Feb. 24, 1953 R. C. BARTON ET AL 2,629,693

LUBRICATING COMPOSITION

Filed July 1, 1947 3 Sheets-Sheet 1

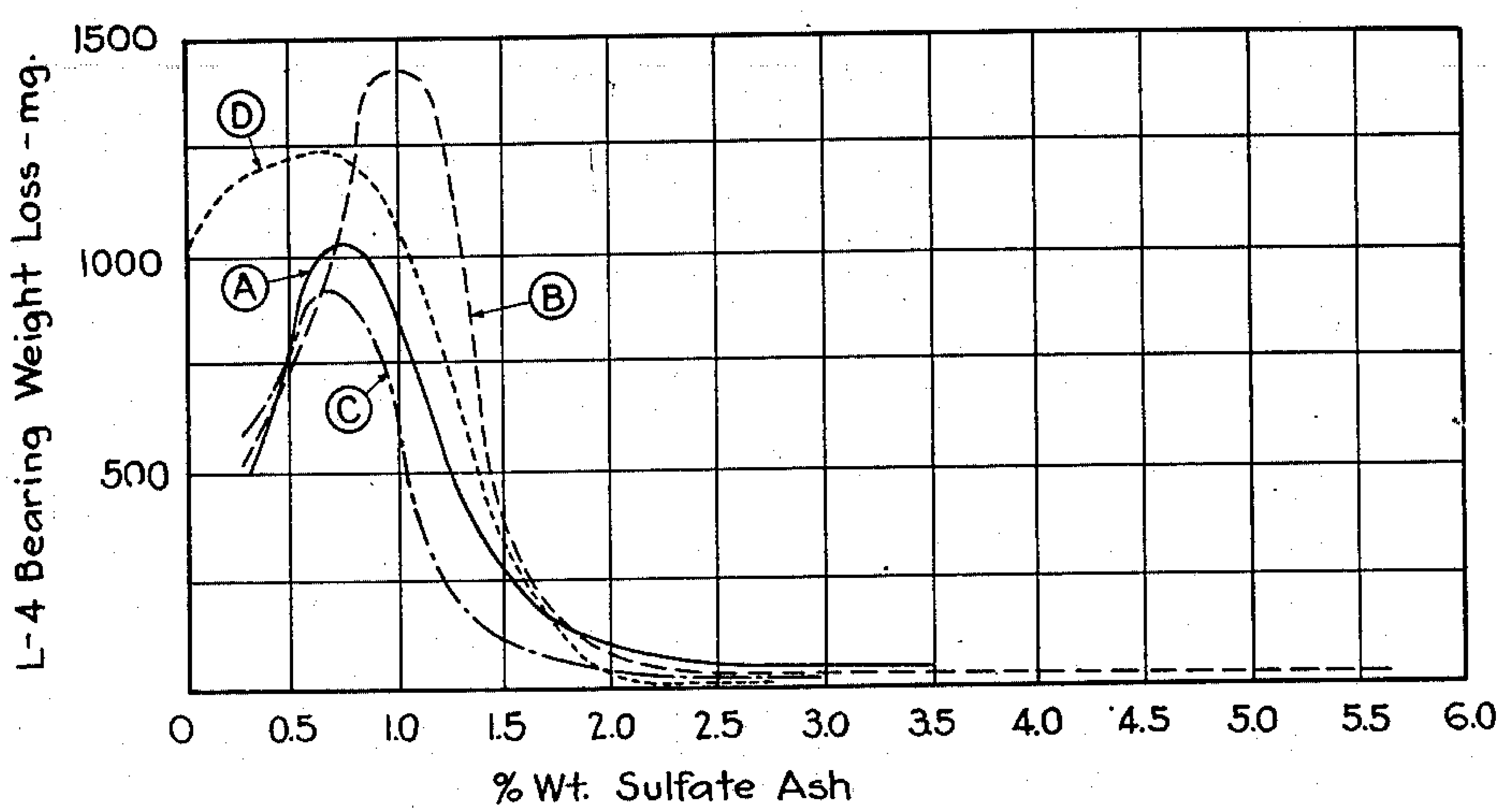

FIG. I

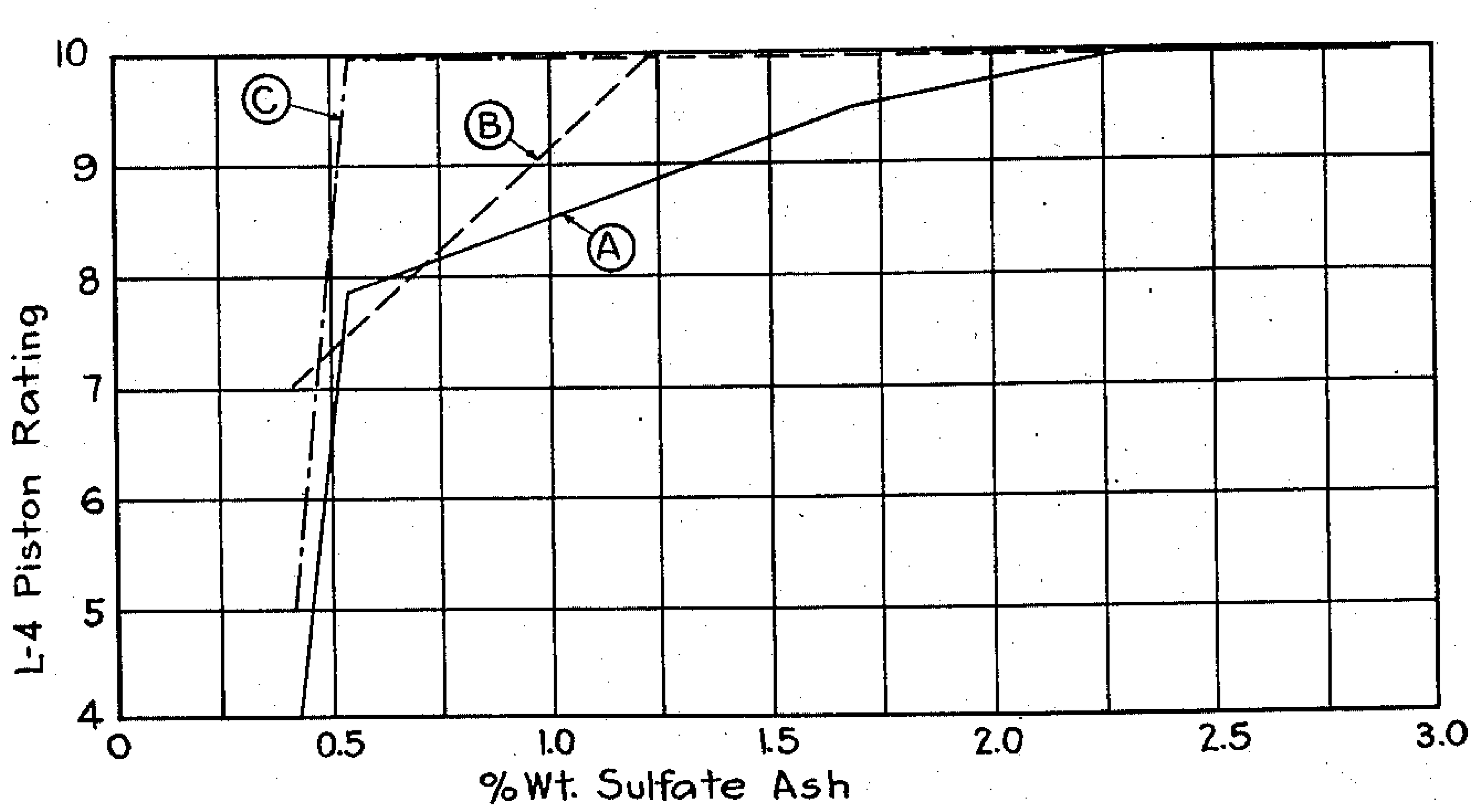

FIG. II

Ⓐ Neutral Calcium Petroleum Sulfonate + Phenyl-α-Napthylamine.

Ⓑ Basic Calcium Petroleum Sulfonate + Phenyl-α-Napthylamine.

Ⓒ Basic Calcium Petroleum Sulfonate + Phenyl-α-Napthylamine +2.6 Di Tertiary Butyl 4 Methyl Phenol.

Ⓓ Ca Salt of Alkyl Phenol-Formaldehyde Condensation Reaction.

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LUBRICATING COMPOSITION

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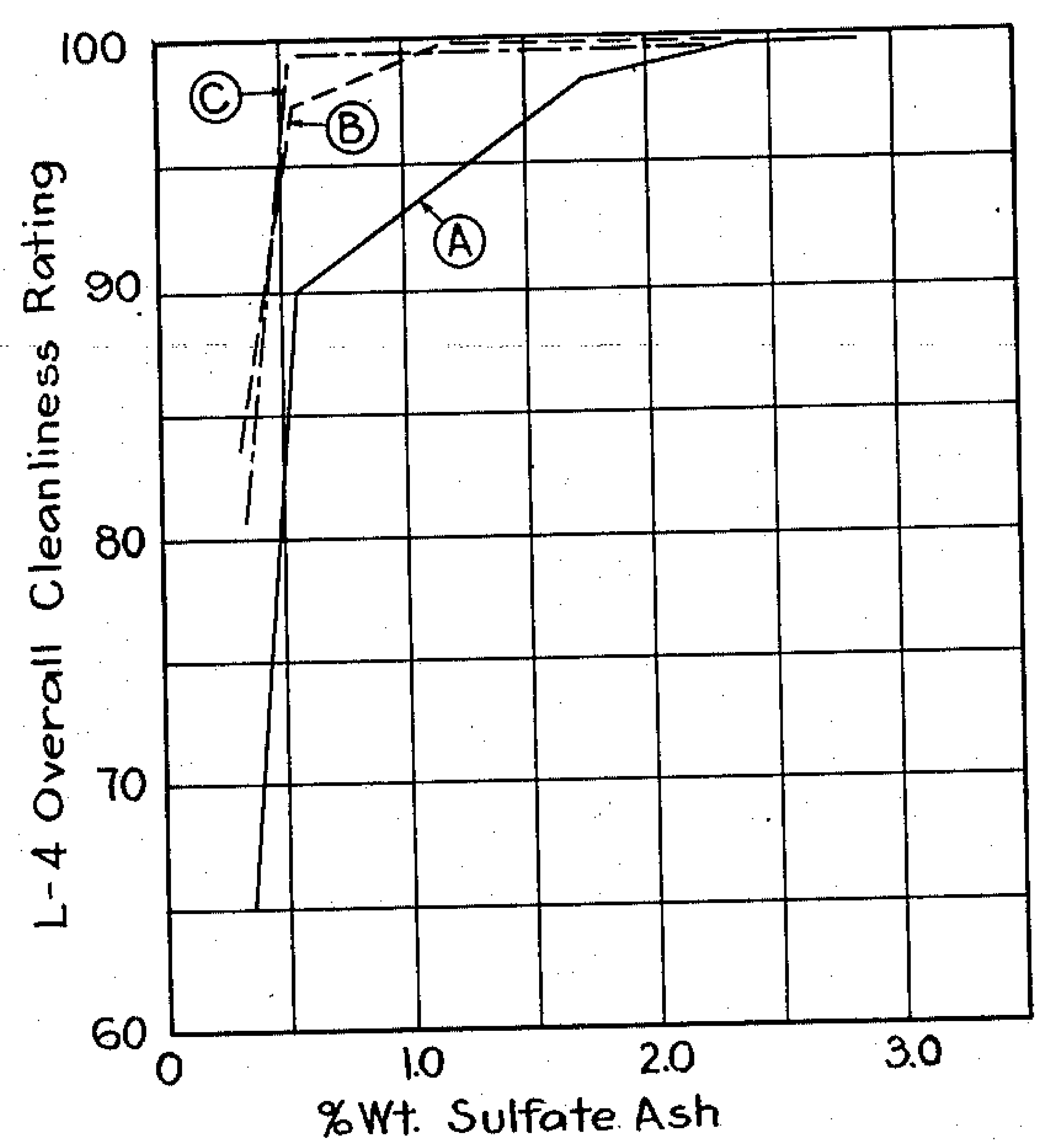

FIG. III

Ⓐ Neutral Calcium Petroleum Sulfonate + Phenyl-α-Napthylamine.

Ⓑ Basic Calcium Petroleum Sulfonate + Phenyl-α- Napthylamine.

Ⓒ Basic Calcium Petroleum Sulfonate + Phenyl-α-Napthylamine +2.6 Di Tertiary Butyl 4 Methyl Phenol.

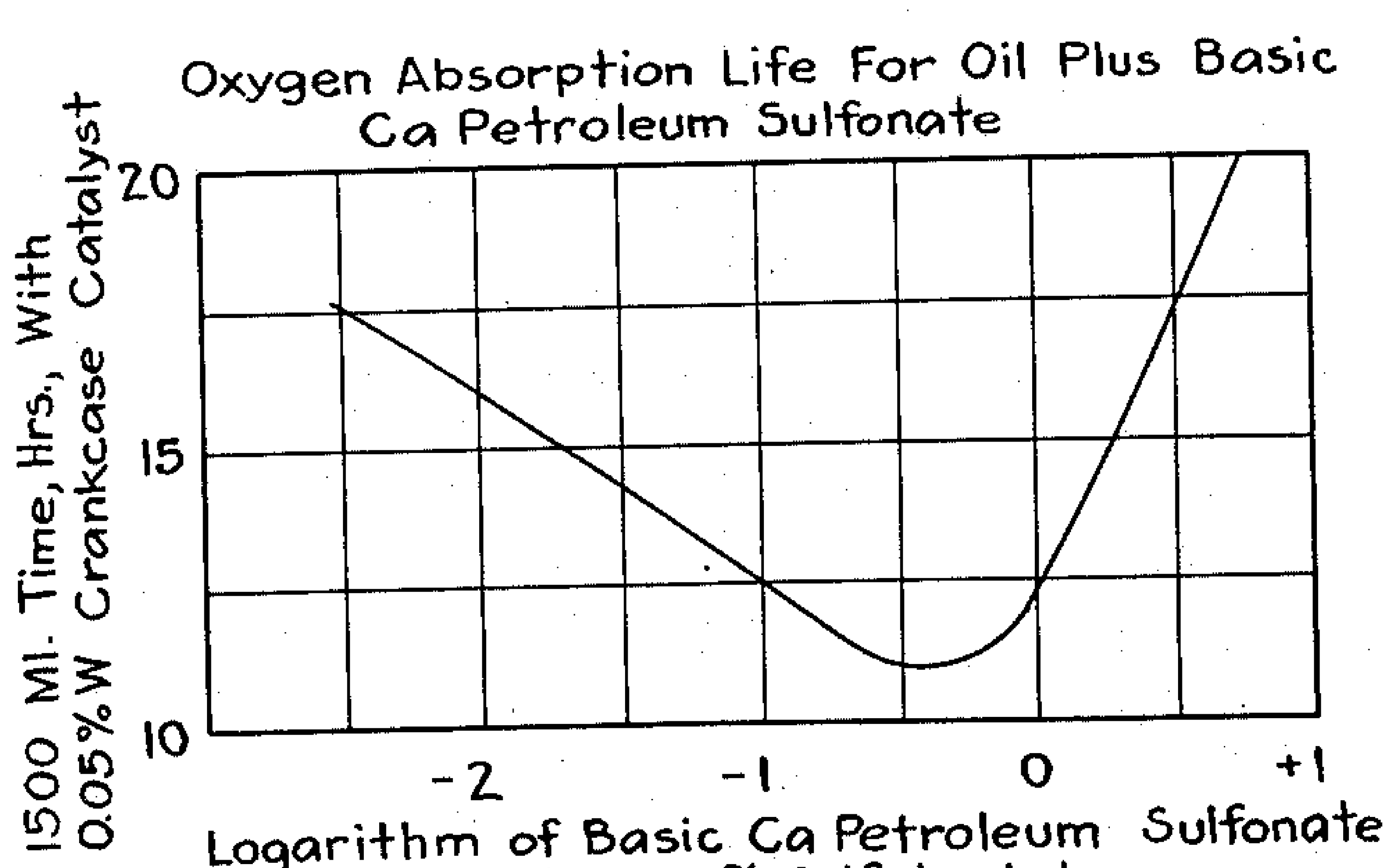

FIG. IV

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LUBRICATING COMPOSITION

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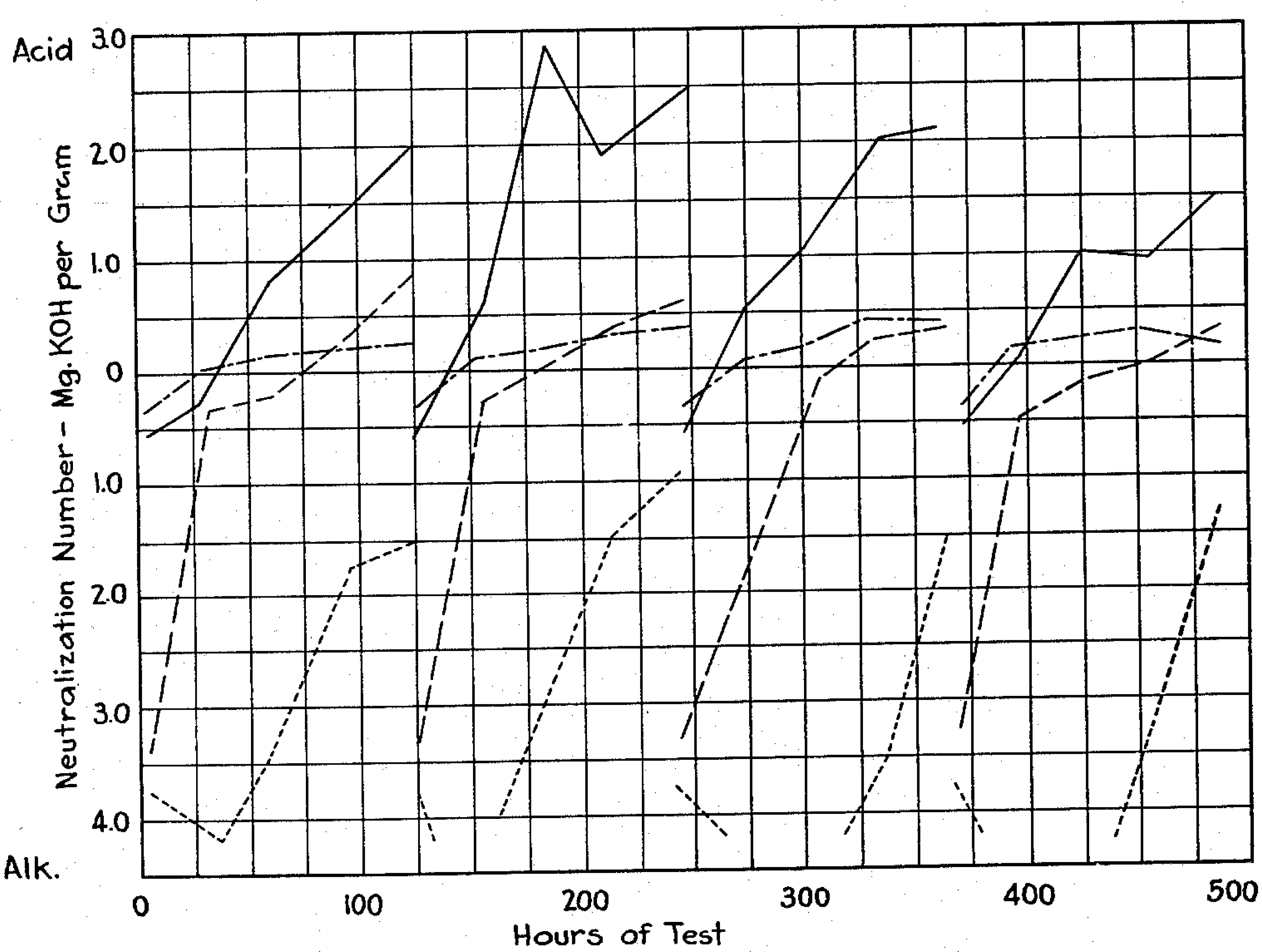

Development of Acidity During Low Temperature Caterpillar Test Using High Sulfur Fuel.

FIG. V

——— Acid Number-Reference Oil
– – – Acid Number-High Ash Oil
–·–·– Strong Acid No.-Reference Oil
------- Strong Acid No.-High Ash Oil

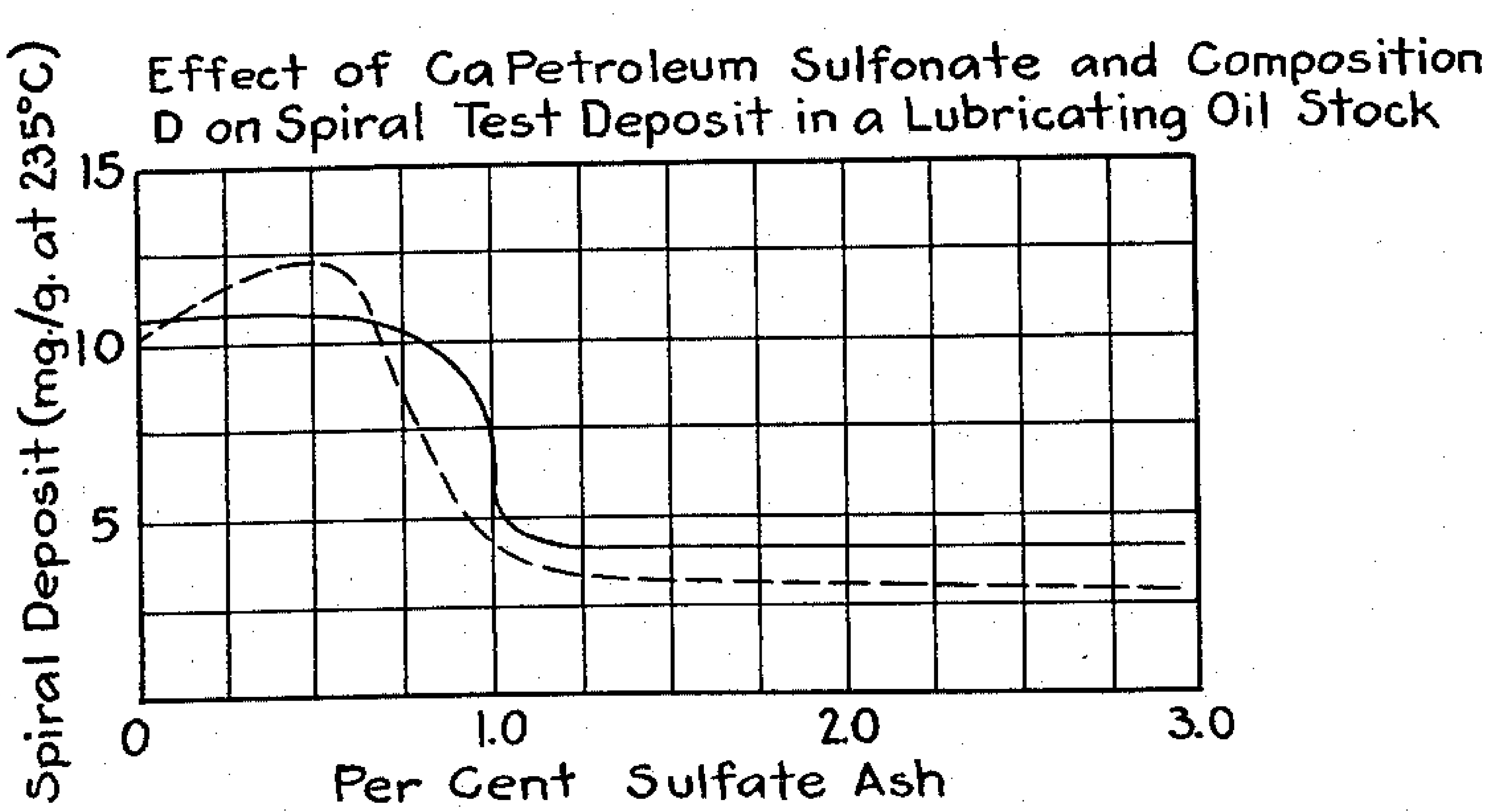

FIG. VI

——— Ca Petroleum Sulfonate
– – – Composition D

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UNITED STATES PATENT OFFICE

2,629,693

LUBRICATING COMPOSITION

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Application July 1, 1947, Serial No. 758,430

12 Claims. (Cl. 252—33.4)

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This invention relates to compounded lubricating compositions, suitable for use in substantially all types of industrial equipment, and particularly in engines operating under adverse conditions. Specifically, this invention pertains to engine lubricants compounded with ash-forming improving agents in amounts above a critical lower limit so as to impart to said lubricants outstanding lubricating properties.

It is well known in the art that lubricants whether doped or undoped, deteriorate and form corrosive bodies, sludge, varnish and other contaminants in engines whether operated under mild conditions (as characterized by low temperature and reduced load) or under extreme pressure conditions as characterized by high temperature, high speeds, high loads, and the like. Under either condition of operation, factors are encountered which contribute to oil deterioration with the formation of resultant products of contamination which causes corrosion, sludge, varnish and lacquer formations; this inevitably results in sticking, wearing, scuffing, scoring and even seizing of metal parts.

Engine fouling and wear under conditions of high temperature operation is generally attributed to oil deterioration caused by oxidation. Lubricating oils under such conditions tend to oxidize rapidly and form corrosive bodies and carbonaceous materials which cause scratching or scuffing of movable metal parts, sticking of valves, piston rings and the like. A condition which may accentuate and accelerate deterioration of lubricants is the presence of small amounts of moisture existing or formed in lubricants, or blowby vapors from fuel (especially if they are high sulfur fuels) which enter the lubricating system and form harmful deterioration products, and the like. The close tolerances to which engine parts are machined as well as the restricted clearances between various engine parts aggravate this condition and aid in the breaking down of the lubricant. This is due to the fact that varnish and/or lacquer coatings on various engine parts such as rings, valves, pistons, cylinder walls, etc., caused by oil deterioration, diminish side clearances, act as heat insulators; both conditions cause increased oil temperature, resulting in its further breakdown.

Lacquer formations are generally attributed to oil oxidation and are hard resinous materials having a tendency to adhere on metal surfaces and form thereon a hard deposit which blisters and on chipping acts as an abrasive capable of scratching surfaces and blocking oil passages.

High temperature and pressure oil decomposition products are highly corrosive, especially towards alloys such as copper-lead, cadmium-silver, etc. Other factors can also account for engine corrosion but they are complex in nature and varied in origin. Thus, acids, found or formed in oils or fuels may attack and corrode copper-lead bearings or the like. At elevated temperatures alloyed bearings are adversely effected by sulfur derived from certain of its compounds or found free in an oil or fuel. Under these conditions sulfur can produce hard brittle, black deposits on copper-lead or silver bearings. Such deposits may adhere and reduce the bearing clearance or they may break out and gouge out the bearing, in either event resulting in bearing failure.

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To withstand wear and protect bearing surfaces under the above stringent operating conditions, lubricants must possess so-called extreme pressure properties whereby the lubricant by forming a film of low shear strength by chemical action or physical adsorption on the contact points, prevents metal welding and seizure. Generally, lubricants are quite incapable of maintaining a continuous protective lubricating film between contacting metal surfaces, unless fortified with special agents possessing extreme pressuring properties. However, such extreme pressure agents when added in amounts to be effective generally increase engine deposits and cause wear because of their corrosive nature and activity.

Although oil oxidation is minimized in low temperature operation, engine fouling from other causes is very serious and aggravating. Engine deposits and sludge under these conditions are generally associated with oil insolubles originating from combustion of the fuel oxidation products. If high sulfur fuels are used, this condition becomes extremely serious, especially if small quantities of water and other contaminants enter the system. Low temperature deposit formations are referred to as mayonnaise emulsions which contribute to engine fouling and wear. The presences of mineral matter, carbonaceous materials also cause wear and contribute toward accelerating corrosivity of metal parts.

To improve the lubricating properties of mineral lubricating oils and synthetic lubricants it has become the practice to blend with or add to the various lubricants one and in most cases more than one, addition agents, which have the property of stabilizing and inhibiting deterioration of lubricants and impart certain beneficial properties to them. Thus additives have been specifically developed which have the property of inhibiting corrosion of alloyed bearings as utilized in automotive, diesel and aircraft engines. Additives have also been developed which possess the property of modifying the carbonaceous matter formed by deterioration of lubricants, so as to be easily removed. Other additives have been developed for the purpose of acting as detergents in lubricants in order to assist in the removal of soot, sludge, varnish, lacquer and the like. Detergents due to their cleaning and dispersing properties prevent the building of deleterious materials on surface and if formed assist in removing them. Still other additive agents have the properties of inhibiting wear, oxidation; impart oiliness, extreme pressure properties, act as solubilizers and the like.

It is an object of this invention to improve the lubricating properties of various lubricating bases by addition thereto of a substantial amount of improving agent and/or agents. Another object of this invention is to provide lubricants with dopes in such concentrations so as to obtain a stable, corrosion resistant product even when subjected to the most adverse operating conditions. Still another object of this invention is to provide a highly effective detergent lubricant capable of preventing ringsticking as well as sticking or seizure of other engine parts. It is also an object of this invention to provide an improved lubricant capable of preventing wear, scuffing, scratching and the like. Still another object of this invention is to provide a stable, non-corrosive, highly detergent heavy duty lubricant suitable for use under varied and adverse conditions. Other objects of this invention will appear as the description proceeds.

The art discloses the addition of dopes and improving agents to lubricants in rather very minor amounts particularly in the case of lubricants compounded with a metallic compound. This has been done apparently due to the belief that because of the pronounced activity of the additives or dopes, these latter if used in high concentrations would become contaminants rather than improving agents and therefore would act as abrasives, wear, sludge, lacquer corrosion promoters, and the like. Because of this and also because of the physical modifying effects dopes have on base lubricants, such as increased viscosity and the like, the addition of large quantities of dopes to lubricants has been frowned upon.

The addition of oil dopes in very minor amounts has been rigorously adhered to in the art; for example, U. S. Patents 2,375,222 and 2,410,652 state that any additives, such as detergents, when incorporated in lubricants should be in such small amounts as to leave substantially a non-volatile ash upon combustion, and that, at most, the total ash content should not exceed about 0.25% (determined as sulfate ash) and preferably should be below about 0.2% ash by weight. Furthermore, U. S. Patent 2,416,192 discloses that the maximum amount of metallic detergent dope which can be added to lubricants with safety should not be in excess of 0.42% ash, calculated as sulfate ash. Navy specifications for lubricating oils suitable for diesel engines and the like impose a rigid limitation as to the maximum ash allowable in lubricants. Thus Navy Department specification 14-0-13*a* places as a maximum allowable ash for diesel lubricants at 0.6% ash by weight. Lubricants containing an ash content above 0.6% ash heretofore have been regarded as unsuited because of the danger of increased corrosion, wear, etc., particularly in the case where metallic salts are used as the dopes.

The desirability of keeping the ash content of lubricants at a minimum, namely, below 0.6% and

preferably below 0.2%, appeared to be a critical limitation substantiated by facts. Thus, within the ranges actually tested heretofore, numerous performance tests such as the CRC tests L1, L2, L3, L4 and L5, as well as actual field tests, disclosed that as the ash content increased, corrosivity also increased at an alarming rate. For example, it was shown that by increasing the concentration of a metallic detergent in a lubricant from 0.2% to about 0.6% wt. ash, corrosivity increased by over 300%. The addition of corrosion and/or oxidation inhibitors had little effect on stabilizing or inhibiting corrosivity due to increased amounts of ash forming dopes present. Since such general alarming results were consistently obtained with lubricants containing ash-forming additives in concentrations approaching 0.6%, the practice of doping lubricants with such additives in very low concentrations, such as around about 0.2% wt. ash, has been rigorously adhered to.

It has now been discovered that improved engine performance can be obtained by doping the base lubricant with additives employed in concentrations capable of forming ash in amounts exceeding at least 1.0% by weight, and up to such large amounts that the only limiting factor is the change in viscosity characteristics of the base lubricant which render it unsuited for engine lubrication. Stated somewhat differently, it has now been discovered that the corrosivity and instability of doped lubricants capable of forming an ash increases with increased concentrations up to a maximum, this range being between 0.2 and about 0.8% and higher. However beyond this maximum value, namely beyond about 1.0% ash, lubricants become more stable, corrosion progressively decreases, and cleanliness as well as general engine performance is improved. The most efficient range for doped lubricating oils is when the additive or additives are in a concentration such that their amounts are between about 1% and about 10% by weight and preferably between about 1.0 and 4% by weight as calculated on the ash basis. With ash forming additives which have little effect on viscosity or gellation of the base lubricant, amounts exceeding 10% and even above 50% by weight ash may be used.

The term "ash forming materials" comprises such ingredients which if ignited per se or as an oil concentrate, will produce an ash free of carbonaceous matter. If certain metallic salts such as of sodium, calcium, etc. are present, the percentage ash may be expressed as percentage of ash as sulfate, while with zinc and aluminum the percentage of ash is expressed as percent oxide ash. This basis of calculation can be accomplished by acidifying the sample tested with dilute sulfuric acid, igniting the sample to free it of carbonaceous matter and expressing the residue as percent sulfate ash. Thus, for example, the following procedure may be followed to determine the amount of ash residue in an oil sample containing a minor amount of calcium petroleum sulfonate. A small portion of the sample may be heated in a crucible allowing the combustible material to burn slowly, igniting the residual ash to free it of carbon and adding a few drops of surfuric acid to convert any reduced calcium sulfide, etc. to sulfate, re-igniting and weighing the residue, which is reported as percent sulfate ash. It is therefore to be clearly understood that all values above and henceforth referred to are on the percent ash basis such as percent sulfate ash in the final product and not the percent by weight or volume of a dope concentrate, which can be further diluted or the final percent by weight of a dope in an oil. The above is substantially the method described in the ASTM (ES-43) of 1945.

Broadly stated this invention relates to improving lubricants by addition thereto of ash forming metallic detergents in amounts exceeding 1.0% by wt. calculated on the ash basin. The metallic detergent salts may be represented broadly by the partial general formula

$$-X-M, \quad -X-M-QH, \quad \text{or} \quad \begin{matrix} X \\ \quad \diagdown \\ \quad\quad M \\ \quad \diagup \\ X \end{matrix}$$

wherein M is a metal or cationic portion of the salt; X is a part of the anionic portion of the salt to which M is linked to form the metallic salt; and Q is an element of the group of O, S, Se and Te.

The metal parts in the above class of compounds may be:

Group 1

lithium
sodium
potassium
rubidium
cesium
copper
silver

Group 2

beryllium
magnesium
calcium
zinc
strontium
cadmium
barium

Group 3

aluminum
gallium
indium
thallium

Group 4

titanium
zirconium
tin
lead

Group 5

vanadium
antimony
bismuth

Group 6

chromium
molybdenum
tungsten

Group 7

manganese

Group 8

iron
cobalt
nickel

The acid-forming part in the above class of compounds may be:

Benzene sulfonic acid
Toluene sulfonic acid
Tri isopropyl naphthalene sulfonic acid
Diphenyl sulfonic acid
Polyalkyl aromatic sulfonic acid, e. g.
Poly amyl naphthalene sulfonic acid
Diwax benzene sulfonic acid
Xylene sulfonic acid
Benzene disulfonic acid
Alkane sulfonic acids, e. g. amyl, octyl, nonyl, lauryl, dodecyl sulfonic acids
Petroleum sulfonic acids derived from various petroleum fractions such as:
- gas oil
- kerosene
- light oil
- turbine oil
- mineral lubrication oil
- heavy oil
- petroleum waxes, e. g.:
  - petrolatum
  - paraffin wax and mixtures of various hydrocarbon fractions
- wax sulfo salicylic acid
- diwax naphthalene sulfonic acids, etc.

Petroleum sulfonic acids are produced by treating suitable petroleum hydrocarbon fractions with sulfuric acid. For example, a turbine oil having a Saybolt universal viscosity at 100° F. of from about 400 to 540 seconds is treated with fuming sulfuric acid, preferably in small increments. After a calculated amount of sulfuric acid has been added to the oil, the sludge which forms is removed and the acid-treated oil containing dissolved oil-soluble sulfuric acid is neutralized with a solution of sodium hydroxide. The aqueous alkali solution is removed from the mixture and the sodium salts of petroleum sulfonic acid extracted with alcohol. The alcohol layer containing the sulfonates can be removed by distillation or by any other suitable means.

Modifications to the above procedure can be made by removing acid sludge after the entire required amount of acid has been added. Also the sulfonic acid can be removed before neutralization rather than after as indicated above. If this is done, it is preferable to give the acid treated oil a clay treatment so as to remove inorganic esters of sulfuric acid and other impurities so as to prevent formation of inorganic salts. Clays which are particularly suitable are highly adsorbent clays such as Attapulgus clay, Floridin, bentonite, bauxite, fuller's earth, etc. Still another modification in preparing pure oil-soluble sulfonates is to add to the sludge free acid-treated oil a solvent such as benzol, carbon tetrachloride, and the like and to neutralize said mixture with a caustic solution. The spent caustic solution is removed. The solvent is distilled off, leaving a substantially pure sulfonate in oil mixture. The product can be air blown and dehydrated to remove impurities. Instead of sulfonating a mineral oil alone a small amount of waxy material may be added to obtain a more improved sulfonate. The sulfonic acids may be formed by acidifying the neutralized sulfonate or a particularly desired salt of a sulfonic acid may be obtained by double decomposition.

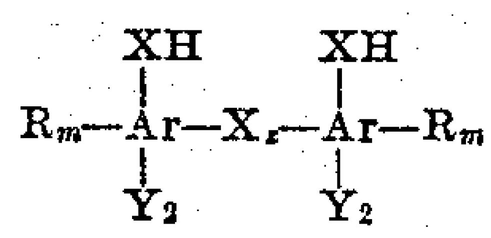
Other oil-soluble organic sulfonic acids may be produced by sulfonating alkyl aromatic hydrocarbons, such as alkyl benzenes, alkyl naphthylenes, alkyl anthracenes, alkyl phenanthrenes, alkyl picenes, alkyl chripenes, alkyl diphenyls, etc., provided the number of carbon atoms in the alkyl chain or chains is sufficient to render the resulting sulfonic acids and their salts soluble in the base. It is desirable that at least one alkly radical be relatively long, i. e. contain at least 8 or more carbon atoms, not only because of solubility in oils, but also for the reason that long alkyl chains improve the anti-ringsticking efficiency of the salts formed with the sulfonic acids. Thus, one may produce an aromatic hydrocarbon suitable for the production of highly efficient sulfonic acids by condensing chlorinated paraffin wax, alkyl chlorides such as octyl, decyl, cetyl, etc.; chlorides, fatty alcohols, long chain olefins such as may be obtained in the cracking of wax, etc., with aromatic hydrocarbons by means of suitable condensing agents such as Friedel-Crafts catalysts, sulfuric acid, phosphorus pentasulfide, phosphoric acid, etc. Sulfonic acids may contain substituent radicals as for example, paraffin wax substituted naphthalene mono sulfonic acids which contain a sulfonic radical attached to one ring of the naphthalene nucleus and a hydroxy or amino radical attached to the other ring.

Phenolic compounds (R—Ar—X—H) wherein

Ar is an aryl nucleus, X is O, S, Se, Te and R is a substituent non-polar and/or polar groups:

Phenol
Alkyl phenol
Dibutyl phenol and its thio phenols
Amyl phenol and its thiophenols
Tertiary butyl
p-Tertiary amyl
Octyl
p-Iso-octyl
Isobutyl
Nonyl
Cetyl phenols and thio phenols
Alkylamino phenol
Alkyl amino naphthol
Catechol
Resorcinol
Pyrogallol

All of these compounds may contain substituent groups as listed under VII B and the like. Substituted products are: hydroquinone, quinone, orcinol, phloro-glucinol, cresols, thymol, saligenin, cinnamyl alcohol, methyl phenyl carbinol, eugenol, cardanols, etc. Also the thio phenolic derivatives of these phenolic compounds may be used as well as various reaction products thereof such as obtained by reacting phenolic compounds with: SCl_2, S_2Cl_2, H_2S, ammonium hydro sulfide —H_2S, S, SO_2 and the like to form sulfide derivatives which may be represented broadly by the formula:



wherein Ar is an aryl nucleus, R is an alkyl, arylalkyl radical and the like, X is O, S, Se or Te and u is an integer of from 1 to 4, and Y may be a polar radical such as listed under VII B either or both m and x on the Ar group may be zero or an integer of 1 or 2.

Phenolic condensation products may also be formed by reacting products under group IX with aldehydes of the aliphatic, aromatic or cyclic type, specifically represented by formaldehyde, acetaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde; furaldehyde and the like. The condensation reaction is carried out at rather an elevated temperature using an acid or basic catalyst. Typical condensation reaction products may be formed between:

Octyl phenol-formaldehyde
Octyl phenol-acetaldehyde
Iso octyl phenol-acetaldehyde
Iso octyl phenol-crotonaldehyde
Octyl phenol-benzaldehyde
Octyl phenol-furaldehyde
Octyl thio phenol-furaldehyde
Octyl thio phenol-formaldehyde
Amyl phenol-formaldehyde
Amyl phenol-furaldehyde

Any of the above metallic salts may be used as well as mixtures of these salts in lubricants which may if desired be doped with corrosion and/or oxidation inhibitors.

The following table gives typical examples of preferred normal or inner basic metallic salts which give outstanding lubricating properties when used in high concentrations so as to form a high ash, such as above 1% by weight ash and preferably above about 1.5% and up around about 2.5% ash. Greater quantities of the salts may be used provided the addition does not increase the viscosity of the base lubricant above that generally suitable for engine lubricating. Mixtures of these salts may be used and the percentage ash may be expressed either as percent sulfate ash, percent oxide ash or as percent ash.

Cation part

Lithium	Vanadium
Sodium	Bismuth
Calcium	Chromium
Barium	Molybdenum
Magnesium	Manganese
Strontium	Iron
Aluminum	Cobalt
Tin	Nickel
Lead	

Acid part

Petroleum sulfonic acid
Triisopropyl naphthalene sulfonic acid
Diaryl naphthalene sulfonic acid
Diwax benzene sulfonic acid
Diwax naphthalene sulfonic acid
Benzene disulfonic acid
Lauryl sulfonic acid
Cetyl phenol sulfide
Octyl phenol sulfide
Octyl thio phenol sulfide
Phenol-formaldehyde
Condensation product
Octyl phenol-formaldehyde condensation product, etc.

Although new and outstanding improved results are obtained by adding to lubricants metallic detergents in amounts sufficient to form an ash of above about 1.0% and preferably above about 1.5 and 2.0% and up to above 2.5% ash or sulfate ash by weight, it is desirable under specific lubricating conditions to admix with said high ash forming metallic detergent doped lubricants minor amounts of a corrosion inhibitor and/or an anti-oxidant.

The corrosion inhibitors which may be used with high ash forming metallic detergents of this invention are:

Inhibitors

(I–*a*).—Organic amines (aromatic, aliphatic, alkylaryl, cyclic, heterocyclic amines and their mixtures):

Paraphenylene diamine
Alpha-naphthylamine
Orthophenylene diamine
Beta-naphthylamine
5-dibeta-naphthyl para phenylene diamine
2,4-diamino diphenylamine
Meta toluylene diamine
2-amino-1,4-naphthohydroquinone
4-amino-1,2-naphthohydroquinone
Thiodiphenylamine
Monobenzyl para amino phenyl
2,4-diamino toluene
2,4-diamino diphenyl amine
Para amino ozobenzene
Octadecyl benzyl amine
Beta phenylamine-alpha-naphthylamine
Phenyl-α-naphthylamine
Phenyl-B-naphthylamine
N,N′ dibutyl para phenylene diamine
Tetra methyl diamino diphenyl methane
p,p′-diamino diphenyl methane
4,4-diamino diphenyl methane
Tetraethyl diamino diphenyl methane
Diisoamyl diamino diphenyl methane

Bis - (B - naphthyl amino methyl) -p-tertamyl phenol
3,3,5 tricyclohexylamine
Dicyclohexylamine
N-phenyl morpholine
N-(parahydroxyphenyl) morpholine
Octadecyl 3-methyl-2-pentylamine
N-octadecyl-2-ethylhexylamine
Hexadecylamine
Octadecylamine
Octadecenylamine
Octadecadienyl amine
Paraffin waxamine
Cocoamine prepared from cocoanut oil acids
N,N'-dimethyl triglycol diamine
Disalicylal ethylene diamine
N-salicylal-N'-ethanol-ethylene diamine
5 methyl
2,4-diamino anisole
Ketone diarylamine
Ketone amine
Ketone amine condensation products
Butyaldehyde aniline derivatives
Condensation products of acetone and aniline
Reaction products of acetone and para amino diphenyl

In addition to the above amine compounds the following mixtures of amines produce good stabilizers:

Mixtures of diphenyl paraphenylene diamine and isopropoxydiphenylamine
Phenyl-α-naphthylamine and meta toluylene diamine
Mixture of dipara methoxy diphenyl amine
Diphenyl para-phenylene diamine and phenyl beta naphthyl amine
Mixtures of phenyl-B-naphthylamine and meta toluylene diamine
Mixture of diphenyl para phenylene diamine and para phenylene diamine
Mixture of stearic acid, meta toluylene diamine and phenyl-α-naphthylamine
Mixture of ditolylamine and petroleum wax, toluidines, xylidines, cymidine, cumidine, pseudo cumidine and the like.

The amines which are particularly preferred are:

Phenyl-α-naphthylamine
Phenyl-B-naphthylamine
Beta phenylamine-alpha-naphthylamine
Tetra methyl diamino diphenyl methane
Meta toluylene diamine, and their mixtures

(I–b).—Polycarboxylic acids:

Octyl succinic acid
Alkyl alkylene malonic acid
Alkyl alkylene thiomalonic acid
Alkyl alkylene glutaric acid
Alkyl alkylene tartaric acid
Alkyl alkylene citric acid
Cyano stearic acid
Cyano palmitic acid
Distearic acid sulfide
α-Hexadecyl thio glycolic acid
P-phenylene dithio distearic acid, etc.

(I–c).—Partial esters of polyhydric alcohols:

Glyceryl mono oleate
Glycol mono propionate
Glyceryl mono stearate
Diaryl maleate
Glyceryl mono ricinoleate
Diaryl succinate
Sorbitan mono oleate
Diamyl tartarate
Sorbitan mono stearate
Sorbitan mono ricinoleate
Erythritol mono oleate
Erythritol mono stearate
Mannitol mono oleate
Diamyl oxalate

(I–*d*).—Sulfur compounds:

Sulfurized oleic acid
Sulfurized sperm oil
Sulfurized cotton seed oil
Sulfurized wax olefins
Dibenzyl disulfide
Bis methylene phenyl sulfide
Bis methylene tolyl sulfide
Butyl arsine disulfide
Thiobenzanilide
Sulfurized mono or dihydric esters of linoleic acid
Triphenyl arsine sulfide
Sulfo-chlorinated mono esters of fatty acids e. g. reaction product of sperm oil and sulfur chloride
Thiobenzophenone

(I–*e*).—Compounds containing phosphorus:

Triphenyl phosphite
Tricresyl phosphite
Tributyl phosphite
Tricresyl phosphate
Diethyl phenylphosphinate
Ethyl diphenyl phosphinate
Naphthenyl phosphite
Reaction products of substituted phenol + PCl_3 tricyclohexyl phosphite
Esters containing trivalent P, e. g.

$$\begin{array}{c}\text{R—CH—COOR'}\\ |\\ \text{—P—}\end{array}$$

(I–*f*).—Compounds containing both sulfur and nitrogen:

O-nitro phenyl thio ethers
O-amino phenyl thio ethers
Thio cyano ethers and thio ethers

$$\begin{array}{c}\text{R—CH—X—R'}\\ |\\ \text{Y}\end{array}$$

where X is O or S, and Y is —CNS or —NCS, e. g. amyl thiocyano methyl ether

Thiobenzanilide
Substituted thiazines and thiazoles e. g. triphenyl thiazole
Compounds containing N═C—S— group in ring, e. g. mercapto benzothiazole
Dianiline disulfide
Thio and isothiocyanates e. g. lauryl thio and isothiocyanate
N-substituted morpholines e. g. N-amyl morpholine
Di morpholine polysulfides

(I–*g*).—Compounds containing both sulfur and phosphorus:

Reaction products of phosphorus sulfide and a phenol or a polyolefin
Thioesters of phosphinous, phosphinic and thiophosphinic acid
Phosphatide e. g. lecithin, etc.

(I–*f*).—Alkyl substituted hydroxy aromatic compounds represented by the general formula:

$$\begin{array}{c}Y_m\\ |\\ R_n\text{—Ar—OH}\end{array}$$

wherein *Ar* is an aromatic radical, R is an alkyl, alkoxy arylalkyl radical, Y is an organic polar radical, m may be zero or integer of 1 or 2 and n is an integer of 1 to 3. Particularly preferred anti-oxidants are the polyalkyl phenols in which the alkyl groups are attached at the 2,6 or 2,4,6 positions. The alkyl radicals which occupy the ortho positions may be methyl, ethyl, n- and isopropyl, n-, iso, secondary and tertiary butyl, primary, secondary or tertiary amyl, hexyl, heptyl, octyl and homologous radicals. Examples of such polyalkyl phenols are:

2,4,6 trimethyl phenol
2,6 dimethyl phenol
2,4 dimethyl-6-secondary butyl phenol
2,4 dimethyl-6-tertiary amyl phenol
2,4 dimethyl-6-tertiary octyl phenol
2,4 dimethyl-6-tertiary butyl phenol
Alpha and beta naphthol
4-tertiary butyl catechol
p-Benzyl amine phenol
Hydroquinone, vanillin, diisobutyl phenol
Pyrogallol
Guaracol
Thymol
Resorcinol
Cinthaquinone
Di-tertiary-butyl-meta-cresol
2,5 ditertiary butyl hydroquinone
Tertiary octyl phenol
Tertiary butyl ether of o-tertiary p-cresol
Cardanol
Bis-(B-naphthylamino methyl)-p-tertiary amyl phenol

(I–*g*).—Phosphorus containing organic compounds:

Phosphatides
Chepalin
Lecithin

(I–*h*).—Organic acids, other than those listed under (I–*b*):

Gallic acid	Phthalic acid
Tannic acid	Uric acid
Cinnamic acid	Fureic acid
Benzoic acid	Abietic acid
Salicylic acid	

(I–*i*).—Sulfur compounds:

Thiodiphenyl amine	Phenyl sulfide
Methyl phenyl disulfide	Phenyl disulfide
Ethyl sulfide	Benzyl disulfide, etc.
Benzyl sulfide	Wax disulfide

(I–*j*).—Terpenes:

Pine oil
Rosine oil
Turpentine oil, etc.

(I–*k*) Organic compounds containing halogen e. g.:

Halogenated diphenylene oxide
Halogenated acid-diphenylene oxide condensation product
Condensation product of two halogenated fatty acids
Condensation product of halogenated wax halogenated organic acid
Halogenated wax condensation product
Halogenated ring compound such as o-dichlorobenzene
Halogenated hydrocarbons e. g. chlorinated hexane
Chlorinated diphenyl benzene
Mono and dichloro derivatives of xylyl-, phenyl-, decyl-, and tolyl hepta decyl ketone
Halogenated naturally occurring esters e. g. chlorinated carnauba wax
Halogenated alkylated aromatic e. g. alkylated toluene
Halogenated petroleum wax
Halogenated aliphatic alcohol
Halogen containing derivatives of diphenyl ether e. g. chlorinated diphenyl ether
Product made by chlorinating a petroleum coal, tar or wood distillate and removing less stable constituents by treatment with $AlCl_3$
Polychlorinated naphthol
Chlorinated resorcinol
Chlorinated cottonseed or castor oil
Chlorine derivatives of polyisobutylene
Halogenated nitrite derivatives from petroleum acids
Tetrachloriobibenzyl or similar compounds
Chlorinated Edeleanu extract
Halogenated nitrile derived from paraffin wax
Halogenated aromatic aldehydes
Halogenated dibutyl phthalate, etc.

The amount of anti-oxidant and/or corrosion inhibitor if added to a base oil containing a metallic detergent in amounts sufficient to form an ash at least above about 0.8%, is generally less than 1% by weight, although greater quantities may be used. The preferred range is between about 0.1% and up to about 5% by weight, depending upon the oil base, concentration of the metallic detergent and condition of use.

Base oils may be selected from a wide variety of natural oils such as paraffinic, naphthenic and mixed base oils having a wide viscosity range, such as a minimum of 90 at 130° F., S. U. S. up to 250 at 210° F., S. U. S. In addition synthetic oils may be used such as polymerized olefins; copolymers of alkylene glycols and alkylene oxides; organic esters, e. g. 2-ethyl hexyl sebacate, dioctyl phthalate, trioctyl phosphate; polymeric tetra hydrofuran; polyalkyl silicon polymers, e. g. dimethyl silicon polymer, etc. Mixtures of natural and synthetic oils can be used also. Under certain conditions of lubrication minor amounts of a fixed oil such as castor oil, lard oil and the like may be admixed with a hydrocarbon oil and/or with a hydrocarbon oil-synthetic oil mixture.

To more fully illustrate the present invention the following are a few examples of compositions of this invention which have been compounded in high concentrations with ash forming metallic detergents and inhibited against corrosion and/or stabilized against oxidation deterioration and found extremely effective for heavy duty lubrication. The base oil used for test purposes was an SAE 30 oil having a viscosity index of 55. High ash containing compositions of this invention passed the CRC tests L–1, L–2, L–3 and L–4 as described in the CRC handbook under the chapter describing engine oil tests. For purpose of illustration the following test results of oil compositions of this invention are listed when subjected to a CRC test L–4–545, which is a 36-hour test in a Chevrolet engine using the following conditions:

	Minimum	Maximum	Average
Engine speed, R. P. M.	3,130	3,165	3,150
Engine load, B. H. P.	29.8	30.5	30
Oil Temp. in Sump., °F	277	284	280
Oil pressure, p. s. i.	13.5	14.1	13.8
Jacket outlet coolant temp., °F	197	203	199
Exhaust pressure, in Hg	0.7	0.9	0.8
Intake depression, in Hg	12.2	12.8	12.5
Fuel consumption, sec. per 300 cc	70.0	72.9	71.3

The following table shows the effect of increased concentration of an ash forming detergent on the average bearing weight loss, piston rating and overall rating, said ash containing base oil being inhibited with an anti-oxidant and/or corrosion inhibitor.

TABLE I

BASIC OIL 600 SUS AT 100° F. MOTOR STOCK

Normal Calcium Salt of Petroleum Sulfonate, Percent Sulfate Ash	Basic Calcium Salt of Petroleum Sulfonate, Percent Sulfate Ash	Phenyl-α-Naphthylamine, Percent Wt.	2,6 ditert. butyl 4 methyl phenol, Percent Wt.	Bearing Weight Loss, mg.	Piston Rating	Overall Rating	Visc. inc. at 100° F. Percent
0.3	--------	0.2	--------	501	4	66	82
0.6	--------	0.2	--------	872	8	90.5	100
0.9	--------	0.2	--------	1,000	8	90.5	100
1.2	--------	0.2	--------	516	------	99.5	96
1.7	--------	0.2	--------	197	9.5	99.5	80
2.3	--------	0.2	--------	70	9.5	99.5	80
--------	0.3	0.2	--------	532	7¼	84.5	80
--------	0.6	0.2	--------	750	8¼	92	--------
--------	0.9	0.2	--------	1,260	9+	99	90
--------	1.2	0.2	--------	1,312	10	100	130
--------	1.7	0.2	--------	282	10	100	81
--------	2.3	0.2	--------	64	10	100	104
--------	5.8	0.2	--------	[1] 22	10	100	--------
--------	0.3	0.2	0.7	570	5	81½	69
--------	0.6	0.2	0.7	810	10	99½	80
--------	1.2	0.2	0.7	350	10	100	48

[1] 17 hrs.

This data is graphically presented by curves in Figures I, II and III. In each of these curves of Figure I, it can be seen that bearing corrosion increases drastically with increased concentrations of detergent until a maximum is reached and thereafter the bearing corrosion unexpectedly begins to decrease with increased concentrations of detergent. Since the corrosion increases well past 0.6% by weight ash it can be seen why the general conjecture in the art is that corrosion would continue to increase with increased concentration of detergent and the apparent reason why the U. S. Navy and Army specification placed an arbitrary critical limit of 0.6% by weight ash as the maximum allowed for engine lubrication. However it has now been discovered that past a critical upper limit corrosion and wear begin to decrease with increased amounts of detergent. Thus the valuable contribution of this invention is that increasing the concentration of a detergent past a critical upper corrosion limit wear and corrosion can be substantially inhibited. Furthermore not only the corrosive and wear tendencies of lubricants diminished in this manner but engine cleanliness and performance is greatly improved as can be seen by references to Table I and Figures II and III.

TEST II

A reference oil and an oil of this invention were subjected to a CRC L-1, at a water jacket temperature of 100° F. and at standard operating conditions with a fuel containing 1.06% sulfur.

Analysis of the reference oil and high ash oil were as follows:

	Reference Oil	High Ash oil, referred to as Composition B [1]
Gravity, °A. P. I. at 60°	23.5	22.8
Flash, C. O. C., °F	400	400
Fire, °F	420	420
Viscosity, S. S. U. at 100° F	343	538
Viscosity, S. S. U. at 130° F	150	227
Viscosity, S. S. U. at 210° F	50	60
Viscosity Index	47	68
Aniline Point, °F	188	260
Sulfur, percent	0.52	0.96
Insol. P. E., Mg/g	0.59	0.54
Oxide ash, percent	0.27	2.08
Carbon Residue, percent	0.38	3.35
Neut. No	0.11 alk	3.34 alk
Strong Base No., Mg/g	0.40 alk	3.86 alk
Free Acidity, Mg/g	--------	--------

[1] Calcium petroleum sulfonate, 2% weight sulfate ash; phenyl-α-naphthyl amine, 0.2% weight; 2,6 ditert. butyl-4-methyl phenol, 0.7% weight.

Analysis of the properties of the test oils reveals that the gross acidity (refer to Fig. V) of the high ash oil was less than that of the reference oil and that no strong acids were detected at any time in the high ash oil, whereas the reference oil revealed the presence of stray acids in as low as 30 hours of testing.

RESULTS OF L-1 ENGINE TEST

Engine Condition	L-1 Except 100° F. Water Temperature		L-1 Operating Condition	
	Reference Oil	Composition B of this invention	Reference Oil	Composition B of this invention
Piston rings	medium deposits	All free and clean	Heavy deposit of sludge around oil ring supports and along bottom rail.	All free and clean.
Grooves	medium deposit of hard carbon and lacquer.	Clean	Covered with black lacquer and medium deposit of hard carbon.	Clean.
Lands	100% Black lacquer	100% clean	100% covered with black lacquer.	Do.
Underside Crown	Covered with black lacquer.	Clean	Covered with dark brown lacquer.	Do.
Ring Wear-Top ring	0.050″ gap increase	0.011″ gap increase	0.028″ gap increase	0.013″ gap increase.
Liner Wear:				
Transverse	0.0049″	0.0055″	0.0028″	0.0010″.
longitudinal	0.0095″	0.0059″	0.0011″	0.0008″.

TEST III

An actual field test in a caterpillar D-4600 engine driving a water well pump and using a high sulfur fuel was operated for a period indicated in the table below using the best available heavy duty lubricant identified in the table as reference oil A which contained a metallic detergent in concentration of less than 0.5% by weight sulfate ash. At the end of the test the condition of the engine was observed. The engine was then overhauled with new cylinder liners, pistons and rings and again operated for 510 hours using reference oil A and thereafter on an SAE 30, 55 V. I. oil doped with a base identified as composition B of this invention comprising:

Basic calcium petroleum sulfonate, percent weight sulfate ash	2.0–2.3
Phenyl-α-napthylamine, percent weight	0.2
2,6 ditertiary butyl-4-methyl phenol, percent weight	0.7

lubricants the acidic materials as they formed are taken up by the alkaline reserve agent thereby preventing sludge formation, whereas in low ash doped lubricants there is insufficient neutralizing material capable of taking up or neutralizing the acidic decomposition materials as they are formed. Increased amounts of sludge on the other hand inactivate the detergent ingredients in the lubricants or admixed with it and the entire mixture is removed as a contaminant.

The unexpected results obtained using a high ash doped oil are further illustrated by subjecting an S. A. E. 30 motor stock oil of 55 VI and doped with various amounts of a basic calcium petroleum sulfonate. Oils thus doped were subjected to a Dornte oxidation test as described in the Industrial and Engineering Chemistry, vol. 35, page 581, 1943, using 0.05% wt. crankcase catalyst, and at a temperature of 150° F., the

	Composition	Time	Average cylinder wear	Condition of rings, ring grooves and pistons
Run 1	Reference Oil A	1,300 hr	0.03(0)	Heavily fouled with sludge.
Run 2	Reference Oil A	500 hr		
	Composition B	1,050 hr. after engine was run for 500 hr. on Reference Oil A.	0.005 in total actual wear	Engine absolutely clean.

Analysis of composition B before and after the above engine run is given below.

	Initial New Oil	Used oil after 1050 hr.	Used oil [1] after centrifuged
Gravity, °A. P. I	22.6	22.2	
Flash, P. M. cc., °F			
Flash, C. O. C., °F	410	420	
Viscosity, S. S. U. at 100° F	579	689	
Viscosity, S. S. U. at 210° F	61.0	64.8	
Viscosity Index	64	63	
Initial pH	10.7	6.4	6.3
TBN-E, mg. KOH/g	5.2	0.2	0.2
TAN-E, mg. KOH/g	0.8	5.0	4.0
Oil Insolubles, percent vol	nil	0.2	
Isopentane Insolubles, percent weight	nil	0.2	
Benzol Insolubles, percent wt	nil	0.2	
Saponification No., mg. KOH/g	1.0 alk	3.9	3.7
Sulfated Ash, percent wt	2.1	2.2	2.3

[1] Oil diluted with equal volume petroleum ether, centrifuged at 6000 R. P. M. for ½ hour and volume precipitate measured. Petroleum ether evaporated from oil prior to subsequent testing.

The above figures are highly significant and illustrate perhaps the reason for the unexpected results obtained using a high ash doped oil. Thus as indicated above the initial new oil had an initial base number by electrometric titration (TBN-E) of 5.2 and after 1050 hours of use dropped to 0.2 indicating that the basicity of the oil was being depleted. Also the average total acid number (TAN-E) increased from 0.8 to 5.0 indicating further formation of acidity materials. However the total sulfate ash in the new and used oil remained substantially constant. This sulfate ash apparently acts as an alkaline reserve reacting with acidity materials as they are formed thereby preventing the formation of corrosion, sludge and the like. On the other hand with low ash doped lubricants the formation of acidic decomposition products takes place without the presences of any reagent capable of acting in the capacity of an alkaline reserve agent. Another surprising factor is that whereas with high ash doped lubricants of this invention the active metallic detergent remains substantially constant acting in the capacity of an alkaline reserve agent, in the case of low ash doped lubricants the metallic detergent becomes depleted rapidly and after relatively short period of use. It appears that with high ash doped

time required to absorb 1500 ml. of oxygen noted. Figure IV discloses the results obtained and illustrates once again applicant's basic discovery. Thus it can be seen that up to a critical value of around about 0.8% wt. ash the oxidation stability of doped oils decreases with increased concentrations, but that past the critical value oxidation stability contiues to increase with increased concentrations of metallic detergent.

TEST IV

In two CFR engines used for evaluating the octane rating of aviation gasolines, normally compounded heavy duty lubricating oils allowed deposits to accumulate on the piston to an extent which interfered with operation. A large increase in the amount of ash forming additives in lubricating oil reduced deposits between normal overhaul periods to a negligible amount as is shown in the table following:

CFR–AFD F–2 ENGINE

BASE OIL (55 VI MOTOR STOCK OIL)

Ca petroleum sulfonate, percent wt. ash	0.27	2.7
Sulfurized sperm oil, percent wt	3.00	---
Phenyl-α-naphthylamine, percent wt	0.2	---
Engine Deposit in 200 hrs	Excessive	Negligible

TEST V

Spiral test procedure

(*a*) A test sample reservoir, a 100 ml. separatory funnel, is filled with the oil to be tested and weighed to 0.1 gram on a beam balance. The reservoir is then placed in position with the tip of the calibrated capillary just above the opening in a feed lead tube, and the oil flow rate controlled at 0.5 gram per minute by a previously calibrated glass capillary tube.

(*b*) A prepared spiral is slipped over the heater and thermocouples attached to the screws on the periphery of the spiral.

(*c*) A tared 100 milliliter beaker is placed in position under the spiral lead off tube to recover the unvolatilized oil.

(*d*) Current is applied to the spiral heater through a standard 115 volt variable transformer (A "Varitram," Model V-1M, equipped with a voltmeter has been found very satisfactory for controlling the power input).

(*e*) Power input is adjusted so that the average temperature of the thermocouples is 280° C. (variation from the average for any one thermocouple should not be more than 10 degrees).

(f) After allowing at least ten minutes for the spiral temperature to equilibrate, the oil flow is started and the heat input is adjusted so that the average temperature of the thermocouples is 275° C.

(g) A qualitative check on slight variations in the oil rate due to room temperature changes may be made by taking a drop count during the run.

(h) At the end of 100 minutes the oil flow is stopped and the power to the heater is turned off.

1.—Reporting of results

(a) The charge reservoir is reweighed and the weight of sample used is recorded.

(b) The recovered oil beaker is reweighed and the per cent sample loss (volatilized) is reported.

(c) The spiral is allowed to cool and then is slipped off the heater and washed by dipping gently in isopentane until successive washings are colorless. The washed spiral is then dried in an oven at 100° C. for approximately thirty minutes, cooled to room temperature and reweighed to the nearest milligram.

(d) Any insoluble deposits that flake off the spiral during the washing are recovered by filtering the isopentane through a tared sintered glass filter. These deposits are dried at 100° C. for thirty minutes, cooled to room temperature, and their weight determined.

(e) The milligrams increase in spiral weight plus the weight, in milligrams, of any deposit recovered from the washings divided by the grams sample charged is reported as "milligrams deposit per gram" at (test temperature) and the results of a spiral test on various concentrations of Ca petroleum sulfonate in mineral oil and composition (referred to in column 13) are represented graphically in Figure VI. Once again it can be seen that an oil is improved with increased concentration of an ash forming salt.

Spiral test results on mixtures of Ca petroleum sulfonate and Ca octyl phenol-formaldehyde condensation product are listed below. It will be noticed that as the concentration of the additive mixture increases to a maximum deposit formation also increases, but thereafter as the additive concentration is increased deposit formation decreases.

SPIRAL DEPOSIT

Ca petroleum sulfonate and Ca octyl phenol-formaldehyde condensation product in mineral lubrication oil.

Additives	Additive Ratio	Total Additive (Per-cent Sulfate Ash) 0	0.25	0.50	1.00
None		7.5			
Ca petroleum sulfonate		7.5	3.1	2.5	1.0
Ca octyl phenol-formaldehyde condensation product		7.5	4.5	2.7	2.4
Ca petroleum sulfonate / Ca octyl phenol-formaldehyde condensation product	3/1	7.5	2.4	2.2	1.0
Ca petroleum sulfonate / Ca octyl phenol-formaldehyde condensation product	1/1	7.5	5.2	2.1	0.9
Ca petroleum sulfonate / Ca octyl phenol-formaldehyde condensation product	1/3	7.5	5.0	3.0	1.0

Improvement of lubricants doped to a high ash value is also illustrated in the Thrust Bearing Corrosion Test as described in the National Petroleum News, September 17, 1941, pp. 294–296.

55 VI, SAE 30 motor oil containing 0.2% wt.

PHENYL-α-NAPHTHAMINE

Additive	Concentration, per cent sulfate ash	Critical Corrosion Temp., °C
None		
Ca petroleum sulfonate	0.60	155+
Do	1.20	165+
Basic Ca petroleum sulfonate	0.60	155+
Do	1.10	160+
Do	1.70	165+
Do	2.30	165+

S. A. E. 30 MINERAL OIL

Additive	Concentration, per cent sulfate ash	Critical Corrosion Temp., °C
Ca salt of alkyl phenol-formaldehyde condensation product	0.2	155
Do	0.5	165
Do	1.0	>175
Do	2.0	>170
Do	3.0	>170
Do	4.0	>170
Ba salt of alkyl phenol sulfide	6.8	160+
Ca salt of alkyl phenol sulfide	4.0	160+

Specific salts and inhibitors referred to in the above examples were only used for illustrative purposes and are not to be construed as limitations of this invention, the present basic invention being that lubricants doped with ash forming compounds in high concentrations of above 0.6% by weight ash produce improved and unexpected results. It is therefore to be understood that while the features of the invention have been described and illustrated in connection with specific compositions, the invention is not to be limited thereto or otherwise restricted, except by the prior art and the scope of the appended claims.

We claim as our invention:

1. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil; a calcium salt of petroleum sulfonic acid in an amount of from about 1% to about 4% calculated as sulfate ash and minor amounts of from 0.1% to about 1% by weight of phenyl alpha naphthylamine and 2,6 ditertiary butyl-4-methyl phenol.

2. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil; a calcium salt of a hydrocarbon aromatic sulfonic acid in an amount of from about 1% to about 4% calculated as sulfate ash and minor amounts of from 0.1% to about 1% by weight of an aryl amine and an alkyl phenol.

3. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil, a basic calcium salt of petroleum sulfonic acid in an amount of from about 1% to about 4% calculated as sulfate ash and minor amounts of from 0.1% to about 1% by weight of phenyl alpha naphthylamine and 2,6-ditertiary butyl-4-methyl phenol.

4. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil, a basic alkaline earth metal salt of petroleum sulfonic acid in an amount of from about 1% to about 4% calculated as sulfate ash and minor amounts of from 0.1% to about 1% by weight of phenyl alpha naphthylamine and 2,6-ditertiary butyl-4-methyl phenol.

5. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil, a basic alkaline earth metal salt of petroleum sulfonic acid in an amount of from about 1% to about 4% calculated as sulfate ash and minor amounts of from 0.1% to about 1% by weight of an aryl amine and an alkyl phenol.

6. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil; a calcium salt of a petroleum sulfonic acid in an amount of from about 0.8% to about 4% calculated as sulfate ash and a minor amount of from 0.1% to about 1% by weight of phenyl alpha-naphthylamine.

7. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral oil, a metal salt of a hydrocarbon aromatic sulfonic acid in an amount of from about 0.8% to about 4% calculated on an ash basis and a minor amount of from 0.1% to about 5% by weight of an aryl amine.

8. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil, a calcium salt of petroleum sulfonic acid in an amount of from about 0.8% to about 4% calculated as sulfate ash and minor amounts of from 0.1% to about 5% by weight of phenyl alpha-naphthylamine and sulfurized sperm oil.

9. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil, a mixture of a calcium salt of petroleum sulfonic acid and a calcium salt of a condensation product of octyl phenol-formaldehyde, the mixture of said salts being in the ratio of 1:3 to 3:1, respectively, and in an amount of about 1% calculated as sulfate ash and minor amounts of from 0.1% to about 1% by weight of phenyl-alpha-naphthylamine and 2,6-ditertiary butyl-4-methyl phenol.

10. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil, a mixture of an alkaline earth metal salt of petroleum sulfonic acid and an alkaline earth metal salt of a condensation product of octyl phenol-formaldehyde, the mixture of said salts being in the ratio of 1:3 to 3:1, respectively, and in an amount of about 1% calculated as sulfate ash and minor amounts of from 0.1% to

about 1% by weight of phenyl-alpha-naphthylamine and 2,6-ditertiary butyl-4-methyl phenol.

11. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil, a mixture of an alkaline earth metal salt of petroleum sulfonic acid and an alkaline earth metal salt of a condensation product of octyl phenol-formaldehyde, the mixture of said salts being present in the ratio of 1:3 to 3:1, respectively, and in an amount of about 1% calculated as sulfate ash and minor amounts of from 0.1% to about 1% by weight of an aryl amine and an alkyl phenol.

12. A finished liquid lubricating composition for use in engines operating on high sulfur fuel comprising a major amount of a mineral lubricating oil, a mixture of a calcium salt of petroleum sulfonic acid and a calcium salt of a condensation product of octyl phenol-formaldehyde, the mixture of said salts being present in the ratio of 1:3 to 3:1, respectively, and in an amount of about 1% calculated as sulfate ash and a minor amount of from 0.1% to about 5% by weight of phenyl-alpha-naphthylamine.

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