



합성윤활유 및 첨가제 관련 특허정보 분석

(I)

고려대학교 화학과
최 주 환 박사

개 요

합성윤활유와 윤활유 첨가제의 생산과 응용에 관련된 각종 특허정보를 몇가지 주요 분야로 나누어서 분석하였다. 본고에서 수집, 분석된 특허정보는 다음과 같다.

합성윤활유 부문

- A. LINEAR ALPHA OLEFIN OLIGOMERS(PAO)
- B. NEOPOLYOL ESTERS
- C. DIBASIC ACID ESTERS

윤활유 첨가제 부문

- A. POLYALKENYL SUCCINIMIDE
- B. ZINC DIHYDROCARBYLDITHIOPHOSPHATES
- C. SULFONATES
- D. ETHYLENE-PROPYLENE COPOLYMERS
- E. ALKYLPHENATES

본고에서 분석된 특허정보가 윤활유 생산 및 응용 등의 연구개발에 관계하는 분들에게 조금이나마 도움이 되었으면 한다.

I. 합성윤활유 특허정보 분석

A. LINEAR ALPHA OLEFIN OLIGOMERS(PAO)

Assignee	Oligomerization		Reaction Conditions	Hydrogenation
	Monomer(s)	Catalyst		
Uniroyal	LAO ≥ 3C	(1) Alkyl aluminum halide (2) Organic halide	Continuous high reaction rates without cooling; no solvent.	Not shown.
Soluble catalyst for oligomerizing olefins for lubricant production.				
Gulf	LAO, such as 1-decene	(1) BF ₃ (2) Promoter such as n-butanol	Not shown.	Special procedure to give desired introduction of desired methyl and ethyl groups onto trimer chains. Unsaturated oligomer is trickled down hydrogenation column. 600 psi and 200°C

Preparation of alpha olefin oligomer synthetic lubricant.

Assignee	Oligomerization		Reaction Conditions	Hydrogenation
	Monomer(s)	Catalyst		
Gulf	LAO, such as 1-decene	(1) BF_3 (2) Promoter such as decanol	2-stage continuous. Tank reactor in first stage and a tube reactor in the second stage. Example had 110°F in first reactor and 120°F in tube reactor; both at 50 psig.	Conventional catalysts such as Pd, Pt, Ni with elevated temperatures and pressure.
Method of making alpha olefin oligomers.				
Gulf	LAO, such as 1-decene	(1) BF_3 (2) Promoter such as n-butanol	Multi-stage continuous. Tank reactors in series. Example had two reactors. 120°-130°F, and 50 psig in both reactors.	Conventional catalysts such as Pd, Pt, Ni with elevated temperature and pressure.
Method of oligomerizing 1-olefins.				
Uniroyal	LAO, $\geq 3\text{C}$	(1) Alkyl aluminum halide (2) Organic halide	Continuous. High reaction rates without cooling; no solvent. 40-60 min, 23°-152°C.	Optional, for added thermal oxidative stability.
Oligomerization catalyst containing aluminum alkyl halide and organic halide for converting olefins to lubricants and hydraulic oils.				
Lion Fat & Oil	LAO, $\geq 6\text{C}$	(1) Multivalent alcohol derivative. (2) Aluminum halide. Catalyst may be used repeatedly for further oligomerization	Example showed 5hrs and 120°C	Not shown.
Polyolefins oil preparation using a catalyst derived from aluminum chloride and a multivalent alcohol derivative.				
Exxon	LAO, preferably 10-14 C atoms	Alumino-silicate molecular sieve	One representative, set of conditions is 600°F, 600 psig and 1 hr residence time.	Conventional hydrofinishing conditions employing conventional catalysts such as Ni and cobalt molybdate. Example showed 500°F, 800 psi hydrogen and 1 hr with 5% Ni catalyst.
Synthesis of low viscosity, low pour point hydrocarbon lubricating oils.				
Uniroyal	LAO, $\geq 3\text{C}$	(1) Aluminum alkyl halide. (2) Organic halide.	Example showed 120°C and 30 minutes.	Not shown.
Oligomerization of alpha olefins using catalyst system containing aluminum alkyl halide, used in production of synthetic lubricating oils.				
Liquichimica S.P.A.	C_{6-24} n-olefins	Friedel-Crafts(NaAlCl_4 used in example)	Example showed 130°C and 2.5 hrs.	Example showed 10% Raney Nickel catalyst 200°F and 50 atm for 4 hrs.
Synthetic lubricating oils.				
Mobil oil	C_{6-12} alpha olefins	(1) BF_3 in presence of water or alcohol Promoter. (2) Low boiling ester of a carboxylic acid.	Examples showed 15° to 50°C and 104 to 205 minutes.	Mentioned but not described.
Controlled oligomerization of olefins.				

Assignee	Oligomerization		Reaction Conditions	Hydrogenation
	Monomer(s)	Catalyst		
Lion Fat & Oil	Olefin or olefin mixture having > 6C atoms	(1) Polyhydric alcohol derivative. (2) Aluminum halide. (3) Metallic aluminum powder.	Examples showed 100°C for 5 hrs.	Raney nickel catalyst, 10 kg/cm ² hydrogen pressure, 150°C, 3 hrs. Catalyst is used 10 times.
Method for preparation of olefin oligomer.				
Lion Fat & Oil	LAO, ≥ 6C	(1) Polyhydric alcohol derivative having all hydrogen atoms of hydroxyl groups replaced by acyl groups and alkyl groups, both groups having 1 to 20 carbon atoms. (2) Aluminum halide.	Examples showed 5 hrs and 100°-130°C.	Raney nickel catalyst, 10kg/cm ² hydrogen pressure, 150°C, 3 hrs.
Stauffer	TMP	Heptanoic acid	Not given.	
Synthetic lubricants, based on a mixture of liquid neopolyol ester and a liquid alpha-olefin oligomer (hydrogenated mixture of trimeric and tetrameric decene-1), plus additives.				
Lion Fat & Oil	Olefins having 6 or more carbon atoms	(1) Aluminum chloride (2) Ketone having 4 or more carbon atoms. (3) Olefin catalyst constituent. (4) Ester, ether, or alcohol.	Examples showed 100°C and 6 hrs.	Raney nickel catalyst, 70kg/cm ² hydrogen pressure, 150°C, 3 hrs.
Method for preparation of hydrocarbon liquid polymers.				
Lion Fat & Oil	Olefins having 6 or more carbon atoms	(1) Polyhydric alcohol completely substituted with 1-20 acyl and/or alkyl groups. (2) Aluminum halides.	Examples showed 100°C and 5 hrs.	Raney nickel catalyst, 150°C, 3 hrs.
Preparation of olefin oligomers in presence of aluminum halide and esterified polyhydric alcohol.				
Uniroyal	LAO, ≥ 3C	(1) Alkyl aluminum halide. (2) Organo-halide compound.	Not shown.	Not shown.
Alpha-olefin oligomerization catalyst system comprising alkyl aluminum halide and organo-aluminum compounds, giving oligomers used as lubricants and hydraulic fluids.				
Lion Fat & Oil	LAO having 8-10 C atoms	(1) Titanium halide and not less than 1 alkyl Al compound. (2) A tertiary catalyst formed from an alkali metal hydride, Al halide and Ti halide.	Examples with EtAlCl ₂ + TiCl ₄ , 20°-40°C, 4 hrs Example with AlCl ₃ + LiHalide 100°-120°C, 4 hrs.	Raney nickel catalyst 150°C, 20kg/cm ² hydrogen pressure.
Polyolefin-based lubricating oils with reduced viscosity at low temperatures, derived from 8-10 C olefin mixtures.				
Lion Fat & Oil	Alpha olefins having 6-14 C atoms	(1) Alkali metal hydride. (2) Boron or aluminum halide. (3) Titanium halide. Above 3 items for ternary catalyst. A quaternary catalyst may be used having (4) Metallic lithium or sodium added to the above	70°-200°C	Raney nickel catalyst.
Method of producing liquid olefin polymer.				

Assignee	Oligomerization		Reaction Conditions	Hydrogenation
	Monomer(s)	Catalyst		
Bray Oil	LAO having 6-12 C atoms	(1) Anhydrous aluminum chloride modified with a nitro paraffin. (2) $TiCl_4$ can also be included and can be replaced by dibutyl or tributyl tin chloride.	180° - 250° F appears to be most desirable temperature range.	Raney nickel catalyst preferred; 50-2500 psig hydrogen pressure. 250° - 500° F, 4-24 hrs.

Polymerization process.

Snamprog-etti	LAO having 4-18 C atoms	(1) Compound of a transition metal from the IV to VIII Group of the Periodic Table plus two coordinated anionic co-catalysts. (2) Aluminum compound of an inorganic nature. (3) Aluminum compound of the conventional Ziegler type.	Examples showed 25° - 80°C for 5 hrs.	Pd on alumina catalyst, 220°C, 80kg/cm ² hydrogen pressure, 5 hrs.
---------------	-------------------------	---	---------------------------------------	---

Production of synthetic lubricants from alpha-olefins through a ternary catalytic system.

Ethyl Corp.	LAO, such as C_6-C_{16} 1-Decene in preferred	(1) BF_3 (2) Water promoter.	Batch. BF_3 in molar excess of water. 0-500 psig, 10° - 60°C, 1-4 hrs.	Pt or Pd on charcoal, Raney nickel, nickel on kieselguhr, copper, chromite, alumina-supported copper and palladium. 100-2000 psig, 150° - 200°C.
-------------	---	-----------------------------------	---	--

Process for producing a C_6-C_{16} normal alpha-olefin oligomer having a pour point below about -50° F.

Ethyl Corp.	LAO, such as C_6-C_{16} 1-Decene is preferred	(1) BF_3 (2) Alcohol promoter	Batch. BF_3 in molar excess of alcohol. 0-500 psig, 10° - 60°C, 1-4 hrs.	Same as above.
-------------	---	------------------------------------	---	----------------

Synthetic lubricants by oligomerization and hydrogenation.

Shell	LAO having 6-12 C atoms	Alkali metal tetrahaloalanate	Examples showed 125° - 150°C from 110 minutes to 4 hrs.	Nickel on kieselguhr catalyst, 200°C, 1500 psig hydrogen pressure, 8 hrs.
-------	-------------------------	-------------------------------	---	---

Synthetic oils from alpha-olefins.

Snamprog-etti	LAO having 4-18 C atoms	(1) Compound of a transition metal from the IV to VIII Group of the Periodic Table. (2) Aluminum compound which is a linear polyimic polymer.	Examples showed 80°C. and 3 hrs.	Pt supported on alumina; 180°C, 50kg/cm ² , 2 hrs.
---------------	-------------------------	--	----------------------------------	---

Process for the preparation of synthetic lubricating oils from olefins.

Snamprog-etti	LAO having 7-17 C atoms	$BF_3 \cdot H_2O$	Examples showed 0-50°C for 30 minutes.	Nickel on kieselguhr catalyst, 250°C, 70 kg/cm ² , 5 hrs.
---------------	-------------------------	-------------------	--	--

Production of synthetic lubricating oils.

Assignee	Oligomerization		Reaction Conditions	Hydrogenation
	Monomer(s)	Catalyst		
Institut Francais Du Petrole	Alpha-olefins having 6-16 C atoms	Organic peroxides	Examples showed 250° -320°C and 3-5 hrs.	Raney nickel catalyst, 200°C, 50kg/cm ² hydrogen pressure (time not given).
Preparation of synthetic lubricants.				
Mobil Oil	1-Decene or mixtures of 1-olefins between 6-12 C atoms having mean of 10 C atoms	(1) BF ₃ (2) Promoter such as 1-decanol	Examples showed 25° -35°C and 1-3 hrs.	Not shown.
Polymerization of olefins with BF ₃ .				
Sun Oil	LAO having 6-14 C atoms	(1) Aluminum alkyl sesquichloride or aluminum dialkyl monochloride or aluminum monoalkyl dichloride. (2) Titanium tetrachloride. (3) Oxygen-containing organic compound which is either an oxirane or a methyl alkyl ether.	Examples showed 30°C and 20 hrs.	Raney nickel catalyst. 150° -250°C, 1000-2000 psig hydrogen pressure.
Preparation of synthetic lubricating oil.				
Sun Oil	LAO having 6-14 C atoms	(1) Aluminum alkyl sesquichloride. (2) TiCl ₄ (3) Oxirane or methyl alkyl ether (4) Diene capable of chelating with a metal component of the catalyst.	Examples showed 30°C and 20 hrs.	Not shown.
Synthetic lubricating oil preparation.				
Gulf	At least two alpha-olefins having 6-16 C atoms. Mean C number per molecule is between 9 and 14.	Any Friedel-Crafts metal halide catalyst, AlCl ₃ preferred.	Examples showed 209° F and 35 minutes.	Not shown.
Copolymerization of low carbon number and high carbon number olefin fractions.				
Sun Oil	LAO having 6-14 C atoms	(1) TiCl ₄ (2) Aluminum alkyl compound. Above can be modified by the addition of certain oxygen-containing compounds.	Deposition of brown gummy film on surfaces within reactor prevented by carrying out reaction in the presence of activated carbon. Examples showed 30°C and 20 hrs.	Raney nickel catalyst 150° -250°C and 1000-2500 psig hydrogen pressure.
Preparation of synthetic lubricating oils.				

Assignee	Oligomerization		Reaction Conditions	Hydrogenation
	Monomer(s)	Catalyst		
Sun Oil	LAO having 6-14 C atoms	(1) Alkyl aluminum sesquichloride. (2) TiCl ₄ (3) Oxygen-containing organic compound which is either an oxirane or a methyl alkyl ether.	—	Raney nickel catalyst, 150°-250°C, and 1000-2500 psig, hydrogen pressure.
Preparation of synthetic lubricating oil.				
Sun Oil	LAO having 6-14 C atoms	(1) Aluminum alkyl sesquichloride. (2) TiCl ₄ (3) A tetraalkyl silicate.	Examples showed 15°-30°C for 20 hrs.	Not shown.
Method of preparing synthetic lubricating oil.				
Mobil Oil	LAO having 10-14 C atoms	Synthetic zeolites	Examples showed 400°-650°C and 1/2-5 hrs.	Not shown. Mention is made of hydrogenation to reduce any unsaturation which may be present.
Production of lubricating oils.				
Socony Mobil	LAO having 6-12 C atoms	Di-tertiary butyl peroxide or Friedel-Crafts catalysts such as BF ₃ or AlCl ₃	Examples showed 20°-150°C and 95 minutes to 5 hrs.	Nickel-on-kieselguhr catalyst, 300° F, 1500 psig hydrogen pressure, 3 hrs.
Polymerized olefin synthetic lubricants.				

B. NEOPOLYOL ESTERS

Abbreviations
 NPG: neopentyl glycol
 PE: pentaerythritol
 TME: trimethylolethane
 TMP: trimethylolpropane

Assignee(s)	Polyol(s)*	Acid(s) †	Reaction Conditions ‡
Texaco	PE	2-12 C atoms	Not given
Synthetic lubricants, suitable for bus or truck turbine engines. Pour points have been depressed by blending with at least one mineral oil and a methacrylate pour point depressant.			
Stauffer	TMP	Heptanoic acid	Not given.
Synthetic lubricants, based on a mixture of liquid neopolyol ester and a liquid alpha-olefin oligomer (hydrogenated mixture of trimeric and tetrameric decene-1), plus additives.			
Snamprogetti	PE, Di-PE, TMP	Heptanoic, caprylic, lauric, hexadecanoic.	210°-240°C, no catalyst, no azeotroping agent.
Synthetic lubricants, suitable for base stocks for internal combustion engines having low volatility in relation to viscosity, high viscosity index, high thermal stability, good resistance against oxidation, good lubricating power and good compatibility with mineral oils.			

Abbreviations
 NPG: neopentyl glycol
 PE: pentaerythritol
 TME: trimethylolethane
 TMP: trimethylolpropane

Assignee(s)	Polyol(s)*	Acid(s) †	Reaction Conditions ‡
I.F.P	TMP	Heptanoic, lauric, isostearic C ₁₀₋₁₆ saturated aliphatic monocarboxylic, adipic, azelaic.	Temperatures not given. No catalyst, no azeotroping agent.

Synthetic lubricants, suitable as base stock for automobile engines, having good additive solvent properties and particularly suitable for formulating multigrade oils(20w-50) with the least amount of viscosity index improver.

I.F.P	TMP Polypropylene glycol	Heptanoic, isostearic, lauric, adipic. Esterification is com- pleted with acetic anhydride.	190°-260°C, either with cata- lyst (p-toluenesulfonic acid) or without catalyst, either with azeotroping agent (xylene) or without azeotroping agent.
-------	--------------------------	---	--

Synthetic lubricants, prepared from esters by using a deficiency of carboxylic acids so that free hydroxyl groups remained. These free hydroxyl groups were then esterified by reaction with lower aliphatic acid anhydrides.

Unilever-Emery N. V.	PE, TMP	Heptanoic, pecargonic, isononanoic, isostearic	225°-250°C, no catalyst, either with azeotroping agent (toluene) or without azeotroping agent.
-------------------------	---------	---	---

Synthetic lubricants, suitable as base stock for piston engines, having low pour point, high flash point, high viscosity index, satisfactory rubber seal swelling, good viscosity stability and good mineral or compatibility.

Hercules Inc.	PE. C ₆₋₁₀ alkanols, average C=8. C ₇ alkanols.	5-9 C atoms, average C=6. 1. Trimellitic.	Not given.
---------------	--	--	------------

Synthetic lubricants, suitable as base stock for jet engines, having low pour point, suitable high and low temperature viscosities.

Texaco	PE(including di-tri-and tetra-), TMP	5-10 C atoms, straight and branched chain aliphatic cycloaliphatic, aromatic and mixtures.	Not given.
--------	---	---	------------

Synthetic lubricants, suitable for gas turbines or jet engines, operative over a wide temperature range and exhibiting good thermal stability, anti-wear, load-carrying and anti-oxidation properties.

Inventa A.G.	NPG, PE, TMP. Polyethylene glycol 200. 2-Ethyl-1- hexanol	Obtained as by-product in oxidation of cyclohexane to cyclohexanol/cyclohexanone. Butyric, valeric, caproic, hydroxycaproic, adipic.	No temperatures given. Sodium bisulfate, sulfuric acid or p-toluenesulfonic acid catalyst; toluene azeotroping agent.
--------------	---	--	---

Synthetic lubricants, suitable for jet engines, having low pour point, high flash point, high viscosity index.

Ethyl Corp.	Di-PE, TMP	Valeric, caproic, caprylic, capric	150°-251°C, either with catalyst(sodium bisulfate or p-toluenesulfonic acid) or without catalyst, either with azeotroping agent(xylene) or without azeotroping agent.
-------------	------------	---------------------------------------	--

Synthetic lubricants, suitable for use in turbines and turbojet engines, suitable for use in subsonic and supersonic jet aircraft engines, having high temperature stability and high and low temperature lubricity.

Abbreviations
 NPG: neopentyl glycol
 PE: pentaerythritol
 TME: trimethylolethane
 TMP: trimethylolpropane

Assignee(s)	Polyol(s)*	Acid(s) †	Reaction Conditions ‡
Ruhrchemie	NPG	Pelargonic, 3, 5, 5-trimethyl-hexanoic	153°C, sulfuric acid catalyst, cumene azeotroping agent.
Synthetic lubricants, suitable for use in turbojet subsonic aircraft engines, noncorrosive and having low pour point, suitable high and low temperature viscosities, high flash point, adequate thermal and oxidation stability.			
Nyco, S.A.	NPG, PE, di-PE, TME. Trimethylolbutane, penta-ediols, hexanediols, trimethylpentanediols	5-9 C atoms. Adipic, sebacic	Not given.
Synthetic lubricants, suitable for use in hydraulic transmissions and in racing-car engines.			
Mobil Oil	NPG, PE, di-PE, TME, TMP	5-10 C atoms.	Not given.
Synthetic lubricants, suitable for use in jet aircraft turbine engines, having high temperature stability and low pour point.			
Ethyl Corp.	Di-TMP	Average 4-9 C atoms. Caprylic, capric, caproic, butyric, pivalic(2, 2-dimethyl propanoic acid).	Di-TMP formation: 2 TMP 100° - 250° C + H ₂ O p-Toluenesulfonic acid catalyst, toluene azeotroping agent. Esterification: Temperatures not given. p-Toluenesulfonic acid catalyst, xylene azeotroping agent.
Synthetic lubricants, suitable for use in gas turbine aircraft engines, having high temperature stability, low viscosity at low temperature and a satisfactory lubricating viscosity at high temperature.			
Mobil Oil	Technical PE, TMP, 2-methyl-2-ethyl-propane, 1, 3-diol	Pelargonic, isopentanoic caprylic. Mono-carboxylic acid having 1 to about 30 C atoms.	-
Synthetic lubricants, suitable for jet aircraft engines, having resistance to high temperature oxidation, complete fluidity at high and low temperatures, low rubber swell, high flash point, and resistant to breakdown.			
Texaco	PE, di-PE, TMP	Straight-chain, branched-chain, cycloaliphatic, aromatic and mixtures of these. 2-12 C atoms.	Not given.
Synthetic lubricants, suitable for aircraft turbine engines, said to have outstanding oxidation and corrosion resistance and deposit-inhibiting properties.			
Esso	2-Hydroxymethyl-2-decyl-1, 3-propanediol	2, 2-Dimethyl pentanoic acid. Pelargonic acid.	No temperatures given. p-Toluenesulfonic acid catalyst, xylene azeotroping agent.
Synthetic lubricants, suitable for SST-type jet engines, having high oxidative stability at engine temperatures up to 500°F (260°C), high viscosity indices, minimal corrosiveness, minimum high temperature evaporation loss and low pour points.			

Abbreviations
 NPG: neopentyl glycol
 PE: pentaerythritol
 TME: trimethylolethane
 TMP: trimethylolpropane

Assignee(s)	Polyol(s)*	Acid(s) †	Reaction Conditions ‡
Deutsche Erdol	2-Butyl-2-hexylpropanediol, 2-hexyl-2-octylpropanediol, 2-octyl-2-decylpropanediol	Caprylic, pelargonic, capric.	Not given.
Synthetic lubricants, suitable for use in aircraft engines and jet turbines, having low volatility and high viscosity index.			
Geigy	PE	Mixture of straight and branched-chain aliphatic monocarboxylic acids. Mean C number of mixed acids within 7.2-8.5. % C atoms contributed by straight-chain acids greater than 60%. Heptanoic, caprylic, 2-ethyl-hexanoic.	200°-220°C, no catalyst, toluene azeotroping agent.
Synthetic lubricants, suitable for jet engines, having low volatility at elevated temperatures and not causing excessive seal swell.			
B. P. Chemicals	Di-PE, TMP, ethoxylated with ethylene oxide of propylene oxide	Heptanoic, pelargonic, butyric, lauric.	115°-195°C, benzenesulfonic acid catalyst, xylene or toluene azeotroping agent.
Synthetic lubricants, suitable for internal combustion engines or stationary jet engines.			
British Petroleum	TMP, PE	Caprylic, sebacic, heptanoic, 2-ethylhexanoic	Not given.
Synthetic lubricants, suitable for jet aircraft engines, having good resistance to oxidation and corrosion, and good load capacity.			
Sinclair	PE, TMP	3, 3-Dimethylpentanoic acid, 5, 5-dimethylhexanoic acid.	161°-210°C, no catalyst, xylene azeotroping agent.
Synthetic lubricants which are subjected to higher temperatures, such as in combustion turbine engines, having higher viscosity indexes, lower pour points and greater heat stability than mineral oils of corresponding viscosity.			
Emery Industries, Inc.	NPG, PE, TMP. 2,2,4-Tri-methylpentanediol	Valeric, pelargonic	210°C, no catalyst, xylene azeotropic agent.
Synthetic lubricants for use in aircraft gas turbine engines, suitable for higher temperatures, showing oxidation and corrosion resistance, also having good low temperature viscosity and pour point.			
Shell	PE, di-PE, TMP	C ₅₋₉ acids. Azelaic acid.	Not given.
Lubricants stable against air oxidation.			
I.F.P.	NPG	Quaternary acids having 5-20 C atoms.	Chlorides of C ₁₃ -C ₁₉ acids + NPG, 80°C.
Thermally stable ester lubricants of low pour point.			
Tenneco	PE, TMP	Pelargonic. Di-2-methyl-pentanoic.	Not given.
Synthetic lubricants, suitable for jet engines, having good lubricity, low pour point, and high flash point.			

Abbreviations
 NPG: neopentyl glycol
 PE: pentaerythritol
 TME: trimethylolethane
 TMP: trimethylolpropane

Assignee(s)	Polyol(s)*	Acid(s) †	Reaction Conditions †
British Petroleum	PE, TMP	Caprylic, capric, caproic, pelargonic, heptanoic, sebacic, azelaic	Not given.
Synthetic lubricants, suitable for jet aircraft engines, having resistance to oxidation and loss of load-carrying ability at high temperatures.			
Drew Chemical Corp.	Technical PE	2-6 alkanolic acids, 5-9 C atoms, 6-7.25 average number of carbon atoms, 60% = maximum number of C atoms contributed by caprylic and pelargonic acids. 45% = maximum number of C atoms contributed by branched-chain acids.	159° - 232°C, no catalyst, no azeotroping agent.
Synthetic lubricants, suitable for jet engines, able to withstand temperatures above 300°F and down to -40°F.			
Socony Mobil	Technical PE	Commercial isopentanoic(2 parts by wt valeric + 1 part by wt isovaleric), pelargonic.	Not given.
Synthetic lubricants, suitable for jet engines, stable and fluid over a wide temperature range, low volatility at high temperatures, thermal stability, no coke or sludge formation			
British Petroleum	TMP	Caprylic, sebacic	Not given.
Synthetic lubricants, suitable for aviation jet engines, resistant to high temperatures, having a high viscosity index, noncorrosive to metal.			
Shell	PE, TME, TMP	Pivalic	Pivalyl chloride + pyridine + PE, 4° - 85°C
Synthetic lubricants, for jet engines, resistant to oxidation and thermal decomposition at the high operating temperatures of such engines.			
Shell	TME	4-10 C atoms, including, 4-6 mol% capric acid or capric halides. At least two different acyl groups. Even number of C atoms preferred.	109-143°C, p-toluenesulfonic acid catalyst, toluene azeotroping agent.
Synthetic lubricants, suitable for use in high temperature machinery operating at 400°F(204°C) or above. For use as aircraft or other gas turbine lubricants.			
Geigy	NPG, PE, TMP	3-10 C atoms. Saturated straight-chain dicarboxylic acid having 4-14 C atoms.	No temperatures given, no catalyst. Toluene azeotroping agent.
Synthetic lubricants having better viscosity characteristics than conventional diester lubricants, particularly suitable for use in aero gas turbine engines subjected to extremes in temperature.			
Geigy	NPG, PE(mono-, di-, tri-), TMP, 2-methyl-2-n-propyl-1,3-propanediol	Acetic, butyric, valeric, caproic, heptanoic.	80° - 160°C. p-Toluenesulfonic acid catalyst. Benzene or xylene azeotroping agent.
Synthetic lubricants, also suitable for use as plasticizers. Made from capryl alcohol by-product in the manufacture of sebacic acids.			

Abbreviations
 NPG: neopentyl glycol
 PE: pentaerythritol
 TME: trimethylolethane
 TMP: trimethylolpropane

Assignee(s)	Polyol(s)*	Acid(s) †	Reaction Conditions ‡
Heyden Newport Chemical Corp.	TME	4-6 C atoms for two hydroxyl groups, 7-10 C atoms for third hydroxyl group. Butyric, iso-butyrlic, n-valeric, isovaleric, 2-ethylbutyric, caproic, heptanoic, caprylic, 2-ethylhexanoic, pelargonic, capric. Average chain length of 5.6-7.0 carbon atoms.	175°C, no catalyst, xylene azeotroping agent.

Synthetic lubricants for jet aircraft engines, having high viscosity indexes, good oxidation stability, good thermal stability, low pour point, high flash point and sufficient viscosity at high temperature.

Tenneco	TME, TMP	Butyric, valeric, caproic, caprylic, pelargonic, capric, lauric.	175°-180°C, no catalyst, xylene azeotroping agent.
---------	----------	--	--

Synthetic lubricants for gas turbine aircraft engines, having high viscosity indexes, high temperature and oxidation stability, high flash points, and good low temperature properties.

Hercules Powder Co.	Di-PE	2-12 C atoms, in proportions to give an average chain length of 5-10 C atoms.	147°-237°C, no catalyst, toluene azeotroping agent.
---------------------	-------	---	---

Synthetic lubricants for gas turbine aircraft engines, suitable for bulk oil temperatures above 150°C.

Celanese	TMP, TME, PE. Also alkanols with 8-10 C atoms	5-8 C atoms. Alkane dioic acids of 6-10 C atoms.	158°-253°C, no catalyst, xylene azeotroping agent.
----------	---	--	--

Synthetic lubricants for use in jet engines and having optimum high and low temperature properties with low degree of elastomer seal swell.

Celanese	NPG, TME, TMP, PE, 2-butyl-2-ethyl-1, 3-prop-enediol, 2, 2, 4-trimethyl-1, 3-pentanediol	Average chain length of between 4 and 12 C atoms, preferably between 5 and 9 carbon atoms. No more than 2 carbon atoms in side chains, if branched chains are used.	216°-259°C, no catalyst, xylene azeotroping agent. Yields: On polyols: 86-95.5% On acids: 90.4-96.6%
----------	--	---	---

Synthetic lubricants, having high thermal stability, for high performance jet aircraft engines, cannot be made from neopentyl polyols and alkanolic acids having an average chain length of between 4 and 12 carbon atoms, if acid catalyst has a dissociation constant higher than that of acetic acid.

Heyden Newport Chemical Corp.	NPG, TME, TMP PE. Trimethylolbutane	Saturated aliphatic dicarboxylic and aromatic dicarboxylic acids having from 2-36 C atoms. Mono-carboxylic acids, including those with branched chains, and having from 2-22 C atoms.	160°-181°C, phosphoric acid catalyst, xylene azeotroping agent.
-------------------------------	-------------------------------------	---	---

Synthetic lubricants suitable for jet aircraft engines, suitable for high and low temperatures can be made from neopolyols, dibasic acids, and monocarboxylic acids.

Abbreviations
 NPG: neopentyl glycol
 PE: pentaerythritol
 TME: trimethylolmethane
 TMP: trimethylolpropane

Assignee(s)	Polyol(s)*	Acid(s) †	Reaction Conditions ‡
E. F. Drew & Co., Inc.	Mono- and di-PE, TME, hexanetriol, glycerol	Mixture of mono- and dibasic acids, sufficient to combine with hydroxyl groups. Adipic, maleic, terephthalate, isophthalic, azelaic, sebacic, capric, caprylic.	147°-230°C, no catalyst.

Synthetic lubricants for aviation engines, suitable from below 0°F to above 500°F can be made from mixed linear esters of polyhydric alcohols and mixtures of mono-plus dicarboxylic acids.

I.C.I.	PE and poly-PE. Also includes other polyhydric alcohols.	more than 10 carbon atoms. Also includes cycloaliphatic. Saturated or unsaturated. Also includes polycarboxylic acids.	260°-280°C with PE. Yield 98-100% theoretical.
--------	--	--	--

Use of heat-activated alumina as catalyst overcomes disadvantage of sulfuric acid catalyst which causes charring of many polyhydric alcohols. Spent alumina is insoluble and can be mechanically separated and reactivated.

- * Technical grade PE is 88 wt % PE plus 12 wt % Di-PE.
- † Acids are linear aliphatic monocarboxylic, unless otherwise specified.
- ‡ Esterification pressure is atmospheric, unless otherwise specified.

C. DIBASIC ACID ESTERS

Inventor(s) or Assignee	Alcohol(s)	Acid(s)	Reaction Conditions
Toa Cosei Chemical Industries	(A) 2-Ethylhexanol, (B) tridecanol	(A) Dodecane diacid, (B) azelaic acid	Tetrabutyl titanate catalyst, 180°-200°C.

Synthetic lubricants, suitable as base stock or as additives to decrease pour points or increase viscosities of mineral oils. Mixture of diesters of dodecane diacid and azelaic acid with higher branched primary alcohols.

Inventa AG	2-Ethylhexanol	Mixture of dicarboxylic acids having 8-12 carbon atoms	Excess alcohol, catalyst, azeotroping agent, 8 hrs reflux. No temperature given.
------------	----------------	--	--

Synthetic lubricants, suitable for jet engines, having pour points below -60°C and flash points above 240°C. Mixture of esters of unbranched dicarboxylic acids having 8-12 carbon atoms and branched aliphatic monoalcohols. Acids are manufactured from cyclodecanol/cyclodecanone mixtures.

Fischer, Hornberger, Wolf	n-Butyl alcohol, l-butanol	Heptadecanodioic acid	No examples given.
---------------------------	----------------------------	-----------------------	--------------------

Synthetic lubricants, shear-resistant and cold-resistant. Mixture of esters of branched-chain dicarboxylic acids of from 16-22 carbon atoms and aliphatic alcohols of less than 6 carbon atoms with polymers of butenes having a molecular weight of from 1,200-4,500.

Ruhrchemie	n-"Oxo"-octanol, n-"Oxo"-nonanol	Trimethyladipic acid	5 hrs under reflux at 155°C, cumene azeotroping agent, p-toluenesulfonic acid catalyst.
------------	----------------------------------	----------------------	---

Synthetic lubricants for turbine engines, which meet MIL-L-7808 specifications. Esters of easily obtainable, commercially available alcohol and acid components. Mixture of diol diester, neopolyol esters, and dibasic acid diester.

Inventor(s) or Assignee	Alcohol(s)	Acid(s)	Reaction Conditions
Monsanto	B,B-Dimethylphenylethyl alcohol	3,3-Dimethylglutaric anhydride	p-Toluenesulfonic acid catalyst, toluene azeotroping agent, 155°C to solution. Esterification temperature not given. Toluene removed until 180°C reached. Further heating for 4 hrs at 165°C. (Acyl chloride examples also given.)

Synthetic lubricants liquid at temperatures well below 32°F and well above 400°F with viscosity relatively unaffected at high temperatures, having high thermal and oxidative stability. Diesters having terminal dimethylphenyl groups and no hydrogen atoms on the beta carbon atoms of the alcohol or diol.

Castrol	Branched aliphatic primary alcohols	C ₅ -C ₁₇ dicarboxylic acids	No examples given.
---------	-------------------------------------	--	--------------------

Synthetic lubricants, suitable for use in gasoline and diesel piston engines and in industrial and gas turbines. Esters of dicarboxylic acids and branched aliphatic primary alcohols. Miscible with mineral oil in all proportions.

Scholven-Chemie AG	n-Butanol, n-hexanol, n-octanol, n-decanol, n-nonanol, n-dodecanol	Trimethyladipic acid	No reaction examples given. Residual acidity removed by magnesium oxide or magnesium hydroxide.
--------------------	--	----------------------	---

Synthetic lubricants, with high viscosity index, low viscosities at low temperatures, high flash point, low evaporation losses at operating temperatures and adequate shearing, oxidation and thermal stability. Lubricants suitable for jet engines. Esters of trimethyladipic acid, preferably with straight chain monoalcohols. Esterification with mixtures of alcohols gave better properties than mixtures of pure esters.

Technochemie GmbH	2-Ethylhexanol	C ₁₉ -dicarboxylic acid	100% excess alcohol, sulfuric acid catalyst, toluene azeotroping agent, 36 hrs reaction. No temperatures given.
-------------------	----------------	------------------------------------	---

Synthetic heavy duty lubricants prepared from esters of dicarboxylic acid having 19 carbon atoms and primary alcohols having 4 carbon atoms.

Technochemie GmbH	2-Ethylhexanol	Heptadecanedicarboxylic acid	Benzene azeotroping agent, conc. sulfuric acid catalyst, 35 hrs reflux. No temperatures given.
-------------------	----------------	------------------------------	--

Synthetic lubricants with suitable viscosity characteristics and high thermal stability, prepared from esters of branched-chain dicarboxylic acids having 19 carbon atoms with straight or branched chain primary alcohols having 3-19 carbon atoms. Lubricants suitable for blending with natural or other synthetic lubricants.

Ruhrchemie	2-Ethylhexanol; 3,5,5-trimethyl-hexanol	(Normal+150)-C ₁₉ -dicarboxylic acid	100% excess alcohol, p-toluenesulfonic acid catalyst or without catalyst, toluene azeotroping agent or without azeotroping agent, 85-90% molar yield. No temperatures given. Up to 24 hrs esterification.
------------	---	---	---

Synthetic lubricants with greater than 300°C range between pour point and flash point. suitable for turbine oils for aircraft. Prepared from esters of dicarboxylic acids having the formula C₁₉H₃₆O₄.

National Distillers & Chemical	2-Ethylhexanol	2,5-Dimethyl-2,5-diphenyladipic acid	16% excess alcohol, 0.5 part tetraisopropyltitanate catalyst, 180°-230°C over a 3-hr period.
--------------------------------	----------------	--------------------------------------	--

Synthetic lubricants suitable for jet engines, prepared from esters of 2,5-dialkyl-2,5-diphenyladipic acids.

II. 윤활유 첨가제 특허정보 분석

A.1 POLYALKENYL SUCCINIMIDE

Objective	Mol Wt Polymer	Amine	Mol Ratio Amine:SA	Solvent	Temperature	Time (hr)
Improve sludge dispersion and varnish inhibition	Approx. 900 min	Polyethylene Polyamines	0.1:1 to 1:1			
Combined dispersant-VI improver	40,000-200,000	Polyethylene-Polyamines	0.5:1 to 0.1:1	Toluene	110°C (230°F)	6
Improved dispersant	900	Tris(5-amino-3-thiapentyl) amine		Methanol	155°C (311°F)	3
Reduce required additive concentration in lube oil	900	Aminoalkoxy-amines	0.4:1 to 0.6:1	Lube oil	140-180°C (284-356°F)	4
Shear-stable VI improver-dispersant	1,700	Polyamines	1:1	Mineral oil	125°C (257°F)	2
Pure amine raw material	1,870	3-(2-Amino-propylamino)-ethane	0.5:1 to 2:1	Toluene	100-200°C (212-392°F)	3
Dispersant-VI improver	1,300-5,000	Ethylene polyamines	0.25:1 to 2:1	Oil	150-210°C (302-410°F)	2-4
Dispersant-detergent		Diamines		Oil	125°C (256°F)	2
ene copolymer.						
Improved dispersant	6,000	(Octadecyl-amino) propylamine			170°C (338°F)	3
High nitrogen content cal initiator, e. g., 0.5-1.25% organic	750-1,500	Mono- or polyamines peroxide	2:1 to 5:1		90°C (194°F)	1-3
Dispersant with corrosion and foam inhibition	1,000	N, N, N ¹ , N ¹ -tetrakis(3-aminopropyl) ethylenediamine	Various	Oil	120-150°C (248-302°F)	4-5
Basic dispersion agent	1,300	Polyethylene-imine		Xylene	160°C (320°F)	3
Antirust dispersant	300-7,000	Alkylene polyamines		Oil	100-200°C (212-392°F)	4

Alkenyl SA reacted with a bis-succinimide or an ester of an alkenyl SA.

Improved dispersant	1,000	Polyamine ether			160°C (320°F)	3
---------------------	-------	-----------------	--	--	---------------	---

Polyamine ether prepared by cyanoethylation and hydrogenation of triethanolamine.

Mixed dispersants	875 and 1,300	TEPA		Toluene	202°C (396°F)	25
-------------------	---------------	------	--	---------	---------------	----

Succinimide based on PIB of 875 mol wt heated with PIB succinic anhydride based on 1,300 mol wt to give mixed imide.

	Objective	Mol Wt Polymer	Amine	Mol Ratio MA:PIB	Solvent	Temperature	Time (hr)
	Economic purification process	900-2,000	Polyethylene-polyamines	0.1:1 to 1:1		100-200°C (212-392°F)	8
Reaction product treated with in ganic base.							
Texaco Inc.	High nitrogen content	900-2,000	Alkylene polyamines	0.5:1 to 2:1		100-200°C (212-392°F)	6
SA made from dehydrohalogenated PIB.							
Texaco Development Corp.	Detergent-dispersant	1,250	Ethylenedi-amine	1:6.25	None	100-200°C (212-392°F)	
Treated with NaOH at 20-150°C (68-302°F) after reaction with amine.							
USSR	Simplified process		Polyamines				
MA removed from condensation produced by hydrolysis.							
Sanwa Kasei Kogyo Co., Ltd.	Dispersant-VI improver	500-5,000	Diethylene-triamine	1:1	Toluene, mineral oil	95°C (203°F)	3
Heated with LiOH · H ₂ O to give final product.							
Texaco Inc.	Dispersant with anticorrosion properties	500-3,000	Ammonia	1:1	Polyisobutene	100-250°C (212-482°F)	2
Used as intermediate for overbased Ca salt.							
Texaco Inc.	Improved thermal stability	700-3,000	Polyethylene-amines	1:1		200°C (392°F)	
Unstable compounds decomposed by heating to 250-300°C, extracting with alcohol.							
Lubrizol Corp.	Minimize emulsion formation	700-5,000	Polyoxyalkolene polyamines	0.1:1 to 2:1		125-250°C (256-482°F)	1.5-6
Preferred amines have mol wt of at least 400.							
Lubrizol Corp.	Increase demulsifying characteristics	700-5,000	Polyoxyalkylene polyamines	0.1:1 to 2:1	Mineral oil	150-200°C (302-392°F)	4-5
Use of polyoxyalkylene amines prevents formation of emulsion in crankcase.							
British Petroleum Co. Ltd.	Highly basic ashless dispersant	840 max.	Polyamine and sec. or tert. monoamine	1:1	Aromatic hydrocarbon	160-170°C (320-338°F)	5
Equimolar quantities of polyamine and monoamine are used. Monoamine is recovered from reaction mixture. High base numbers result partly from low molecular weight alkenyl group.							
USSR	Increased high temperature perf or mance		Polyethylene-polyamine			145-155°C (293-311°F)	
Reaction carried out in presence of a sulfo acid and a cation exchange resin.							

A.2 POLYALKENYL SUCCINIC ANHYDRIDE

	Objective	Mol Wt Polymer	Mol Ratio MA:PIB	Promoter	Temperature	Time (hr)	% PIB Conversion
Texaco Inc.	Simplify process	300-3,500	0.5:1 to 2.0:1	Oxygen(air)	180-225°C (356-437°F)	5-10	45-52
Orobis, Ltd.	Make polyalkenyl bis(succinic anhydride)	500-2,100	1:1 to 3:1	Nickel iodide	230-250°C (446-482°F)	6-12	70
Reaction carried out under 30-45 psig N ₂ . Product is mixture containing up to 40% bis(succinic anhydride).							
Shell oil Co.	Reduce Cl ₂ content of product	300-200,000	1.7:1	Chlorine	180°C (356°F)	9	83
Ratio Cl ₂ :MA=0.67:1. Chlorination time:5 hr at 180°C, thermal treatment: 4 hr at 180°C.							
Texaco Inc.	Improve yield, reduce tar formation	800-1,500	0.9:1	Brominated phenol, e.g., orthobromo- phenol	235-265°C (455-509°F)	6	
Preferred Br concentration: 10-250 ppm.							
Shell International Research Maatschappij B.V.	Increase conversion of PIB	500-250	1:1 to 2:1	Chlorine	160-210°C (320-410°F)	3-7	78-90
After chlorination, mixture heated at 160-210°C for about 2 hr under reflux. Tars and excess MA removed by washing with alcohol-water mixture.							
Lubrizol Corp.	Reduce Cl ₂ consumption	750-3,000	1:1	Chlorine	175-200°C (347-392°F)	12-18	
Molar ratio Cl ₂ :MA=0.5:1.0 to 0.7:1.0 Cl ₂ may be added intermittently.							
Texaco Inc.	Increase nitrogen content of succinimide	900-2,000	0.2:1 to 2:1	Chlorine	100-250°C (212-482°F)	4-24	
Polyalkene chlorinated at about 120°C then dehydrochlorinated at about 235°C to increase reactivity with MA.							
Standard Oil Co. (Indiana)	Improve yield, reduce tar formation	300-3,000	0.9:1.0	Chlorinated or brominated carboxylic or sulfonic acid	249°C (480°F)	6	64-74
Additive concentration 5-200 ppm, based on PIB, e.g., 75 ppm N-bromosuccinimide.							

MA = Maleic anhydride.

PIB = Polyisobutene.

B. ZINC DIHYDROCARBYLDITHIOPHOSPHATES

Earliest Date	Assignee	Objective
6/19/80	Chevron Research Co.	Inhibit oxidation and corrosion
Zinc salt of lower(2-3 carbon atoms) dialkyldithiophosphoric acid reacted with an oil-soluble alkenyl or alkyl succinimide.		
2/25/80	Shell International Research	Extreme pressure antioxidant
Zinc salts prepared from acid based on alcohols containing oxyalkylene groups, e.g., alkylsalicylates.		
5/31/79	Lubrizol Corp.	Extreme pressure antioxidant
Additive consists of mixed metal salts of di(hydrocarbyl)dithiophosphoric acid and an aliphatic or alicyclic carboxylic acid.		
4/2/79	Chevron Research Co.	Extreme pressure additive with improved wear prevention properties.
Additive is zinc salt of alkylphenyl, oly(oxyalkylene)dithiophosphate. Example compound prepared by reacting tetraprop lenephenol with 1,2-epoxybutane, P ₂ S ₅ , and ZnO.		
3/9/79	Orogil SA	Novel extreme pressure antiwear additive
Additive is a metallic(preferably Zn) dithiophosphate made by reacting ZnO with		
$\begin{array}{c} \text{R}_2 \quad \quad \text{S} \\ \quad \quad \\ (\text{R}_1 - \text{COO} - \text{CH}_2 - \text{C} - \text{CH}_2\text{O})_2\text{P} - \text{SH} \\ \\ \text{R}_3 \end{array}$		
Where R ₁ is an alkyl, olefinyl, cycloaliphatic aryl, or heterocyclic radical and R ₂ and R ₃ are alkyl radicals containing 1-4 C atoms.		
3/9/79	Orogil SA	Novel extreme pressure antiwear additive with improved heat stability
Zinc dithiophosphate of composition shown in (486145) is reacted with an alkyl ester with the aid of a sulfurization agent.		

Earliest Date	Assignee	Objective
3/1/79	Mobil Oil Corp.	Antiwear, antioxidant additives with improved oil solubility, odor, and corrosivity characteristics
Additive is made by reacting the reaction product of alkyl- or aryl dithiophosphoric acids and a sulfurized olefin with a reactive olefin, epoxide, unsaturated aldehyde, or other reactive compound.		
12/29/78	Standard Oil Co.(Indiana)	Haze-free zinc dihydrocarbyl-dithiophosphates
Surface active agent added to reactants just before addition of zinc oxide.		
6/29/77	Chevron Research Co.	New method for preparing mixed alkyl-aryldithiophosphates
Dialkyl- and diaryldithiophosphoric acids mixed and heated at 55-95°C to form approximately 20-25 mol% di(alkylaryl)dithiophosphoric acid, which is then neutralized with ZnO.		
5/23/77	Standard Oil Co.(Indiana)	Improve neutralization, reduce amount of excess metal base required
Acidic promoter (e.g., nitric acid) used for neutralization. Excess promoter neutralized a nitrogen-containing base which forms a salt and does not replace metal in the dithiophosphate (e.g., ammonia or urea).		
3/28/77	Standard Oil Co.(Indiana)	Continuous neutralization of dithiophosphoric acids
Neutralization mixture pumped through a static mixer, cooler, and a small holding vessel to increase contact time. Water of reaction removed by blowing with nitrogen in stirred tanks. Reaction temperature 100-170°F (38-77°C); excess ZnO, 20-60%.		
3/10/77	USSR	Increased antioxidant and detergent properties
Hydroxyl compound is 0.15-1:1 mol ratio mixture of polyalkylene glycol C ₁₋₁₀ alkylphenyl ether and polyalkylene glycol C ₃₋₂₀ alkylphenyl ether.		
3/10/77	USSR	Improved additives
Mono- and polyglycol ethers of alkylphenols with 1-10 C atoms in the alkyl group and 1-7 glycol groups reacted with P ₂ S ₅ at 176-266°F (80-130°C) and neutralized at 140-212°F (60-100°C).		
3/1/77	Standard Oil Co.(Indiana)	Improved neutralization process for diaryldithiophosphates
C ₃ -C ₈ dialkyldithiophosphoric acid (0.11-0.22 mol per mol of aryl dithiophosphoric acid) used as a neutralization promoter.		

Earliest Date	Assignee	Objective
3/27/76	Edwin Cooper and Co., Ltd.	Improve neutralization for zinc diaryldithiophosphates
Reaction of ZnO with acid promoted by conducting it in mineral oil treated with NO ₂ .		
2/25/76	Chevron Research Co.	Prepare mixed dialkyldithiophosphates
Mixture of primary and secondary alcohols reacted with P ₂ S ₅ at 176°F (80°C), added to slurry of ZnO in oil at 212°F (100°C) to form Zn-dialkyldithiophosphates.		
12/19/74	Texaco Inc.	Improved additive for automatic transmission oil
Additives prepared from long, straight-chain alcohols, acids, and thiols, e.g., n-octadecyloxyethoxyethyl alcohol.		
12/1/72	USSR	Antiabrasive additive
Dialky- or dialkylaryldithiophosphoric acids neutralized with KOH solution and the resultant salt treated with a Cl-containing hydrocarbon.		
10/12/7	Texaco Development Corp.	Improve stability
Mixture of methylisobutyl alcohol and dimethylcarbinol used.		
1/10/72	Czechoslovakia	Improve thermal stability
Mixture of 2-ethylhexanol and isobutyl alcohol reacted with P ₂ S ₅ , diluted with ethanol, reacted with ZnO in benzene.		
12/9/70	Texaco Inc.	Nitration inhibition
Mixture of Zn-dialkyldithiophosphate and Zn-bis[(2-alkyl-phenoxy)ethyl] dithiophosphate added to lubricating oil.		
7/24/70	Standard Oil Co.(Indiana)	High temperature stability
Dinonyl dithiophosphoric acid neutralized with ZnO in presence of a promoter such as Zn(NO ₃) ₂ .		

(계속)