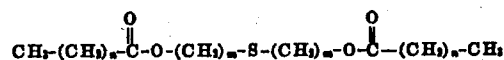
The groups R_2 and R_3 in the above general formula are either similar or dissimilar hydrocarbon radicals, especially aliphatic radicals which may be saturated or may contain one or more unsaturated linkages of olefinic or acetylenic character and furthermore may contain elements such as sulfur, nitrogen, phosphorus, selenium and tellurium. Preferably, however, each of these radicals is a saturated hydrocarbon radical, and still more preferably is a saturated straight chain hydrocarbon radical forming a primary linkage with the sulfur atom, giving the following general configuration:



wherein R_1 and R_4 are hydrocarbon radicals and R_2 and R_3 are saturated aliphatic radicals. Of this group of thio-ether derivatives, those having similar ester groups and similar aliphatic radicals form the most suitable grease bases and have the general formula:



When the grease bases have the above configuration, those giving the most satisfactory results have R_1 's which are saturated hydrocarbon groups having 4 to 11 carbon atoms, and R_2 's which are saturated straight chain hydrocarbons having 1 to 8 carbon atoms, and preferably from 2 to 5 carbon atoms to give the formula



in which n is an integer of from 3 to 10 and m is an integer of from 2 to 6. The outstanding grease bases having this latter preferred general formula are those in which m is an integer of from 2 to 4.

Compounds having this latter general formula are readily prepared by the reaction of hydrogen sulfide with an olefinic alcohol, such as allyl alcohol to give the bis-(gamma hydroxypropyl) sulfide. This in turn is esterified with an acid, such as trimethylacetic acid or 2-ethylhexoic acid, to give di-esters of thio-ether derivatives. A typical preparation is as follows:

Five hundred cc. allyl alcohol and 124 g. hydrogen sulfide were subjected in a bomb to the radiation from a 250 watt mercury arc lamp. During the first hour the pressure in the system rose steadily from 160 to 220 lbs./sq. in. after which it fell slowly to 170 lbs./sq. in. at the end of the radiation period. In this time the temperature of the reactor increased from 15° C. to 100° C., in part due to the exothermic character

5

of the reaction, but mainly from the heat emitted by the mercury arc lamp. The reaction product was then distilled to remove unreacted allyl alcohol and the gamma-mercaptopropyl alcohol formed during reaction, leaving the desired product, namely, bis-(gamma-hydroxypropyl) sulfide, which boils above 134° C.

In place of ultraviolet light, other free-radical promoting catalysts (preferably in the absence of metallic salts) may be used.

A mixture consisting of 150 grams of bis-(gamma-hydroxypropyl) sulfide, 432 grams of 2-ethylhexoic acid, 8 grams of para-toluene sulfonic acid and 400 cc. of toluene was heated to boiling under a separating still head. This heating was continued until no further water was distilled off. All of the toluene was then evaporated, and the remaining product was distilled to yield 0.865 (348 g.) moles of bis-(gamma-2-ethylhexoxypropyl) sulfide.

Other ingredients

Greases having the compositions of the present invention may be used in unmodified form, or may be compounded with several other materials as stated hereinbefore to give greases having preferred properties for specific purposes.

The subject greases may be modified by the inclusion of a free fatty acid, either similar to an acid radical of the esterifying group, or to the acid radical of the soap, or it may be of a dissimilar nature. The function of the free fatty acid appears to be that of a peptizing agent, giving the soap a better texture, and allowing the use of a smaller amount of soap than if the free fatty acid were absent. When a free acid is present, care must be taken that too much acid is not used, as the grease then becomes unduly soft for general use. Consequently, the composition should preferably contain from about 3% to about 30% (preferably 6% to 15%) lithium soap; from about 0.01 to about 1.0% (preferably 0.05% to 0.5%) free fatty acid; the remainder of the grease comprising the thio-ether derivative as specified hereinbefore.

The free fatty acid may be any within the fatty acid series, but preferably is a saturated fatty acid, such as lauric, myristic, palmitic, stearic, arachic, behenic, hydroxystearic, etc. The free fatty acid may be excess fatty acid added at the time of saponification in the sulfide base. Alternatively, the acid may be added to the thio-ether derivative prior to grease formation, or the grease may be modified therewith at any time prior to use.

Since the grease base is a thio-ether compound, it may show a tendency to oxidize under severe operating conditions, thus allowing the formation of decomposition products which may in time prove detrimental to optimum engine operation. Consequently an oxidation inhibitor, e. g., a phenolic compound or a substituted aromatic amine, may be added to the composition to improve its stability.

Phenolic materials which improve the greases of the present invention include mixed petroleum alkylphenols boiling from about 200° to about 240° C., 2,4-di-tertiary-butyl-6-methylphenol, pentamethylphenol, etc., as well as their homologues and analogues.

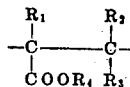
Aromatic amines which are of special utility in the present grease compositions are preferably the N-alkylated para-phenylenediamines or the polynuclear aromatic amines. These include N-butyl para-phenylenediamine, N-N'-dibutyl-

6

paraphenylenediamine, alpha- or beta-naphthylamine, phenyl-alpha- or beta-naphthylamine, alpha, alpha-, beta, beta-, or alpha, beta-dinaphthylamine, etc.

When the greases of the present invention contain these substituted phenols or amines, the compositions should comprise from about 4% to about 40% lithium soap (4% to 10% is preferred), and from about 0.01% to about 2.0% oxidation inhibitor (0.05-1% is preferred), the balance comprising the thio-ether derivative base defined hereinbefore.

When thio-ether derivatives of the above-described structure are gelled with a polymer of one or a mixture of esters of acrylic acid or of an alkylated derivative thereof, the compositions ordinarily obtained have a rubbery texture which has only limited utility as greases. However, when a minor amount of such an ester is incorporated in the compositions of the present invention, the resulting grease is substantially toughened, becomes substantially waterproof and is resistant to syneresis or solution at low and high temperatures, respectively. This toughened composition broadens the utility of the novel greases, since they thereby become useful for heavy duty purposes or where a water-proof grease is required. The acrylic acid ester polymers have structural units of the general structure



wherein R₁, R₂ and R₃ are either hydrogen or alkyl groups, and COOR₄ is an ester radical. Preferably R₁ is either hydrogen or a lower alkyl group, such as methyl, ethyl, isopropyl, butyl, isobutyl, amyl, etc., while R₂ and R₃ are preferably hydrogens. The most satisfactory degree of water-proofing is obtained when R₄ is an alkyl group having 3 or more carbon atoms, and preferably has 4 to 8 carbon atoms. Optimum results are obtained when the polymeric ester is a polymer of isobutyl methacrylate.

When the homologues and analogues of polymerized acrylic acid esters are used as water-proofing and toughening agents for the greases of this invention, optimum over-all results are obtained when the composition comprises the following ingredients:

Polymerized acrylic ester	0.1-10% (preferred 0.5%-4%)
Lithium soap	4-40% (preferred 4%-10%)
Thio-ether derivative	Balance (preferred 86%-95%)

Preparation of the grease and grease components

The lithium soaps are prepared by direct saponification of either fatty acids or of fats, which generally are glycerides of the fatty acids. The saponification is normally carried out by heating the fat or fatty acid with Li₂O, its hydrates, or LiOH. The lithium soaps thus formed, for example, at temperatures of about 100° C. usually contain a small amount of free fatty acid and water of neutralization. This latter may be removed by distillation, preferably at about 110° C. or at lower temperatures if reduced pressures are employed. In some greases its presence is not objectionable.

A second method of forming the lithium soap comprises mixing the fatty acid material with the thio-ether derivatives which comprise the grease base, and subsequently adding a normal lithium oxide, preferably in small amounts and at mod-

erate temperatures, so as to cause saponification of the fatty acid material, without allowing any substantial reaction to occur between the thio-ether derivative and the normal lithium oxide.

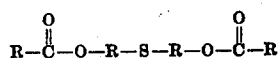
A unique process for the formation of the greases of the present invention comprises mixing a dihydroxyalkyl thio-ether and a fatty acid, causing esterification to take place, then adding a normal lithium oxide and proceeding as described in the paragraph above. The reaction may contain unreacted fatty acids, or dihydroxyalkyl thio-ethers and/or solvents which may be removed by distillation, extraction or other means subsequent to or during esterification of the dihydroxyalkyl thio-ether and the preparation of the lithium soap.

An alternative process which has been discovered comprises mixing the dihydroxyalkyl thio-ether and fatty acid material adding a normal lithium oxide at such temperatures and under such conditions that reaction will occur substantially only between the lithium oxide and the fatty acid, and subsequently adjusting conditions, so that esterification of the dihydroxyalkyl thio-ether takes place, either with remaining free fatty acid or with a subsequently added fatty acid. If necessary, the composition may be purified as noted above.

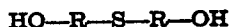
The simultaneous formation of the esterified dihydroxyalkyl thio-ether and of the lithium soap is also contemplated.

The best method of preparing the subject greases which involves no after-treatments or other steps such as dehydration, solvent removal, extraction of diluents or removal of excess reactants comprises the addition of a preformed lithium soap to a preformed dicarboxyalkyl thio-ether, usually at elevated temperatures to facilitate solution.

The thio-ether derivatives comprising the bases of the greases of this invention include those having the general formula:



These are usually prepared by the esterification of a dihydroxy thio-ether having the general formula:



The esterifying acid and dihydroxy thio-ether are usually purified by distillation, extraction, or usually heated together, preferably in the presence of an esterification catalyst and an inert solvent such as benzene, toluene, xylene, etc. The reaction may be carried out with continuous or intermittent distillation of water formed during the esterification, or may be conducted in the presence of a dehydration catalyst, such as zinc chloride. Subsequent to esterification, the product may be purified by distillation, extraction, or other means for the removal of water, solvent, catalysts, dehydration agents, and unreacted esterifying acid and/or dihydroxy thio-ether. The acids and dihydroxy thio-ethers, from which these esters are prepared, are listed in the section of this specification entitled "The grease base." A typical esterification also is described in the latter section.

Other ingredients which may be added include various corrosion inhibitors, extreme pressure additives, anti-wear agents, stabilizers, viscosity index improvers, and the like, provided they do not interfere with the operation and utility of the grease.

As pointed out hereinbefore, the lithium soap may be present in the subject greases to the extent of from about 4% to about 40% of the composition. Preferably, however, the soap concentration will be from about 4% to about 10%. When an aromatic amine, a substituted phenol, a free fatty acid, or a waterproofing amount of lithium naphthenate is present in the grease in the amounts described hereinbefore, the amount of lithium soap may be reduced, since each of these substances exerts a certain peptizing action of its own.

The greases of this invention are particularly applicable for lubricating mechanisms, including ball bearings, especially where mineral oil base greases have proved to be unsatisfactory. They are suitable for use in aircraft or for other purposes where unduly harsh conditions, either hot or cold, are encountered.

The following examples illustrate the products of the present invention:

Example I

A grease having a composition according to the present invention was prepared as follows:

Bis-(gamma-2-ethylhexoxyloxypropyl) sulfide was prepared as described hereinbefore. Substantially neutral lithium stearate was added to the sulfur compound while it was heated at about 185° C. The soap disperses at this temperature, after which it is rapidly cooled. The grease so formed was then homogenized to remove any lumps that might be present therein. Amounts of the ingredients were such that the grease contained 10% of lithium stearate and 90 per cent of the sulfide derivative. The grease was of buttery consistency at room temperature, and showed substantially no indications of syneresis. The buff-colored composition maintained suitable grease structure as high as 160° C.

Example II

Bis-(gamma-trimethylacetoxypopyl) sulfide was prepared by the method previously described for bis-(gamma-ethylhexoxyloxypropyl) sulfide, substituting trimethylacetic acid as the esterifying agent in place of 2-ethylhexoic acid. Ten parts neutral lithium stearate was dispersed in 90 parts of the sulfide at 185° C. The grease so formed was homogenized. It had a smooth texture which showed no tendency to synerize, was the color of cream, and had a satisfactory texture as high as about 194° C.

Example III

Using the mixed naphthenic acids derived from petroleum as the esterifying agent bis-(gamma-naphthenoxypropyl) sulfide was prepared. The esterification of bis-(gamma-hydroxypropyl) sulfide with this agent, was carried out by the process substantially as described hereinbefore for the preparation of bis-(gamma-2-ethylhexoxyloxypropyl) sulfide. The naphthenic ester was mixed with lithium stearate at 185° C. to form a 90:10 mixture of ester and soap. Upon rapid cooling followed by homogenizing the composition exhibited excellent grease properties, being light brown in color, showing no tendency to synerize, and maintaining its proper grease structure as high as 170-190° C.

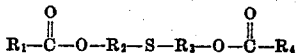
We claim as our invention:

1. A lubricating grease composition comprising as the major lubricating constituents thereof bis-(gamma-2-ethylhexoxyloxypropyl) sulfide and

9

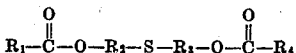
lithium stearate, from 4% to 40% of said major lubricating constituents being said stearate.

2. A stable lubricating grease composition comprising as the major lubricating constituents thereof a thio-ether derivative having the general formula

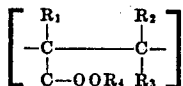


wherein R_1 and R_4 are hydrocarbon radicals, R_2 and R_3 are aliphatic radicals, a lithium soap, from 4% to 40% of said major constituents being said soap and an oxidation inhibitor.

3. A water-resistant lubricating grease composition comprising as the major lubricating constituents thereof a thio-ether derivative having the general formula



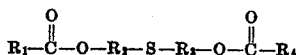
wherein R_1 and R_4 are hydrocarbon radicals, R_2 and R_3 are aliphatic radicals, a lithium soap and a minor amount of a polymer having recurring structural units of the general formula



wherein R_1 and R_3 are radicals selected from the group consisting of hydrogen and alkyl radicals, and COOR_4 is an ester radical.

4. A water-resistant lubricating grease composition according to claim 14, wherein the polymer is present in said composition in amounts from about 0.1 to about 10%.

5. A lubricating grease composition comprising as the major lubricating constituent thereof a thio-ether derivative having the general formula



wherein R_1 and R_4 are hydrocarbon radicals and R_2 and R_3 are aliphatic radicals, and a lithium soap from 4% to 40% of said major constituents being said soap.

6. A lubricating grease composition according to claim 5, wherein the lithium soap comprises lithium naphthenate.

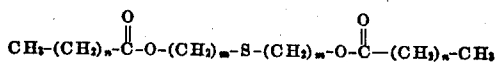
7. A lubricating grease composition according to claim 5, wherein the lithium soap is derived from a mono-olefinic fatty acid.

8. A lubricating grease composition according to claim 5, wherein the lithium soap is derived from a saturated fatty acid having at least 12 carbon atoms.

9. A lubricating grease composition according to claim 5, wherein the lithium soap contains at least 12 carbon atoms.

10. A lubricating grease composition according to claim 5, wherein the lithium soap comprises from about 4 to about 40% of said composition.

11. A lubricating composition comprising 4-40% of a lithium soap and, as the major lubricating component, a thio-ether derivative having the general formula

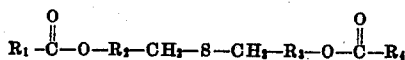


wherein m is an integer from 2 to 4, n is an integer from 1 to 4, the groups $(\text{CH}_2)_m$ are identical saturated straight chain radicals, and the groups $(\text{CH}_2)_n$ are identical saturated straight chain radicals.

12. A lubricating grease composition compris-

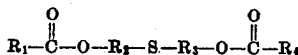
10

ing as the major lubricating constituents thereof a thio-ether derivative having the general formula



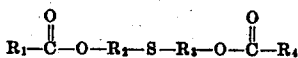
in which R_1 and R_4 are hydrocarbon radicals and R_2 and R_3 are saturated aliphatic radicals, and a lithium soap from 4% to 40% of said major constituents being said soap.

13. A lubricating grease composition comprising as the major lubricating constituents thereof a thio-ether derivative having the general formula



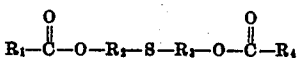
wherein R_1 and R_4 are hydrocarbon radicals and R_2 and R_3 are saturated aliphatic radicals, and a lithium soap from 4% to 40% of said major constituents being said soap.

14. A lubricating grease composition comprising as the major lubricating constituents thereof a thio-ether derivative having the general formula



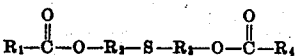
wherein R_1 and R_4 are saturated aliphatic radicals having from 4 to 11 carbon atoms and R_2 and R_3 are aliphatic radicals, and a lithium soap from 4% to 40% of said major constituents being said soap.

15. A lubricating grease composition comprising as the major lubricating constituents thereof a thio-ether derivative having the general formula



wherein R_1 through R_4 are saturated aliphatic radicals, and a lithium soap from 4% to 40% of said major constituents being said soap.

16. A lubricating grease composition comprising as the major lubricating constituents thereof a thio-ether derivative having the general formula



wherein R_1 through R_4 are aliphatic radicals, and a lithium soap from 4% to 40% of said major constituents being said soap.

ELLIS ROSS WHITE.
DENHAM HARMAN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,422,869	Kranzlein et al.	July 18, 1922
2,164,393	Evans	July 4, 1939
2,274,673	Earle	Mar. 3, 1942
2,274,674	Earle	Mar. 3, 1942
2,351,280	Morgan	June 13, 1944
2,351,384	Woods et al.	June 13, 1944
2,356,586	Hentrich et al.	Aug. 22, 1944
2,362,767	Morgan	Nov. 14, 1944
2,366,042	Morgan	Dec. 26, 1944
2,383,146	Morgan	Aug. 21, 1945
2,403,104	Lien	July 2, 1946