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LUBRICATING COMPOSITIONS

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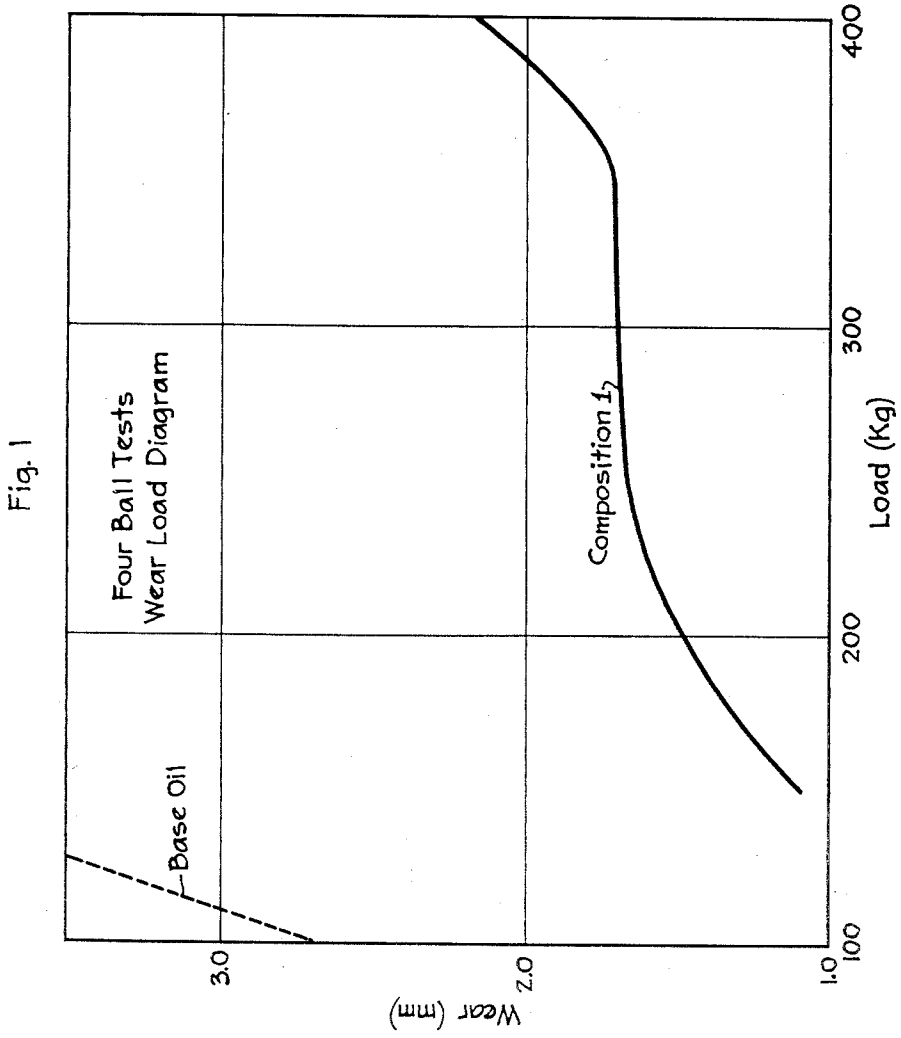


Fig. 1

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LUBRICATING COMPOSITIONS

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This invention relates to extreme pressure lubricants capable of withstanding high pressures at elevated temperatures under severe and adverse operating conditions. More specifically this invention pertains to improvement of extreme pressure lubricants by enhancing their extreme pressure properties and at the same time rendering them substantially non-corrosive and stable, by addition of a novel additive thereto, in relatively minor amounts.

Natural and/or synthetic lubricants per se are not capable of withstanding extreme pressures at high temperatures, high speeds and under severe loading conditions as generally encountered in present day lubricating such as internal combustion engines of various types, transmission devices, certain types of gears, e. g. hypoid gears, metal fabrication such as in cutting and drawing and the like. Under such conditions of lubrication, the protective film formed between contacting surfaces, by the lubricant, so as to prevent direct metal-to-metal contact, breaks down or ruptures and seizure or even welding of metal parts occurs, resulting in serious damage to the elements being lubricated. To overcome this serious weakness generally inherent in undoped lubricants, extreme pressure agents are added which form protective films between contacting surfaces and which possess among their properties the function of imparting film strength and oiliness to lubricants, thus preventing their breakdown and rupture under the above-described lubricating conditions.

The action of extreme pressure agents is largely a physico-chemical phenomenon and this accounts primarily for their effectiveness as extreme pressure agents. These agents or materials in addition to increasing the film strength of lubricants, become reactive with contacting surfaces forming thereon an alloying protective coating or film of great strength and thermal stability. This tenaciously adhering adsorbed protective film not only reduces friction between relatively moving parts such as encountered in internal combustion engines but also acts as an impermeable film which prevents corrosive acids and other contaminants from attacking the metal surface and the like. To be effective, therefore, extreme pressure agents must, to a degree, be reactive with contacting surfaces and form thereon a protective film which prevents welding of moving parts and aids lubrication. Since the reaction is normally between the additives in the lubricants and contacting surfaces at elevated temperatures of around about 500° C. and higher,

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the performance of a given lubricant must depend upon its composition, the composition of the contacting surface being lubricated, as well as the conditions to which the combination is subjected.

Although extreme pressure additives to be effective should be reactive with contacting surfaces, this reactivity should not be corrosive to the reactive surface. This is generally a serious drawback of known extreme pressure agents, for serious damage to metal surfaces, particularly such as alloy bearings and the like, might result. Such additive should also not tend to promote oxidation which generally prompts formation of corrosive acidic materials, sludge, lacquer and varnish which results in sticking and fouling of movable engine parts and the like.

Numerous compounds and mixtures of compounds have been proposed and tried as extreme pressure agents for lubricants, the best of which have only moderately improved the extreme pressure properties of the lubricant and generally at the expense of increased corrosiveness and instability of the lubricant. Among such compounds may be mentioned organic oxygen containing compounds such as fatty acids, esters, ketones, oxidized petroleum fractions; organic compounds containing sulfur or oxygen and sulfur such as sulfurized fatty oils, acids, etc.; organic compounds containing chlorine usually obtained by chlorinating organic compounds or petroleum fractions: organic compounds containing phosphorus; organic compounds containing lead and especially such compounds when in conjunction with an active sulfur compound.

Of the general classes of extreme pressure compounds enumerated, sulfur and/or halogen-containing compounds appear to be most effective and are therefore preferred. However, these have serious defects in that most sulfur compounds to be effective must contain a major amount of sulfur in an active state which is highly corrosive and has a tendency to separate out and form sludge. Materials of this type, when in combination wiith halogen-containing compounds, have a deleterious effect by liberating highly corrosive acids from the halogenated compounds and also interfere with their function as an extreme pressure dope. Halogen-containing compounds when used alone, become highly corrosive to alloy metals such as cadmium-silver, copper-lead, etc., so as to render them useless after short periods of use.

It is an object of the present invention to provide an improved extreme pressure type lubricant capable of effective lubrication under high pres-

sures at elevated temperatures and adverse operating conditions. Still another object of this invention is to provide an improved, stable, sludge free, non-corrosive extreme pressure lubricant. Also, it is an object of this invention to provide an improved extreme pressure lubricant by addition to any lubricating carrier or base a minor amount of a novel reaction product of this invention. Still another object is to form an improved non-corrosive extreme pressure additive from the reaction products of this invention. Other objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, this invention consists of features which will be hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain embodiments of the invention, these being illustrative of but a few variations in which the principle of the invention may be employed.

Broadly stated, this invention is directed to the use in lubricants of various organic compounds, and mixtures, thereof, which compounds contain at least one trihalomethyl group indirectly attached to an aromatic group and represented by the general formula:

$$Y_m—Ar—Q—(CX_3)_n$$

wherein Q is a five or six atom membered cyclic acetal such as dioxalane or dioxane, the X's are halogen atoms from the group consisting of chlorine, bromine, iodine and mixtures thereof; n is a positive integer of at least one; said radical CX_3 being indirectly attached to the aryl radical Ar through Q; the Y's may be polar radicals, non-polar radicals, and mixtures thereof and attached to the aryl nucleus Ar, and m may be a whole number ranging from zero to 3; the preferred polar radical Y being selected from nitro, nitroso, amino, mercapto, sulfo, halo, hydroxyl, carboxyl groups, and if Y is non-polar it may be a saturated or unsaturated oleophilic aliphatic hydrocarbon radical having at least 8 carbon atoms.

The compounds, some of which are specifically illustrated below may be prepared by reacting phenolic compounds such as phenol, nitrophenol or aromatic compounds having the formula Ar—X—C—XH or



wherein Ar is an aryl radical and X may be O, S, Se and/or Te with one or more moles of chloral or chloral hydrate. Thus, 2,4-di(trichloromethyl)-6-nitro-1,3 benzodioxane may be prepared by condensing paranitro phenol with two mols of chloral hydrate, while 2-trichloromethyl-4-phenyl-5-keto-1,3 dioxolane may be prepared by condensing one mol of mandelic acid with one mol of chloral hydrate. By properly selecting the starting materials and reacting them in proper proportions under conditions to form the five or six-membered cyclic acetals the compounds listed below may be prepared.

Specific compounds exemplifying the compounds under (*a*) and broadly described by the formula $Y_m—Ar—Q—(CX_3)_n$ include:

2,4-di(trichloromethyl) 6-nitro-1,3 benzodioxane
2,4-di(tribromomethyl) 6-nitro-1,3 benzodioxane
2,4-di(trichloromethyl) 6-nitroso-1,3 benzodioxane

2,4-di(trichloromethyl) 6-amino-1,3 benzodioxane
2,4-di(trichloromethyl) 1,3 benzodioxane
2,4-di(trichlorobromomethyl) 1,3 benzodioxane
2,4-di(trichloromethyl) 7-nitro-1,3 naphthodioxane
4,4-di(trichloromethyl) 6-nitro-1,3 benzodioxane
2-trichloromethyl-4-phenyl-5-keto-1,3 dioxolane
2-trichloromethyl-4-ethyl-1,3 benzodioxane
2-trichloromethyl-4-octyl-6-nitro-1,3 benzodioxane
4-trichloromethyl-2-octyl-6-nitro-1,3 benzodioxane
4-trichloromethyl-2-phenyl-6-nitro-1,3 benzodioxane
2-trichloromethyl-4-octyl-1,3 naphthodioxane
4,4-diethyl-2-trichloromethyl-1,3 benzodioxane
4 - ethyl - 4 - ethoxyoctyl - 2 - trichloromethyl - 1,3 benzodioxane
4 - octyl - 4 - chloro - octyl - 2 - trichloromethyl - 1,3 benzodioxane
4 - octyl - 4 - chloro - octyl - 2 - trichloromethyl - 6-nitro-1,3 benzodioxane
2 - ethyl - 2 - chloroethyl - 4 - trichloromethyl - 1,3 benzodioxane
2 - butyl - 2 - chlorobutyl - 4 - trichloromethyl - 6-nitro-1,3 benzodioxane
2-trichloromethyl-4-phenyl-1,3 dioxolane
2-trichloromethyl-4-phenyl-5-keto-1,3 dioxolane
2-trichloromethyl-4-naphthyl-5-keto-1,3 dioxolane
2-trichloromethyl-4-phenyl-5-nitro-1,3 dioxolane
5-trichloromethyl-4-phenyl-2-keto-1,3 dioxolane
5-trichloromethyl-2-phenyl-4-keto-1,3 dioxolane
5-trichloromethyl-2-phenyl-4-nitro-1,3 dioxolane
4-trichloromethyl-2-phenyl-5-nitro-1,3 dioxolane
4-tribromomethyl-2-phenyl-5-amino-1,3 dioxolane
2-trichloromethyl-4-phenyl-5-keto-1,3 dioxolane
2 - trichloromethyl - 4 - keto - 6,8 - diisopropyl - 1,3 benzodioxane
2 - tribromomethyl - 4 - keto - 6,8 - diisopropyl - 1,3 benzodioxane

Of the extreme pressure additives within the ambit of this invention those are preferred which are sufficiently soluble in the lubricant under treatment to an extent sufficient to give the compounded lubricant desired extreme pressure properties. It is possible however to produce excellent extreme pressure lubricants by dispersing the additives in the lubricant in the form of a stable coloidal suspension and thus even those additives which are not readily soluble in the base lubricant can be employed. Whether in the form of solutions or of dispersions suitable stabilizing and solubilizing agents may be added such as long chain fatty alcohols having 8 to 20 carbon atoms, organic sulfonates and the like.

In general good results can be obtained by addition to a base lubricant of from a fraction of 1% up to 10%, and the preferred range is from 0.1% to about 5% by weight, of the additive of the invention.

The base lubricant may be selected from a wide variety of natural and synthetic lubricants. Mineral oil fractions and their mixtures varying in viscosity from 100 to 2000 SUS at 100° F. may be used, said mineral oils being obtained from various petroleum crudes such as paraffinic or asphaltic and if desired may be refined by any

of the well known processes such as treatment with sulfuric acid, solvent extraction, or solvent dewaxing. Mixtures of mineral oil and fixed oils such as castor oil, lard oil, and the like, can be used as well as synthetic oils and mixtures of synthetic oils with mineral and/or fixed oils and their derivatives.

Synthetic lubricants which can be used in compositives of this invention are:

I. Synthetic lubricants produced by the Fischer-Tropsch, Synthol, Synthine, and related processes, e. g.:

A. Polymerization of olefins such as ethylene, butylene, and the like, and their mixtures in presence of a Friedel-Crafts or other type catalyst under elevated temperatures and pressures.

B. Polymerization of unsaturated hydrocarbons in presence of a catalyst and then condensing said polymerized product with an aromatic such as xylol, benzol, naphthalene, etc.

C. Oxidation of polymerized olefins of lubricating range as noted under A and B.

D. Process of converting natural gas to carbon monoxide and hydrogen, followed by catalytic reaction under elevated temperature and pressure to produce hydrocarbons of lubricating range (Synthol process).

II. Bergius process for producing synthetic lubricants, e. g.:

A. Hydrogenation of coal, peat, and related carbonaceous materials under pressure and elevated temperature in presence of a catalyst.

B. Hydrogenation of asphalts, petroleum residues and the like.

III. Voltolization process for producing synthetic lubricants, e. g.:

A. Voltolization of fatty materials such as fatty oils.

B. Voltolization of mixtures of fatty oils and petroleum hydrocarbons.

C. Voltolization of unsaturated hydrocarbons, their mixtures, and the like.

IV. Organic synthetic lubricants:

A. Alkyl esters of organic acids, e. g.—alkyl lactates, alkyl oxalates, alkyl sebacates (2-ethyl hexyl sebacate), alkyl adipates, alkyl phthalates (dioctyl phthalates), alkyl ricinoleates (ethyl ricinoleate), alkyl benzoates.

B. Alkyl, alkylaryl esters of inorganic acids, e. g.—trixylenyl phosphate, tributyl phosphate, triethyl phosphate.

V. Synthetic lubricants made by polymerization of alkylene oxides at elevated temperatures in the presence of catalysts such as iodine, hydriodic acid, etc.:

A. Polymers of—ethylene glycol, trimethylene glycol, propylene glycol, tetramethylene glycol, hexamethylene glycol, pentamethylene glycol.

B. Copolymers of—trimethylene glycol and triethylene glycol, trimethylene glycol and hexamethylene glycol, trimethylene glycol and B-methyltrimethylene glycol, trimethylene glycol and diethylene glycol.

C. Copolymers prepared from certain peroxides at elevated temperatures and in presence of KOH or BF_3-ether catalyst, e. g.—ethylene oxides and propylene oxide, isobutylene oxide and propylene oxide, epichlorohydrin and propylene oxide.

D. Sulfur containing polymers obtained by treating allyl alcohol, divinyl ether, diallyl ether, dimethallyl ether, glycols, with H_2S in presence of a catalyst such as toluene sulfonic acid, e. g.—dihydroxy diethyl sulfide, dihydroxy dipropyl sulfide, trimethylene glycol and dihydroxy dipropyl sulfide, trimethylene glycol and dihydroxy diethyl sulfide.

VI. Polymers obtained from oxygen-containing heterocyclic compounds, e. g.—polymerization of tetrahydrofuran in the presence of a catalyst.

VII. Silicon polymers, e. g.—polyalkyl silicon polymers, alkylaryl silicon polymers, dimethyl silicon polymers, etc.

VIII. Fluorocarbon oils, e. g.—fluorinated petroleum fraction etc.

General formulation of compositions of this invention can be represented by:

	Amount (% by weight)
Organic compound of this invention containing at least one CX_3 group wherein X is a halogen indirectly attached to an aromatic group	0.1 to 10% (0.1–5%)
Other additives such as sulfonates, corrosion inhibitors, detergents, etc.	0 to 2% (0.01–5%)
Base lubricant (natural and/or synthetic)	Balance

The following table illustrates lubricating compositions of this invention:

	1	2	3	4	5	6	7
1, 1, 1-trichloro-4(4'chlorophenyl) but-2-en-4-one	---	---	---	x	---	---	---
diethyl (1-phenyl-2, 2, 2-trichloroethyl) phosphite	---	---	---	---	---	---	---
2, 4-di(trichloromethyl) 6-nitro- 1, 3-benzodioxane	x	---	---	---	x	---	---
2-trichloromethyl-4-keto-6, 8-diisopropyl-1, 3-benzodioxane	---	x	---	---	---	---	---
2-trichloromethyl-4-phenyl-5-keto-1, 3-dioxolane	---	---	x	---	---	x	x
Ca petroleum sulfonate	---	---	---	---	---	---	---
Stearyl alcohol	---	---	---	---	---	---	x
Oleyl alcohol	---	---	---	---	---	---	x
Mineral Oil	x	x	x	---	---	---	---
Dioctyl sebacate	---	---	---	x	---	---	---
Mineral Oil+Alkyl naphthalene	---	---	---	---	x	x	---

Compositions of this invention were evaluated as anti-wear agents by use of the four-ball tester similar in principle to the Boerlage apparatus described in the magazine "Engineering," volume 136, July 13, 1933. This apparatus comprises four steel balls arranged in a pyramid formation. The top ball is rotated by spindles against the three bottom balls which are clamped in a stationary ball holder. The balls are immersed in the compositions to be tested. Tests were run with undoped mineral oil and with 1% by weight of compositions 1 and 3 as indicated in the table above under various loads and the wear at these loads was measured. (The results of the tests were plotted and are shown in Figure I.) The fixed conditions under which the tests were conducted are:

Speed: 1500 R. P. M.
Test duration: 60 seconds
Temperature: ambient
Hoffmann steel balls

Lubricants of this invention were also tested on the I. A. E. 3¼ in. centres gear rig and the two-ball machine. The results obtained are summarized in the table below:

Two-ball machine:
Sliding speed, 172 ft./min.
Rolling ratio, 4.2:1
1½'' diam. steel balls
Temperature, 60° C.

I. A. E. 3¼ centres—pinion speed, 2000 R. P. M. Gear rig:

Gears $1\frac{5}{16}$ tooth

The gear material was En 39 and En 34

Base oil: Mineral oil

Additive Conc. Per cent Weight	Additive	Two-Ball Machine Breakdown load (lbs.)
		380
2	2, 4-di(trichloromethyl) 6-nitro-1, 3-benzodioxane	554
0.57	2-trichloromethyl-4-phenyl-5-keto-1, 3-benzodioxolane	450

Additive [1] conc. Per cent Weight	IAE 3¼" Gear Rig Scuffing Load (lbs.)	
	50° C.	100° C.
	17	10
0.4	140	
0.58	90	65

[1] Additive same as above tabulation, respectively.

Because of its synergistic effect the reaction product of this invention can be combined with other additives in lubricants, such as blooming agents, pour point depressants or viscosity improvers, extreme pressure agents, antifoaming agents and the like. Among the specific additives which can be used are oil-soluble detergents which include oil-soluble salts of various bases with detergent forming acids. Such bases include metal as well as organic bases. Metallic bases include those of the alkali metals and of Cu, Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn, Pb, Cr, Mn, Fe, Ni, Co, etc. Organic bases include various nitrogen bases as primary, secondary and tertiary amines and quaternary ammonium bases.

Examples of detergent forming acids are the various fatty acids of, say, 10 to 30 carbon atoms, wool fat acids, paraffin wax acids (produced by oxidation of paraffin wax) chlorinated fatty acids, rosin acids, aromatic carboxylic acids including aromatic fatty acids, aromatic hydroxy fatty acids, paraffin wax benzoic acids, various alkyl salicylic acids, phthalic acid monoesters, aromatic keto acids, aromatic ether acids, diphenols as di-(alkyl-phenol) sulfides and disulfides, methylene bis alkyl phenols; sulfonic acids such as may be produced by treatment of alkyl aryl hydrocarbons or high boiling petroleum oils with sulfuric acid; sulfuric acid monoesters; phosphoric, arsonic and antimony acid mono and diesters, including the corresponding thiophosphoric, arsonic and antimony acids; phosphonic and arsonic acids and the like.

Additional detergents are the alkaline earth phosphate diesters, including the thiophosphate diester; the alkaline earth diphenolates, specifically the calcium and barium salts of diphenol mono and poly sulfides.

Non-metallic detergents include compounds such as the phosphatides, such as lecithin and cephalin, certain fatty oils as rapeseed oils, voltolized fatty or mineral oils and the like.

An excellent metallic detergent for the present purpose is the calcium salt of oil-soluble petroleum sulfonic acids. This may be present advantageously in the amount of about 0.025% to 0.2% sulfate ash. Also alkaline metal salts of

alkyl phenol-aldehyde condensation reaction products are excellent detergents.

Antioxidants comprise several types, for example, alkyl phenols, such as 2,4,6-trimethyl phenol, pentamethyl phenol, 2,4-dimethyl-6-tertiary - butyl phenol, 2,4 - dimethyl - 6 - octyl phenol, 2,6-ditertiary - butyl - 4 - methyl phenol, 2,4,6-tritertiary-butyl phenol and the like; amino phenols as benzyl amino phenols; amines such as dibutyl-phenylene diamine, diphenyl amine, phenyl - beta - naphthylamine, phenyl - alpha - naphthylamine, dinaphthyl amine.

Corrosion inhibitors or anti-rusting compounds may also be present, such as dicarboxylic acids of 16 and more carbon atoms; alkali metal and alkaline earth salts of sulfonic acids and fatty acids; organic compounds containing an acidic radical in close proximity to a nitrile, nitro or nitroso group (e. g. alpha cyano stearic acids).

Extreme pressure agents which may be used comprise: esters of phosphorus acids such as triaryl, alkyl hydroxy aryl, or aralkyl phosphates thiophosphates or phosphites and the like; neutral aromatic sulfur compounds of relatively high boiling temperatures such as diaryl sulfides, diaryl disulfides, alkyl aryl disulfides, e. g. diphenyl sulfide, diphenol sulfide, dicresol sulfide, dixylenol sulfide, methyl butyl diphenol sulfide, dibenzyl sulfide, corresponding di- and trisulfides, and the like; sulfurized fatty oils or esters of fatty acids and monohydric alcohols, e. g. sperm oil, jojoba oil, etc.; in which the sulfur is strongly bonded; sulfurized long chain olefins such as may be obtained by dehydrogenation or cracking of wax; sulfurized phosphorized fatty oils or acids, phosphorus acid esters having sulfurized organic radicals, such as esters of phosphoric or phosphorus acids with sulfurized hydroxy fatty acids; chlorinated hydrocarbons, such as chlorinated paraffin, aromatic hydrocarbons, terpenes, mineral lubricating oil, etc.; or chlorinated esters of fatty acids containing the chlorine in position other than alpha position.

Additional ingredients may comprise oil-soluble urea or thiourea derivatives, e. g., urethanes, allophanates, carbazides, carbazones, etc.; polyisobutylene polymers, unsaturated polymerized esters of fatty acids and monohydric alcohols and other high molecular weight oil-soluble compounds.

Depending upon the additive used and conditions under which it is used, the amount of additive used may vary from 0.1 to 2% or higher. However, substantial improvement is obtained by using amounts ranging from 0.1 to 0.5% in combination with polyhalogen containing organic carbonyl compound and organic thiol, selenol and/or tellurol compound reaction products of this invention.

The novel reaction products of this invention, in addition to being excellent lubricating oil improving, agents are potent oxidation inhibitors for fuels, natural and synthetic rubber, wax coating compositions and other organic materials.

It is to be understood that while the features of the invention have been described and illustrated in connection with certain specific examples, the invention, however, is not to be limited thereto or otherwise restricted, except by the prior art and the broad scope of the disclosed invention.

I claim as my invention:

1. A lubricating composition comprising a mineral lubricating oil having incorporated therein in an amount sufficient to impart ex-

treme pressure properties thereto nitro-1,3-benzodioxane containing from one to two trichloromethyl radicals directly attached to the dioxane ring, said nitro group being attached directly to the 6-position of the benzodioxane.

2. A mineral oil having incorporated therein in an amount sufficient to impart extreme pressure thereto of 2,4-di(trichloromethyl) 6-nitro-1,3-benzodioxane.

3. A mineral lubricating oil having incorporated therein from 0.1 to 10% of 2,4-di(trichloromethyl) 6-nitro-1,3-benzodioxane.

WILLIAM CYRIL WEBBER.

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