



합성윤활유 및 첨가제 관련 특허정보 분석 (II)

고려대학교 화학과
최 주 환 박사

C. SULFONATES

Earliest Date Shown	Assignee	Product	Objective of Patent
8/28/80	Chevron Research Co.	Overbased alkaline earth sul- fonates	Increase degree of overbasing
Sugar solution (20-35% sucrose) added before or after carbonation.			
12/13/79	Exxon Research & Engineering Co.	Basic Mg sulfonate	Process for basic Mg sulfonate dispersant
Neodecanoic acid added to reaction mixture. Carbonation carried to 70-90% of theoretical.			
10/12/79	Tenneco Chemicals Inc.	Overbased Mn salts of organic acids	Overbased Mn salts containing at least 1.3% Mn
Carbonation conducted above 2 atm pressure.			
10/2/79	Ethyl Corp.	Overbased alkaline earth sul- fonates	Recover sulfonic acids from fil- ter cake
Filter cake slurried with aqueous HCl and organic solvent (e.g., hexane). Sulfonic acid recovered from organic phase.			
8/31/79	Exxon Research & Engineering Co.	Overbased Ca sulfonate	Improve solubility of Ca sul- fonate in oil
Water content of initial reaction mixture adjusted to 1-3 wt% of excess CaO used.			
3/26/79	Nalco Chemical Co.	Overbased Mg sulfonate	Product with high Mg content
Sulfonic acid neutralized in presence of a fatty acid (e. g., oleic) and an alkanol amide. After removal of water and methanol, diluent oil, MgO, and Co ₂ are added.			
12/13/78	Exxon Research & Engineering Co.	Overbased Mg sulfonates	Improved promoter, improved filtration
Water may be added. C ₁₀ acids preferred.			
12/13/78	Exxon Research & Engineering Co.	Overbased alkaline earth metal sulfonates	Improved promoter
Water may be added. Carbonation temperature, 50-150°C.			

Earliest Date Shown	Assignee	Product	Objective of Patent
12/13/78	Exxon Research & Engineering Co.	Overbased Mg sulfonates	Improved promoter and reaction system
Reaction mixture includes water (0.5-2 parts by wt based on MgO).			
12/13/78	Exxon Research & Engineering Co.	Overbased Mg sulfonates	Simplified process
Carbonation is conducted between 50°C and reflux temperature until 80-120% of CO ₂ required for excess MgO has passed through reaction mixture and for sufficient time to reach 70-90% of CO ₂ required for excess MgO.			
6/30/78	Chevron Research Co.	Ca polyisobutenyl sulfonate	Prepare neutral, saturated Ca sulfonate
Ca polyisobutenyl sulfonate prepared by metathesis of Na salt with CaCl ₂ .			
6/29/78	USSR	Ca sulfonate	Process for Ca sulfonate
Based on product of alkylation of toluene with C ₂₀₋₈ α-olefins.			
Neutralizing Agent	Solvents	Promoters	
Ca(OH) ₂ , Ba(OH) ₂	Mineral oil	Alcohols, sugar (e. g., sucrose)	
MgO	Toluene	C ₁₋₅ alcohol (e. g., methanol), or C ₃₋₆ ketone	
MnO	25-40% alcohol (e. g., methanol) or ether and alcohol (e. g., methoxyethanol), 60-75% inert hydrocarbon (e. g., naphtha)	Ammonium halides, metal halides and alkanolic acid (e. g., acetic or formic acid)	
Alkaline earth hydroxides			
CaO	Oil, aromatic or aliphatic hydrocarbon	C ₁ to C ₅ alcohol (e. g., methanol)	
MgO	No. 2 fuel oil, low odor paraffinic solvent, toluene	Methanol, formic acid ethylene diamine	
MgO	Oil, aliphatic or aromatic hydrocarbon (e. g., heptane, toluene)	C ₈ -C ₁₀ carboxylic acid (e. g., n-decanoic acid). Copromoters may include alcohols, aldehydes, amines, diketones, etc.	
MgO	Oil, aliphatic or aromatic hydrocarbon (e. g., hexane, toluene)	C ₄ -C ₆ diketone (e. g., acetyl acetone), copromoters may include alcohols, aldehydes, amines, carboxylic acids, etc.	
MgO	Oil, aliphatic or aromatic hydrocarbon (e. g., hexane, toluene)	C ₃ -C ₆ ketone (e. g., acetone), carboxylic acids or salts, amines, diketones	
MgO	Oil, aliphatic or aromatic hydrocarbon (e. g., heptane, toluene)	C ₁ -C ₅ alcohol or C ₃ -C ₆ ketone plus an amine, amine salt, carboxylic acid, or diketone	
NaOH, CaCl ₂	Hydrocarbons or chlorinated hydrocarbons (e. g., 1, 2-dichloroethane)	Methanol	
Ca(OH) ₂			

Earliest Date Shown	Assignee	Product	Objective of Patent
6/20/78	Phillips Petroleum Co.	Overbased Ca petroleum sulfonates	Improved process for high TBN Product
Higher total base numbers (TBN) achieved with moderate agitation than with intensive mixing. Excess methanol promotes gelling.			
5/1/78	Bray oil Co.	Overbased Mg sulfonate	Process adaptable to all commercial grades of MgO
Carbonation rate adjusted according to reactivity of MgO—always less than maximum possible rate.			
5/1/78	Witco Chemical Corp.	Overbased Mg sulfonates	Stable product with minimum Mgo usage
Reaction temperature 70–125° F. No refluxing necessary. Product TBN over 500.			
4/3/78	Calumet Industries, Inc.	Overbased Mg sulfonates	Economical process for fluid, highly basic Mg sulfonate
Sulfonic acid neutralized with basic Mg sulfonate, carbonated in two stages after addition of MgO and promoters.			
2/20/78	USSR	Ca petroleum sulfonate	Process for Ca sulfonate
Mixture of petroleum oil and bis(n-alkylnaphthalene) sulfonated.			
11/22/77	Standard oil Co. (Indiana)	Overbased Mg sulfonates	Single stage process for highly basic, gel-free sulfonate
Sulfonic acid reacted with NH ₃ before addition of MgO. Methanol removed from reaction mass before carbonation.			
8/4/77	Exxon Research & Engineering Co.	Overbased Ca sulfonate	Reduce foaming
Based on sulfonic acids made from alkyl-o-xylenes or alkyltoluenes mixed with an overbased Ca alkylbenzenesulfonate.			
7/14/77	Instytut Technologii Nafty	Ba sulfonate	Low freezing additive
Alkylbenzene sulfonic acid heated with Ba(OH) ₂ ·8H ₂ O until all water was driven out, diluted with oil.			
7/4/77	Exxon Research & Engineering Co.	Highly basic Ca sulfonates	Process for overbased Ca sulfonate
Carbonated with CO ₂ for 4 hr, additional Ca(OH) ₂ then added.			
6/27/77	Standard oil Co. (Indiana)	Overbased aminoguanidine sulfonates	Ashless detergent
Alkybenzene sulfonic acid neutralized at 340° F.			
6/14/77	Edwin Cooper & Co., Ltd.	Overbased Ca or Mg sulfonate	Single stage process yielding a TBN of 200 or more and high metal ratio
Amounts of methanol and water must be limited to prevent gelling, e. g., 0.5–1.0 mol methanol and 0.2–0.8 mol water per mol CaO.			
12/16/76	Chevron Research Co.	Overbased sulfonates	Prepare various metallic sulfonates
Sulfonates based on polyisobutylene.			
10/8/76	Lobofina SA	Overbased Ca sulfonate	Detergent anticorrosion additives
Purified alkylbenzene sulfonic acid reacted with CaO, which has a medium reactivity toward water.			

Neutralizing Agent	Solvents	Promoters
Ca(OH) ₂	Oil, naphtha, monoalkylbenzene (e. g., toluene)	Methanol
MgO	Oil, aliphatic or aromatic hydrocarbons (e. g., xylene)	Alcohols, alkoxyalcohols, ammonia, amines
MgO	Oil, aliphatic or aromatic hydrocarbons	Ammonium hydroxide, methanol, water
MgO	Oil, aliphatic or aromatic hydrocarbons	Lower alkanols, preferably methanol, ammonia, naphthenic acid
Ca(OH) ₂		
MgO	oil, aliphatic or aromatic hydrocarbons	Lower alkanols (methanol), water
Ca(OH) ₂		
Ba(OH) ₂	Aromatic oil with low pour point	None
Ca(OH) ₂	Toluene	Methanol
Aminoguanidine bicarbonate	oil	Water
CaO or MgO	Oil, aliphatic or aromatic hydrocarbon (e. g., hexane/heptane)	Methanol, ammonium formate
Ca(OH) ₂ , NaOH, LiOH		
CaO	Oil, aromatic hydrocarbon	Methanol, water, ammonia or amine

Earliest Date Shown	Assignee	Product	Objective of Patent
7/31/76	Instytut Technologii Nafty	Ca sulfonate	Prepare overbased Ca sulfonate
Reaction mixture contained dispersion of reaction product of polyisobutylene and p ₂ S ₅ .			
7/15/76	Surpass Chemicals, Ltd.	Overbased Mg sulfonates	One step process for overbased Mg sulfonates
Reaction temperature 120-170°F. Water and alcohol may be added gradually during a portion of the carbonation time.			
6/30/76	Surpass Chemicals, Ltd.	Overbased Mg sulfonates	One step process for overbased Mg sulfonates
This patent is identical in most respects to 486186.			
6/24/76	VEB Petrochemisches Kombinat Schwedt	Alkaline earth metal sulfonates	Gelation-free process
0.1-5% alkylphenol inhibits gel formation and improves corrosion inhibiting properties.			

Earliest Date Shown	Assignee	Product	Objective of Patent
5/27/76	Witco Chemical Corp.	Neutral or slightly basic Ca sulfonates	Corrosion inhibitors for diesel engines
Dialkylbenzenesulfonic acids neutralized with Ca(OH) ₂ and water. Air bubbled through mixture to aid in removing water.			
4/29/76	Lubrizol Corp.	Basic Mg-containing complexes	Oleophilic Mg-containing compositions for lube oil and fuel additives
Thixotropic liquids or gels prepared by reacting MgO and alkylbenzenesulfonic acid with water. No carbonation is used.			
4/29/76	Lubrizol Corp.	Mg complex	Process for Mg additive
Mg(OH) ₂ reacted with alkylbenzene sulfonic acid and water to form an MgO-sulfonate complex gel.			
9/8/75	Phillips Petroleum Co.	Borated amine petroleum sulfonate	Detergent for motor oil and gasoline
Mixture of petroleum sulfonic acid and polyamine treated with slurry of boric acid and water in oil.			
7/30/75	Czechoslovakia	Overbased Ca sulfonate	Detergent-dispersant additive
Ca sulfonate mixed with Ca(OH) ₂ suspended in oil, gasoline, water and methanol, carbonated.			
6/9/75	Chevron Research Corp.	Metal polyisobutenyl sulfonates	Improved detergent
Ca polyisobutenyl sulfonate prepared from reaction of O-chlorophenyl vinyl-sulfonate and polyisobutenyl chloride.			
3/28/75	Standard oil Co. (Indiana)	Purified sulfonic acids	Improve overbasing process and overbased sulfonate quality
Crude sulfonic acid treated with water and, after phase separation, with ground limestone to remove water soluble acids, tars, and sludge.			
1/17/75	East Germany	Overbased Ca sulfonates	Additive for marine oils
Mixture may also contain polyalkenyl-succinimide.			
11/19/74	Council of Scientific & Industrial Research (India)	Ba-Ca petroleum sulfonates	Detergent-dispersant additives
Solid hydroxides used as powders 30-60 B. S. mesh.			

Neutralizing Agent	Solvents	Promoters
Ca(OH) ₂	Oil	Urea, stearylamine
MgO	Oil, aliphatic or aromatic hydrocarbon (e. g., naphtha)	Lower carboxylic acid (e. g., acetic acid) or salts, water, methanol
MgO	Oil, aliphatic or aromatic hydrocarbon (e. g., naphtha)	Oil-insoluble lower carboxylic acid, salts, anhydrides, esters containing 1-5 C atoms
Ba(OH) ₂ or Ca(OH) ₂		Alkylphenol
CaO or Ca(OH) ₂	Mineral oil	None
MgO	Mineral oil, naphtha, benzene, toluene, etc.	Alcohols, phenols, amines

Neutralizing Agent	Solvents	Promotere
MgO or Mg(OH) ₂	Toluene	
Tetraethylene-pentamine or polyethyleneamine	Mineral oil	
Ca(OH) ₂	Oil, gasoline	Methanol
NaOH, CaCl ₂	1, 2-Dichloroethane	
CaCO ₃	Hexane, heptane, lube oil	
Ca(OH) ₂ or CaO		Methanol, monoalkanolamine, alkylated nonylphenol
Ba(OH) ₂ or Ca(OH) ₂	Hydrocarbon oil	

Earliest Date Shown	Assignee	Product	Objective of Patent
7/25/74	USSR	Overbased sulfonates	Improved process
Ammonium sulfonate neutralized with metal hydroxide.			
3/29/74	Institute Francais du Petrole des Carburants et Lubrifiants	Overbased Ca sulfonate	Increased basicity reserve
Salt of polyisobutenylsuccinimide amine added to reaction mixture.			
2/1/74	USSR	Highly alkaline sulfonate	Simplify purification
A polysiloxane added before carbonation.			
11/20/73	Lubrizol Corp.	Alkali sulfonate dispersion	Ashless detergent-dispersant
Made from alkylated benzenesulfonic acid and polybutenyl succinic anhydride.			
10/5/73	Lubrizol Corp.	Basic alkali sulfonates	Prepare stable solutions or dispersions
Solution of sulfonic acid, sodium hydroxide, and promoters carbonated at about 85°C. Methanol and other volatiles stripped with nitrogen.			
8/15/73	Tobata Kagaku Co., Ltd.	Highly basic Ca sulfonate	Process for Ca sulfonate
Carbonation in presence of water (2-35 wt% of methanol).			
7/3/73	Institute Francais du Petrole, des Carburants et Lubrifiants	Overbased Ca sulfonates	Process for Ca sulfonates
Mixture of sulfonic acid and C ₁₂₋₁₄ alkyl substituted amine acids neutralized with Ca(OH) ₂ , carbonated under pressure.			
2/2/73	Nippon Oil Co., Ltd.	Ca sulfonate	Improved performance and cost
Conjugated diene polymer from butadiene and toluene hydrogenated and sulfonated, neutralized with NaOH, reacted with Ca(OH) ₂ .			

Earliest Date Shown	Assignee	Product	Objective of Patent
12/20/72	Standard Oil Co. (Indiana)	Overbased Mg sulfonates	One-step carbonation
Sulfonic acid neutralized with ammonia before addition of MgO and carbonation. Reaction temperature 175-200°F.			
12/20/72	Chevron Research Co.	Overbased Mg sulfonates	Simplified economical process
Neutral Mg sulfonate obtained by metathesis of Na sulfonate. Naphthenic acid present from 0.2 to 0.75 equivalent per sulfonic acid equivalent during carbonation.			
10/20/72	Standard Oil Co.	Overbased Ba sulfonates	Prepare overbased Ba alkenyl sulfonates
Alkenyl sulfonic acid neutralized with ammonia, reacted with a precarbonated mixture of BaO in water and methanol.			
4/19/72	Continental Oil Co.	Overbased Mg sulfonate	Low cost, large scale process
Ammonia present at about 1 part per 100 parts by weight of sulfonic acid. Process unsatisfactory with CaO or with aromatic solvents.			
2/4/72	Karonite Chemical Co., Ltd.	Overbased Ca sulfonate	Highly basic detergent
Carbonation and dehydration carried out below 110°C (230°F) to minimize filtration difficulties.			

Neutralizing Agent	Solvents	Promoters
Alkaline earth metal hydroxide	Hydrocarbon	Ammonia and low molecular weight carboxylic acid
Ca(OH) ₂	Toluene	Methanol
Alkaline earth metal hydroxides	Oil, hydrocarbon	Not specified
NaOH	Oil	Methanol
Alkali metal hydroxides or other compounds	Oil, aliphatic or aromatic hydrocarbons	Lower alcohols (e. g., methanol), oil-soluble carboxylic acid compounds, (e. g., polybutenylsuccinic anhydride)
CaO or Ca(OH) ₂	Low boiling point hydrocarbon	Methanol
Ca(OH) ₂	Toluene, oil	Methanol
Ca(OH) ₂ -CaCl ₂	Isooctane	
MgO	Oil, inert hydrocarbon (e. g., xylene)	Methanol, water
MgO	Oil, aliphatic or aromatic hydrocarbon	Lower alcohol (e. g., methanol), naphthenic acid (mol wt = 150-600)
BaO	Oil	Methanol, water
MgO (low density)	Oil, aliphatic hydrocarbons (e. g., hexane)	Lower aliphatic and alkoxy alcohols, water, ammonia
CaO	Mineral oil, dodecylbenzene	Ethylene glycol, tridecanol

Earliest Date Shown	Assignee	Product	Objective of Patent
12/27/71	Bray Oil Co.	Overbased alkaline earth metal sulfonates	Prevent gel formation during overbasing
Reaction mixture treated with limited amount of water after stripping off most of methanol, evaporated, treated with additional water, and dehydrated.			
10/25/71	USSR	Sulfonate additive	Increased effectiveness
Sulfo acid present at 3% by weight during neutralization.			
8/3/71	Continental Oil Co.	Ca(OH) ₂ dispersions	Prepare diesel engine lubricants
CaO mixed with Ca sulfonate solution, refluxed, hydrolyzed, and distilled.			
6/14/71	Esso Research & Engineering Co.	Basic Ba sulfonate	Highly basic dispersant
Mixture of steam and CO ₂ used for carbonation. TBN=165.			
5/12/71	Witco Chemical Corp.	Overbased Ba sulfonate	Highly overbased Ba sulfonate
Alcoholic solution of Ba compound added to sulfonic acid solution in inert solvents carbonation to 50-85% completion at 0-100°C, to 100% completion at 115-130°C.			
6/14/71	Esso Research & Engineering Co.	Overbased Ba sulfonate	High TBN
Carbonation with CO ₂ and steam.			
6/4/71	Witco Chemical Corp.	Basic Mg sulfonate	Stable colloidal Mg dispersion
Mg methylate reacted with CO ₂ , added to sulfonic acid in oil.			
5/7/71	Continental Oil Co.	Borated amine sulfonates	Process for anionic metal-containing sulfonates
Dialkylbenzene sulfonic acid and triethanolamine refluxed with H ₃ BO ₃ and water.			
5/3/71	Mobil Oil Corp.	Overbased Mn compounds	Overbasing process for Mn compounds
Sulfonates or carboxylates may be made by this process.			
3/10/71	Esso Research & Engineering Co.	Overbased sulfonate	Process for highly basic noncarbonated detergent
Sulfonic acid, oil, CaCl ₂ , CaO, H ₂ O, and phenol heated at 140-250°C until CaO is digested.			
12/28/70	Lubrizol Corp.	Mg sulfonates	Prevent formation of insoluble surface films
Ca salts of alkylated phenol-formaldehyde condensation products plus high molecular weight carboxylic acids added to solutions of Mg sulfonates.			
10/17/70	USSR	Overbased petroleum sulfonate	Process for heavy oil raw material
Mixture of residual oils and distillate sulfonated, purified of asphalt and heavy aromatics before neutralization.			
Neutralizing Agent		Solvents	Promoters
CaO, Mg methylate		Naphtha, xylene, toluene	Methanol
Alkaline earth oxide or hydroxide		Sulfo acid of 300-400 molecular weight	

Neutralizing Agent	Solvents	Promoters
CaO	Mineral oil	Lower alkoxyethanol
Ba(OH) ₂	Mineral oil, low boiling hydrocarbon	Alcohol, phenol (e. g., nonylphenol), or amine
BaO (in alcohol solution)	Aliphatic or aromatic hydrocarbons (e. g., naphtha, toluene)	alcohol, water
Ba(OH) ₂ , BaCl ₂	Mineral oil, low boiling hydrocarbon	Alcohol, phenol, or amine
Mg methylate	Mineral oil, naphtha	Methanol
Amino-alcohol, e. g., triethanolamine	mineral oil, hexane	
MnO	Oil	Methanol, CaCl ₂ , chlorobenzene, NH ₄ Cl
CaO	Hydrocarbon oil	Phenol
MgO	Oil	
Alkaline earth hydroxide	Xylene	

Earliest Date Shown	Assignee	Product	Objective of Patent
9/9/70	Bray Oil Co.	Overbased sulfonates	High TBN without gel formation
Carbonation conducted in stages with anhydrous methanol and CO ₂ . In each stage, methanol is removed, product treated with water then dehydrated. Process may be continuous using up to four stages for a TBN of 500-600.			
7/27/70	Czechoslovakia	Basic Ca sulfonate	Stable colloidal Ca salt dispersion
Solution of Ca petroleum sulfonate added to CaO gradually during carbonation for control of temperature and decrease in sediment.			
7/27/70	Czechoslovakia	Ba-Ca sulfonate	Stable Ba salt colloidal dispersion
Ca petroleum sulfonate mixed with BaO dispersion in methanol and xylene, then carbonated. TBN=107. No hydrolysis step.			
7/17/70	Continental Oil Co.	Overbased Ca sulfonate	Stable dispersion
CO ₂ neutralization carried to 80-90% instead of completion.			
7/3/70	Esso Research & Engineering Co.	Overbased Ca isobutenyl sulfonate	Improved detergent additive
Based on alkylbenzene sulfonic acid and a long chain monocarboxylic acid, e. g., polyisobutenepropionic acid.			
6/1/70	Texaco Inc.	Overbased alkalene earth metal sulfonates	Increase metal ratio
Solution of alkaline earth metal sulfonate mixed with alkaline earth hydroxide and boric acid in methanol carbonated with CO ₂ ; mol ratio boric acid:hydroxide between 2:1 and 1:2.			
5/12/70	Esso Research & Engineering Co.	Overbased Ca isobutenyl sulfonate	Improved detergent additive
Based on mixture of alkylbenzene sulfonic acid and polybutenylpropionic acid. Two stage carbonation under pressure. TBN=520.			

Neutralizing Agent	Solvents	Promoters
CaO, MgO, BaO	Aliphatic or aromatic hydrocarbons (e. g., xylene, naphtha)	Methanol, water
CaO (burnt lime)	Mineral oil, xylene	Methanol
BaO	Mineral oil, xylene	Methanol
Ca(OH) ₂	Hexane	Methanol
CaO	Toluene	Methanol, ammonium formate
Alkaline earth hydroxide	Aromatic or aliphatic hydrocarbons (e. g., isooctane)	Boric acid, methanol
CaO	Toluene	Methanol, NH ₄ Cl

D. ETHYLENE-PROPYLENE COPOLYMERS

Assignee	Priority Date	Function	Reactants
Edwin Cooper Inc.	10/27/80	VI improver, dispersant	Maleic anhydride, C ₁₋₁₀ alkanol (e. g., 1-butanol), substituted propanediamine (e. g., N-oleoylamino-propyl-1, 3-propanediamine)
EPDM polymer dissolved in hydrogen treated mineral oil, reacted with maleic anhydride in presence of free radical catalyst. EPDM-maleic anhydride graft copolymer esterified with alkanol, amidated with substituted propanediamine.			
Standard Oil Co. (Indiana)	10/10/80	VI improver, dispersant	Sulfur, polyalkylene amine (e. g., tetraethylene pentamine)
Oxidized EP or EPDM copolymer reacted with sulfur in oil solution, then reacted with amine in presence of formaldehyde, which acts as amination promoter.			
Orobis, Ltd.	10/21/80	VI improver, dispersant	EP or EPDM polymer, air, alkali or alkaline earth metal or compound e. g., an oxide, hydroxide, carbonate, bicarbonate, or peroxy compound of lithium, sodium, or potassium
Method for reducing polymer molecular weight by oxidative shearing. Solution of polymer in oil contacted with air at 100-250°C (212-482°F) in presence of alkali or alkaline earth metal or compound. Degraded polymer may be reacted with amine to form dispersant.			
Standard Oil Co. (Indiana)	10/10/80	VI improver, dispersant	Amine, sulfur or sulfur-yielding compound, polyiso-butylene
Reaction product resistant to increase in viscosity and molecular weight during production.			
Rohm & Haas Co.	12/31/79	VI improver, detergent	Chlorosulfonyl isocyanate, polyamine (e. g., dimethyl-aminopropylamine)
EPDM polymer dissolved in inert solvent (e. g., hexane), reacted with chlorosulfonyl isocyanate, stripped of solvent, dissolved in oil, reacted with amine. Reaction product neutralized with NaOH, stripped under vacuum to remove excess amine and water.			
Agip Petrole, S.p.a.	9/10/79	VI improver	None
Thermal cracking method for reducing molecular weight of EP copolymer. EP copolymer in oil solution heated at 250-350°C (482-662°F) in inert atmosphere for 15-45 minutes in presence of free radical scavenger (aromatic quinone, phenol, or amine compound).			

Assignee	Priority Date	Function	Reactants
Ube Industries	8/30/79	VI improver	Nitrogen-containing monomer, e. g., 2-vinylpyridine
Ethylene-propylene copolymer made by Ziegler-Natta polymerization, continuously grafted to N-containing monomer in tubular reactor at temperature above decomposition temperature of peroxide initiator.			
Ube Industries	8/30/79	VI improver	Nitrogen-containing monomer, e. g. 2-vinylpyridine, dimethylaminoethyl-methacrylate
Ethylene copolymerized with propylene in presence of Ziegler-Natta catalyst. Molecular weight degraded by heating at 80-150°C (176-302°F). N-containing monomer grafted to degraded EP copolymer at 80-150°C for 0.5-10 hr.			
Exxon Research & Engineering Co.	7/3/79	VI improver, dispersant	Maleic anhydride, 8-20°C alkyl-substituted primary amine
Oil solution of EP copolymer reacted with MA so that part of MA is grafted onto oil and part onto EP copolymer.			
Exxon Research & Engineering Co.	2/14/79	VI improver, dispersant	Maleic anhydride, diamines containing one primary and one tertiary amine group, and C ₂₋₆₀ Polyamines
Maleated EP copolymer grafted with 4-(3-aminopropyl) morpholine and diethylenetriamine, reacted with alkylbenzenesulfonic acid. Product inhibits varnish formation.			
Orobis, Ltd	1/9/79	Oxidation resistant VI improver	Thiol acids
EPDM terpolymer reacted with thiol acid obtained by reacting phosphorus pentasulfide with C ₇ to C ₉ primary alcohols or alkyl phenols, e. g., p-dodecylphenol.			
Exxon Research & Engineering Co.	1/9/79	VI improver, dispersant	Alkylene polyamine
EP copolymer containing 2, 5-norbornadiene readily degradable by mastication and oxidation without formation of insoluble gels which may occur with other dienes. Reaction product with amine has favorable low temperature viscosity effects.			
B. F. Goodrich Co.	12/7/78	VI improver	-
EP copolymer stabilized by 0.1-5% of Na dimethyl dithiocarbamate, tetramethylthiuram disulfide, or diethyl dithiocarbamate.			
Rhone-Poulenc Industries S. A.	9/29/78	VI improver, dispersant	sec-Butyllithium, N, N-dimethyl-1, 2-ethanediamine, 2, 2-bipyridine
EPDM containing 1, 4-hexadiene metalated with Li, reacted with bipyridine at 60°C (140° F).			
Rhone-Poulenc Industries S. A.	4/29/78	VI improver, dispersant	sec-Butyllithium, N-methylpyrrolidone
EPDM containing 1, 4-hexadiene metalated with Li, reacted with N-methylpyrrolidone in presence of N, N-dimethyl-1, 2-ethane-diamine.			
Lubrizol Corp.	4/17/78	VI improver, dispersant	Maleic anhydride, amine (e. g., an N-amino-alkyl-morpholine)
EPDM polymer reacted with maleic anhydride in oil solution at 210-220°C (410-428°F), then with amine.			

Assignee	Priority Date	Function	Reactants
Rohm GmbH	2/11/78	VI improver, dispersant, detergent	Polymerizable lactam (e. g., N-vinyl pyrrolidone), poly-merizable N-heterocyclic compound (e. g., N-vinyl imidazole)
EP copolymer graft polymerized with N-vinylpyrrolidone and N-vinyl imidazole in an extruder at 100°C (212°F). Presence of N-vinyl imidazole increases graft yield.			
Rohm & Haas Co.	12/5/77	VI improver, dispersant	Maleic anhydride, ethylenically unsaturated monomer (e. g., methyl methacrylate) and polyamine [e. g., N-(3-aminopropyl)] morpholine
Copolymer of maleic anhydride and unsaturated monomer grafted onto EP polymer by free radical polymerization. Product is post reacted with polyamine, molecular weight reduced by mechanical homogenization.			
Ethyl Corp.	11/14/77	VI improver, dispersant	KMnO ₄ , N, N-dimethyl-1, 3 propane-diamine
EPDM oxidized by aqueous KMnO ₄ solution, amidated with N, N-dimethyl-1, 3-propanediamine. Esterification (e. g., with pentaerythritol) may be used instead of amidation.			
Shell Internationale Research Maatschappij B. V.	9/1/77	VI improver, dispersant	Ozone, 1-18°C amine or alkanepolyol
EPDM reacted with ozone, then with amine (e. g., imidazole) or polyol. Trichloromethane used as solvent for ozonation.			
Exxon Research & Engineering Co.	7/28/77	VI improver,	Dicarboxylic acid anhydride, (e. g., maleic anhydride) 2-60°C and 2-12 N polyamine with at least two primary amine groups, acetic anhydride
Graft polymer of EP and maleic anhydride reacted with amine, then with acetic anhydride. Final reaction with anhydride inhibits viscosity increase on aging.			
Texaco Development Corp.	7/28/77	VI improver, dispersant	Polar olefinic compounds with primary, secondary, or tertiary amine function capable of free radical polymerization with a hydrocarbon, e. g., dimethylamino ethyl acrylate, 2- and 4-vinylpyridine.
EP or EPDM polymers graft polymerized with amines in presence of free radical initiator at 60-160°C (140-320°F). Acrylate esters may be included to improve low temperature properties.			
Exxon Research & Engineering Co.	4/29/77	VI improver, dispersant	Maleic anhydride, N-(3-aminopropyl) morpholine, alkylarenesulfonic acid
Addition of alkylarenesulfonic acid to grafted EP polymer reduced turbidity and improved detergency.			
Texaco Development Corp.	3/30/77	VI improver	-
Addition of N, N'-bis(2-hydroxy-5-alkylbenzyl) ethylenediamine and its Ca, Mg, and Zn salts (0.01-1.0%) to EP copolymer stabilized color and viscosity.			
Shell Oil Co.	3/11/77	VI improver, dispersant	α , β unsaturated dicarboxylic acids anhydrides, or esters (e. g., maleic anhydride and chlorinated compounds), amines with 1-18°C, or alkanepolyol
EP copolymer chlorinated, reacted with maleic anhydride at 180-200°C (356-392°F), then with tetraethylenepentamine. Molecular weight of product reduced by homogenization.			

Assignee	Priority Date	Function	Reactants
Exxon Research & Engineering Co.	4/26/76	VI improver, dispersant, antiwear agent, pourpoint depressant	Amino compounds or oxygen compounds (e. g., hydroxides, epoxides, or, ethers) or sulfur, boron, or phosphorus compounds
Oxidized EP copolymer reacted with alkyllithium compound to form anion which is further reacted with one or more additional reactants to form multifunctional additive.			
Texaco Inc.	9/13/76	VI improver, dispersant	Polyamine containing primary and tertiary amino groups (e. g., dimethylaminopropylamine)
EP copolymer dissolved in benzene, hydroperoxidized by air in presence of free radical initiator, reacted with amine after adding oil and stripping solvent.			
Exxon Research & Engineering Co.	4/26/76	VI improver, dispersant	Ethylenically unsaturated nitrogen-containing monomer e. g., acrylonitrile
EP or EPDM polymer degraded by oxidation or oxidation-mastication, catalytically condensed with nitrogen-containing monomer. Catalyst is a strong base, e. g., NaOH.			
Exxon Research Engineering Co.	4/26/76	VI improver, dispersant	Unsaturated, polar, anionically polymerizable nitrile monomer (e. g., acrylonitrile). Catalyst is butyllithium
EP or EPDM polymer degraded by oxidation or oxidation and mastication, catalytically polymerized with nitrogen-containing monomer.			
Exxon Research & Engineering Co.	3/19/76	VI improver, dispersant	Acrylonitrile or N, N-dimethylaminoethyl methacrylate
EPDM polymer reacted with acrylonitrile, hydrolyzed with KOH and treated with diethylenetriamine gave increased nitrogen content and good shear stability.			
Standard Oil Co. (Indiana)	12/5/75	VI improver	Benzene sulfonic acids or salts
EP or EPDM polymers oxidized with air at 100-400°F in presence of 0.1-1.0% benzene sulfonic acid or salt of benzene sulfonic acid.			
Rohm & Haas Co.	7/31/75	VI improver, dispersant	Vinylpyridine or N-vinylpyrrolidone
EP copolymer mixed with nitrogen-containing monomer and peroxide catalyst at low temperature, polymerized by raising temperature above initiation point. Resulting graft polymer degraded by mechanical homogenization to reduce molecular weight.			
Exxon Research & Engineering Co.	6/25/75	VI improver, dispersant	Ethylenically unsaturated carboxylic acid material (e. g., maleic anhydrides), polyamine (e. g., diethylenetriamine) or polyol (e. g., pentaerythritol), or hydroxyamine (e. g., tris-hydroxymethyl aminoethane)
EP or EPDM polymer graft polymerized with maleic anhydride, post-reacted with amine or polyol.			
Exxon Research & Engineering Co.	5/3/75	Depressant, VI improver	Polyols, e. g., pentaerythritol
EPDM polymer solution chlorinated, stirred with pentaerythritol sodium salt at 180°C (356°F).			

Assignee	Priority Date	Function	Reactants
USSR Ethylene copolymerized at higher pressure with vinyl ethers of phenol or alkylphenols.	4/30/75	Thickener	Vinyl esters of phenol or alkylphenol
USSR EP copolymers degraded to mol wt of 2,000-4,000 by heating at 350-380°C (622-716°F) at 10-80 torr for 5-40 min.	3/7/75	Thickener	-
Exxon Research & Engineering Co. EP copolymer mixed with amine and degraded by mastication and oxidation in a blade type mixer at 345-368°F.	3/5/75	VI improver, dispersant	Aliphatic saturated amines (e. g., triethylenetetramine, tetraethylenepentamine)
Exxon Research & Engineering Co. EP copolymer masticated at 177-200°C (354-392°F) then treated with amine.	3/5/75	VI improver, dispersant	Polyamines, e. g., diethylenetriamine, triethylenetetramine
Lubrizol Corp. Oxidized, degraded EP copolymer reacted with maleic anhydride, esterified with alcohol in presence of sulfuric acid catalyst.	3/3/75	VI improver, dispersant	Maleic anhydride, mono- or polyhydric alcohol (e. g., pentaerythritol)
Enterprise de Recherches et d'Activités Pétrolières EP copolymer polymerized with N-vinylimidazole.	12/12/74	VI improver dispersant	N-vinylimidazole
Exxon Research & Engineering Co. EP copolymer degraded by oxidation and mastication in a Bramley Beken blade mixer, dissolved in oil, reacted with polyamine 400 at 140°C (284°F).	7/31/74	VI improver, dispersant	Polyamine
Texaco Inc. EPDM polymer converted to nitro peroxydicrate by reaction with O ₂ and N ₂ O ₄ at 0°C (32°F), then to nitroketone by addition of dimethylformamide. Nitroketonized polymer reacted with amine.	6/3/74	VI improver, dispersant	Oxygen, N ₂ O ₄ , dimethylformamide, amine (e. g., dimethylaminopropylamine, hexamethyldiamine)
Exxon Research & Engineering Co. EPDM polymer degraded by air oxidation at 170°C (338°F), reacted with ethylenediamine 1.5 hr at 130°C (266°F).	4/25/74	VI improver, dispersant	Polyamines, e. g., ethylenediamine
Exxon Research & Engineering Co. EP copolymer a EPDM terpolymer chlorinated, reacted with sodium pentaerythritol to form hydroxylated polymer.	10/1/73	VI improver, dispersant	Halogen (e. g., chlorine), metal alcoholate (e. g., sodium salt of pentaerythritol)
Exxon Research & Engineering Co. Chlorinated EP or EPDM polymer reacted with pentaerythritol sodium salt.	10/1/73	VI improver, dispersant	Chlorine, polyol metal salt, e. g., pentaerythritol sodium salt
Texaco Inc. EPDM polymer nitroketonized by reaction with N ₂ O ₄ , oxygen, and DMF then reacted with (dimethylamino) ethanol to form an amino ester.	7/23/73	Dispersant	N ₂ O ₄ , dimethylformamide (DMF), (dimethylamino) ethanol

Assignee	Priority Date	Function	Reactants
Texaco Inc.	7/23/73	Dispersant	N_2O_4 , dimethylformamide, amino esters
EPDM polymer nitroketonized and converted to an amino ester. See 486522.			
Exxon Research & Engineering	6/5/73	VI improver, dispersant	Chlorine, polyamine, e. g., tetraethylenepentamine
Chlorinated EPDM polymer reacted with polyamine.			
Texaco Inc.	4/18/73	VI improver, dispersant	Butyllithium, methacrylate polymer
EPDM polymer reacted with butyllithium using N, N, N', N'-tetramethylenediamine as promoter, grafted to polymethacrylate.			
Uniroyal Inc.	1/23/73	VI improver, dispersant	None
Shear stability of EPDM polymer improved by degrading a 2-25% solution in oil by one or more passages through a Mantin-Caulin homogenizer at a pressure of at least 280 bars (4060 psia).			
Texaco Inc.	4/18/73	VI improver, detergent-dispersant, pour point improver	Alkyl- or dialkylaminoalkyl methacrylate
EPDM polymer metalated and grafted to methacrylate polymer.			
E. I. du Pont de Nemours & Co.	12/29/72	VI improver	None
EPDM tetrapolymer has superior shear stability and bulk handling properties over EPDM terpolymers. Polymer derived from ethylene 25-55% (wt basis), propylene 37-75%, 5-18°C nonconjugated diolefin with one double bond (e. g., 1, 4-hexadiene) 0.1-10%, 5-18°C nonconjugated diolefin with two polymerizable double bonds (e. g., 2,5-norbornadiene) 0.1-2%.			
Lubrizol Corp.	10/2/72	VI improver	Primary C_{11} - C_{14} tert-alkylamines
EP or EPDM polymer and mixture of C_{11} - C_{14} amines dissolved in oil, oxidized with air at 150-160°C (302-320°F).			
Standard Oil Co. (Indiana)	8/8/72	VI improver, dispersant	Aldehydes or amines
EP copolymer made by Ziegler-Natta polymerization, degraded by oxidation, reacted with paraformaldehyde at 79°C (174°F).			
Standard Oil Co.	8/8/72	VI improver, dispersant	Aliphatic amines or diamines, or polyalkylene polyamines (e. g., tetraethylenepentamine)
EP copolymer degraded by oxidation at 310°F, reacted with tetraethylenepentamine at 300°F.			
Exxon Research & Engineering Co.	3/16/72	VI improver, dispersant	Epoxidizing agent, e. g., m-chloroperbenzoic acid, amine
EPDM polymer epoxidized with m-chloroperbenzoic acid to give product which can be used as such or further reacted with an amine, e. g., N, N-dimethyl-1, 3-propanediamine.			
E. I. du Pont de Nemours & Co.	12/22/71	VI improver	None
EPDM terpolymer continuously degraded in an extruder under nonoxidizing conditions. Polymer first melted at low temperature (150-280°C) then heated at degradation temperature (300-500°C) for about 2 minutes until viscosity was reduced.			

Assignee	Priority Date	Function	Reactants
Esso Research & Engineering Co. EP polymer made with Ziegler catalyst degraded by extrusion through 1.59mm openings at 400-425°C (752-797°F).	12/6/71	VI improver	None
Chevron Research Co. Atactic EP copolymer hydroperoxidized by air in presence of free-radical initiator [e. g., azobis(isobutyronitrile)], reacted with amine.	6/1/71	VI improver, varnish inhibitor	Mono- or polyamines containing primary or secondary amino groups, e. g., diethylenetriamine
E. I. du Pont de Nemours & Co. EPDM polymer reacted with P ₂ S ₅ then with N, N-dimethyl-1, 3-propanediamine for 10 hr at 205-210°C (401-410°F).	5/23/71	VI improver, dispersant	P ₂ S ₅ , N, N-dimethyl-1, 3-propanediamine
Chevron Research Co. EP copolymer degraded by mastication and oxidation at 157-217°C (315-423°F), diluted with oil, reacted with amine.	2/26/71	VI improver, dispersant, varnish inhibitor	Alkylene polyamines (e. g., diethylenetriamine)
Burmah Oil Trading, Ltd. EP or EPDM polymer masticated at 230°C (446°F) for 10 min or until shear stability index decreased to less than 30%.	1/7/71	VI improver	None
Esso Research & Engineering Co. Mixture of two EP copolymers improves VI without affecting pour point. Ethylene content of first copolymer is 50-95 mol%, of second copolymer 5-80 mol%. First copolymer contains at least 5% more ethylene than second.	6/2/70	VI improver	None

E. ALKYLPHENATES

Assignee	Priority Date	Product	Objective of Patent
Societe Orogil Suspension of MgO in methanol added to solution of sulfurized alkylphenol (e. g., dodecylphenol) in oil reacted with Co ₂ at 20°C (68°F) under pressure of 10kg/sq cm (142 psig).	3/7/80	Overbased sulfurized Mg alkylphenate	Simplified process
Texaco Inc. C ₁₀ -C ₁₂ alkylphenol reacted with Ca methoxyethoxide in two steps at 160-220°C (320-425°F), reacted with S between steps. Total Ca between 130 and 300% stoichiometric, based on original alkylphenol. After hydrolysis and carbonation, product contains about 20% carbonate and 80% hydroxide overbased sulfurized alkylphenate.	9/24/79	Overbased sulfurized Ca phenate	Improved corrosion prevention and increased basicity (TBN=10)
Exxon Research & Engineering Co. Sulfurized nonylphenol dissolved in oil, reacted with solution of Mg ethoxyethoxide in ethoxyethanol hydrolyzed, and carbonated at 100°C (212°F). Viscosity of product is reduced if amount of free ethoxyethanol present during hydrolysis is minimized.	7/27/79	Overbased sulfurized Mg alkylphenate	Reduced viscosity of product
Exxon Research & Engineering Co. Sulfurized nonylphenol dissolved in oil reacted with solution of Mg ethoxyethoxide in ethoxyethanol and water, hydrolyzed, and carbonated at 100°C (212°F). Viscosity reduced by using from 2.5 to 4 mols of water for every gram atom of Mg in excess of that required to react with the sulfurized phenol.	7/29/79	Overbased sulfurized Mg alkylphenate	Reduced viscosity

Assignee	Priority Date	Product	Objective of Patent
Witco Chemical Corp.	6/20/78	Overbased sulfurized Mg alkylphenate	Cost reduction by using MgO instead of metallic Mg to make product with high TBN
Two stage process in which sulfurized alkylphenol (e. g., nonylphenol) is dissolved in methyl Cellosolve* and neutralized by stoichiometric amount of MgO to give normal phenate. In second stage, normal phenate is overbased by reaction with carbonated Mg methoxyethoxide dissolved in methyl Cellosolve*.			
Orogil SA	2/8/78	Overbased sulfurized Ca alkylphenate	Highly basic detergent-dispersant
Mixture of dodecylphenol and Ca alkylbenzenesulfonate reacted with lime and S in presence of ethylene glycol. Reaction mixture carbonated and treated with lime and ethylene glycol twice.			
Orogil SA	12/20/77	Overbased sulfurized Mg alkylphenate	Detergent-dispersant additive
Mg complex prepared by suspending active MgO in methanol and carbonating the suspension. Sulfurized dodecylphenol in oil solution treated with excess Mg complex.			
Exxon Research & Engineering Co.	1/28/77	Overbased sulfurized Ca or Mg alkylphenates	Antirust detergents
Ca or Mg alkoxide reacted with mixture of sulfurized alkylphenol and dihydroxy alkylbenzenes. Overbasing accomplished by carbonating excess metal alkoxide.			
Maruzen Oil Co. Ltd.	12/29/76	Overbased sulfurized Ca phenate	Simplified process for preparing highly alkaline overbased phenates
Alkylated phenol (e. g., nonyl- or dodecylphenol), sulfur, and CaO reacted at about 135°C (275°F) in presence of ethylene glycol. Ratio of Ca equivalent to phenol hydroxy group 0.99 or less. Reaction product carbonated with CO ₂ .			
Texaco Inc.	12/27/76	Overbased chlorinated sulfurized Ca alkylphenate	Highly alkaline additive with improved anticorrosion protection for silver
Mixture of sulfurized alkylphenol (e. g., dodecylphenol) and chlorinated sulfurized alkylphenol dissolved in oil, reacted with Ca methoxyethoxide, hydrolyzed, carbonated with CO ₂ .			
Texaco Inc.	12/27/76	Overbased sulfurized Ca alkylphenate	Improved antiwear properties and high alkalinity
C ₁₀ -C ₁₂ alkylphenol reacted with Ca methoxyethoxide in two steps at 160-220°C (320-425°F), reacted with S between steps. Total Ca is between 100% and 200% stoichiometric, based on original alkylphenol. After hydrolysis and carbonation, product contains 6-7.4% Ca and 0.5-12% S. Ca metal-to-alkylphenol ratio is 2.9:2 minimum.			
Czech	3/16/76	Sulfurized Ba alkylphenate	Detergent with antioxidant and anticorrosion properties
Dodecylphenol reacted with S and NaOH at 170°C (338°F) then with Ba(OH) ₂ at 80-160°C (176-266°F).			
Liquichimica Robassomero SpA	12/5/75	Overbased sulfurized Ca alkylphenate	Low viscosity detergent
Alkylphenol sulfided by reaction with SCl ₂ -S ₂ Cl ₂ , reacted with Ca(OH) ₂ and blown with CO ₂ .			
Exxon Research & Engineering Co.	6/27/75	Overbased sulfurized Mg alkylphenate	Highly based Mg phenate with oxidation and rust inhibiting properties.
CO ₂ is introduced into a reaction mixture containing a sulfurized phenol (e. g., nonylphenol sulfide), alkyl benzene sulfonic acid, an alcohol, MgO, a promoter (e. g., carboxylic acid or ammonium or amine salt of carboxylic acid), and diluent oil. Reaction temperature: 50-70°C (122-158°F).			

Assignee	Priority Date	Product	Objective of Patent
Exxon Research & Engineering Co. Sulfurized nonylphenol dissolved in oil, mixed with Mg ethoxyoxide in ethoxyethanol and water (one mol per gram atom of excess Mg). Mixture is hydrolyzed by heating to 50-100°C (122-212°F) and carbonated with CO ₂ below 100°C (212°F).	5/23/75	Overbased sulfurized Mg alkylphenate	Reduce viscosity of reaction product during manufacture
Institut Francais des Carburants en Inbrifiants Dodecylphenol reacted with suspension of Ca (OH) ₂ in methanol-toluene and sulfonic acid mixture carbonated at 50°C (122°F) to give various Ca contents according to carbonation time.	3/8/75	Overbased Ca alkylphenate	Manufacture hyperbasic detergent additive
Texaco Inc. Three step process in which: 1. Alkylphenol (e. g., dodecylphenol) reacted 45-90% stoichiometric Ca in form of Ca methoxyethoxide. 2. Reaction product reacted with S at 227-238°C (440-460°F) in presence of 13-20 wt% lubricating oil. 3. Sulfurized product reacted with additional Ca methoxyethoxide sufficient to raise Ca to 100-120% stoichiometric. Second stage temperatures and oil concentration are critical.	8/6/74	Sulfurized Ca alkylphenate	Improved antioxidation and anti-corrosion properties
Texaco Development Corp. Mixture of CaO, acetic acid or ethyl acetate, and alkoxyethanol heated at 100-250°C (212-482°F) with sulfurized Ca alkylphenate. Excess CaO results in overbasing.	3/29/74	Overbased sulfurized Ca alkylphenate	Alkaline detergent dispersant
Institutul de Cercetari si Protectarii Technologice pentru Rafinaii si Instalatii Petrochemice (Romania) Mixture of C ₈ -C ₁₈ alkylphenol, BaSO ₄ , and Ba(OH) ₂ · 8H ₂ O in oil heated at 90-145°C (194-293°F) to reduce H ₂ O content to 1%, carbonated at 145°C (293°F) and 200-400mm Hg to eliminate all H ₂ O.	2/4/74	Overbased Ba alkylphenate	Lube oil detergent and antismoke additive for diesel fuel
Texaco Inc. Alkylphenol (e. g., dodecylphenol) nitrated with aqueous HNO ₃ , reacted with Ca methoxyoxide, then sulfurized with s. Product is concentrate of sulfurized normal Ca salt of a 2-nitrated-4-dodecylphenol.	12/21/73	Sulfurized nitrated Ca alkylphenate	Increased antithickening and anticorrosion properties
Chevron Research Co. Mg metal dissolved in methanol and treated with CO ₂ to form solution of carbonated Mg methoxide, which is reacted with alkylphenol (e. g., dodecylphenol at 65-85°C (149-185°F). Reaction product is treated with S at 175-190°C (347-374°F), dissolved in oil, and overbased with additional carbonated Mg methoxide at 65-85°C.	11/9/73	Overbased sulfurized Mg alkylphenate	Improved process which does not require sulfurized alkylphenol as starting material
Texaco Development Corp. Dodecylphenol reacted with Ca methoxyethylate, S, and CO ₂ then with additional Ca methoxyethylate.	7/27/73	Sulfurized Ca alkylphenate	Improved antioxidation, anticorrosion properties
Texaco Development Corp. Dodecylphenol reacted with Ca methoxyethylate and powdered S at 210°C (410°F) under atmospheres of N ₂ and CO ₂ in sequence.	7/18/73	Sulfurized Ca alkylphenate	Detergent-antioxidant
Texaco Inc. Dodecylphenol reacted with Ca methoxyethoxides then with S with sequential blowing with N ₂ and CO ₂ , then with additional Ca complex.	7/6/73	Sulfurized Ca alkylphenate	Improved antioxidant and anticorrosion properties

Assignee	Priority Date	Product	Objective of Patent
Texaco Inc.	2/22/73	Overbased sulfurized Ca alkylphenate	Improved process
An alkylphenol (e. g., dodecylphenol), sulfur, and alkali metal hydroxide (e. g., NaOH) heated at 150-170°C (302-338° F) to form sulfurized alkylphenol, which is then reacted with alkaline earth metal base (e. g., Ca(OH) ₂) in presence of ethylene glycol and an alkanol at 140-180°C (284-356° F). Mixture then carbonated with CO ₂ at 160°C (320° F). Quantity of NaOH is 0.3-0.9 mol, and Ca(OH) ₂ is at least 2 mols per mol alkylphenol.			
Texaco Inc.	10/19/72	Overbased sulfurized Ca alkylphenate	Product with reduced viscosity and improved filterability
Reaction mixtures must be blown with N ₂ at specified rates. Sulfurized normal Ca alkylphenate reacted with Ca methoxyethoxide while blowing with N ₂ at 0.25-0.6 scfh/gallon, stripping with N ₂ at 0.25-0.6 scfh/gallon and then hydrolyzing with steam while blowing with N ₂ at 0.1-0.2 scfh/gallon.			
Chevron Research Co.	8/18/72	Sulfurized Ca alkylphenate	Improved antioxidant, dispersant, and anticorrosion properties
Intermediate reaction product prepared by reacting 1.5-3 mols S, 0.2-1 mol CaO, and 0.2-1 mol ethylene glycol per mol of alkylphenol at 177-185°C (350-365° F) in diluent oil solution. In second step, sulfurized intermediate is reacted with an additional 0.2-0.6 mol CaO and 0.5-2 mols ethylene glycol at 121-232°C (250-450° F).			
Texaco Inc.	6/27/72	Overbased sulfurized Ca alkylphenate	Reduced processing costs from low cost solvent and accelerator
Solution of sulfurized normal Ca alkylphenate in oil reacted at about 210°C (410° F) with solution of Ca methoxyethoxide prepared by dissolving CaO in 2-methoxyethanol, with acetic acid as an accelerator. Mixture is carbonated with CO ₂ at 150-225°C (302-437° F) using at least 1 mol CO ₂ per mol CaO. Use of alkanolic acid necessary for effective overbasing.			
Continental Oil Co.	11/10/71	Overbased sulfurized alkylphenols	Simplified one step process
Alkylphenol mixed with oil, process solvent, and water. Overbasing amount of carbonated Ca or Mg methoxyethoxide added at temperature below reaction temperature. Neutralizing amount of carbonated Ca or Mg methoxyethoxide and sulfur added at higher temperature to complete reaction. Volatiles removed by distillation after blowing with CO ₂ .			
Texaco Inc.	9/15/71	Sulfurized normal Ca alkylphenate	Improved anticorrosion and anti-oxidation properties
Alkylphenol (e. g., dodecylphenol) in oil solution reacted with Ca methoxyethoxide at 160-220°C (320-425° F) in two stages, reacted with S at 205-220°C (400-425° F) between stages. Total Ca addition is 100-120% of stoichiometric, based on original alkylphenol.			
Continental Oil Co.	5/17/71	Overbased sulfurized alkylphenates, especially Mg alkylphenates	Improved process
Alkylphenol mixed with oil, process solvent and water (1.0-2.5 mols per mol of Mg present in final product). Overbasing amount of Mg (or other alkaline earth metal) in methoxyethanol solution added at temperature below reaction temperature 20-55°C (68-131° F) Neutralizing amount of Mg in methoxyethanol solution at higher temperature so reaction will occur. Volatile materials removed by distillation. Water must be added before addition of Mg.			
Texaco Inc.	9/14/70	Normal Ca alkylphenate	Reduced raw material costs
Alkylphenol in lubricating oil solution reacted with CaO or Ca(OH) ₂ in presence of acetic acid. Reaction mixture may also include methoxyethanol.			
Texaco Inc.	9/14/70	Normal Ca alkylphenate	Improve yield
Mixture of alkylphenol methoxyethanol and CaO in oil blown with O ₂ -containing gas (e. g., air) at 75-250°C (167-482° F) during reaction.			

(계속)