

PATENT SPECIFICATION

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(54) BLOCK COPOLYMERS AND ORGANIC COMPOSITIONS CONTAINING THE SAME

(71) We, MOBIL OIL CORPORATION, a Corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to block copolymers suitable for use in organic fluid compositions.

U.S. Patent No. 3,050,511 describes block copolymers obtained from polystyrene and alkylene oxide. The technique involves forming a "living polymer" of the styrene in the presence of an anionic catalyst, then adding the alkylene oxide to it. Such products, however, would not be suitable as hydrocarbon fluid additives and lack suitable terminal groups for thermal and oxidative stability. They would have insufficient solubility in lubricating oils during use to retain their effectiveness. U.S. Patent No. 3,219,725 describes block polymer of oxymethylene and styrene or alpha-methylstyrene produced by polymerizing styrene and adding formaldehyde to produce a polyoxymethylene block. It is understood that the resulting block copolymer may be terminated by esterification. Olefin oxide, higher aldehydes, isocyanates and the like may replace the styrene. Again, the use of styrene polymer as the first block-forming monomer or replacement by a polar monomer would not produce a useful multifunctional additive for lubricating oils.

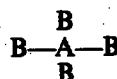
U.S. Patent No. 3,281,499 describes block copolymers of oxymethylene and olefins, such as styrene. The resulting products are mouldable polymers which are of little solubility in lubricating oils or other organic fluids. U.S. Patent No. 3,318,813 describes a tert-butyl-styrene polymer prepared in an anionic polymerization using n-butyl lithium as the initiator. Polymerization is terminated in methanol. This polymer is said to be useful as a viscosity index (VI) improver. The polymers used in this reference contain no polar groups. Hence, these homopolymers are distinguishable from the copolymers of the present invention. U.S. Patent No. 3,175,997 claims a process of preparing terminally reactive polymers, such as butadiene-styrene copolymers, by reacting with ethylene oxide and acidifying the alkali metal group to —OH. The products are used in adhesives, potting compounds and binders. U.S. Patent No. 2,835,658 describes treating styrene-lactone block polymers with diisocyanates. The polymers are elastomers prepared from free-radical bulk polymerization. G.B. Patent Specification No. 1,304,289 describes hydrogenated butadiene-styrene copolymers as VI improvers. These polymers contain no polar polymer blocks.

We have now discovered novel block copolymers of the AB or BAB type. The invention provides a block copolymer having within its molecular structure at least

two segments A and B, segment A being a hydrogenated copolymer of (i) a diene and (ii) styrene or a nuclear-substituted alkyl styrene or mixture thereof, segment B being a segment of polymerized alkylene oxide or alkylene sulfide and constituting from 1 to 50 per cent by weight of the block copolymer.

These copolymers may contain end groups, Z, derived from an organic or inorganic compound capable of reacting with an alkoxide or alcohol. For example, Z may be hydroxy, alkoxy, metaloxy of the alkali metal series, carboxylate, sulfonate, carbamate, isocyanate, diisocyanate, halocarbonyl or heterocyclic nitrogen or oxygen. Organic industrial fluid compositions containing such polymers have improved combined detergent and viscosity index characteristics. Lubricants such as automotive lubricating oils, Diesel oils, cross-graded oils and greases, and fuels, such as gasoline and fuel oils, are suitable media for these polymers.

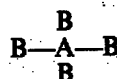
The copolymers are generally of the AB or BAB types. Included in the BAB category are



The invention further provides a method of making a hydrogenated block copolymer, which comprises: (a) copolymerising a mixture of (i) a diene and (ii) styrene or nuclear-substituted alkylstyrene under anionic polymerisation conditions to form an intermediate copolymer, (b) polymerising an alkylene oxide or alkylene sulfide in the presence of a catalyst therefor and in the presence of the intermediate copolymer to form a block copolymer of the intermediate copolymer with segments of the alkylene oxide or alkylene sulfide blocked on to the intermediate copolymer and (c) hydrogenating the intermediate copolymer or the block copolymer.

In the first step of producing the copolymers a mixture of diene, preferably a conjugated diene such as butadiene, and styrene is polymerized by anionic polymerization to form the A block. The initiator for this reaction is suitably an organometal compound; of the alkali metal group: lithium, sodium, potassium, cesium and rubidium. The formula for these initiators is RMy, wherein R is organo, mono- or polyvalent and may be alkyl, alkenyl, aryl, aralkyl, and alkaryl, and may contain from 1 to about 50 carbon atoms; and y is 1 to 4, and preferably 1 or 2. Such initiators as methyl lithium, ethyl lithium, methyl sodium, propyl lithium, n-butyl lithium, sec-butyl lithium, tert-butyl lithium, butyl sodium, lithium naphthalene, sodium naphthalene, potassium naphthalene, cesium naphthalene, phenyl sodium, phenyl lithium, benzyl lithium, cumyl sodium, cumyl potassium, methyl potassium, ethyl potassium, and so forth may be used in this reaction. Also, metal initiators containing a dianion, such as the alkali metal salts of 1,1-diphenyl-ethylene and alpha-methylstyrene tetramer and the radical anion initiators of the sodium naphthalene type, could lead to the formation of the BAB copolymer.

Preparation of



copolymers may be achieved through multifunctional initiators, for example 1,3,5-trilithiocyclohexane and 1,4,7,10-tetrapotassiododecane. In anionic polymerization of this type each molecule of the initiator starts one anionic polymer chain; it is also understood that a multiple anion can permit addition of a second polar block on the A polymer.

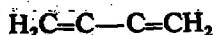
The anionic polymerization reaction is generally carried out in the presence of either a polar or nonpolar solvent. Suitable solvents include hexane, heptane,

octane, benzene, toluene, xylene, tetrahydrofuran, ethyl ether, methyl ethyl ether, 1,4-dioxane, and other alkanes, ethers and aromatic solvents, oils and mixtures thereof. Tetrahydrofuran is the preferred solvent, since it is an excellent solvent for both polymerization steps.

In the preparation of the block A, the mixture is normally dissolved in solvent and polymerized in the presence of from 10^{-1} to 10^{-4} mole of anionic initiator per 100 grams of the monomers. Alkylstyrene comonomers may be used in this step of the process including propylstyrene, n-butylstyrene, i-butylstyrene, t-butylstyrene, n-amylstyrene, i-amylstyrene, hexylstyrenes, heptylstyrenes, methylpropylstyrene, and methylbutylstyrene but styrene itself is preferred. If an alkyl styrene is used we prefer a butyl styrene. Mixtures of different alkylstyrenes or an alkylstyrene with styrene may also be used. Polymerization is carried out for sufficient period of time to provide a block of diene-styrene polymer until no further polymerization occurs. Molecular weights in this first step may range from 1,000 to over 250,000.

The final group on the living polymer consists of —OM derived from the organometal initiator. This group permits addition of the polar block B in the subsequent polymerization step. The term "living polymer" is meant to indicate that the polymerization reaction involving the diene-styrene or -alkylstyrene copolymer has no termination step and may continue until no further monomer remains. One polymer chain starts with each equivalent of the initiator and uses up available monomer until depletion thereof. Control of molecular weight is achieved by adjustment of styrene/initiator ratio.

The diene-styrene and diene-alkylstyrene copolymers possess the desirable solubility in petroleum and other industrial fluids. Conjugated dienes such as butadiene and isoprene (preferred), and 2,3-dimethylbutadiene, 2,3-diphenylbutadiene, and others of the structure



the dangling valences being substituted by hydrogen or alkyl or aryl groups of C_1 to C_{10} , and styrene or the aforementioned alkylstyrenes provide suitable copolymers.

This step of the polymerization may be carried out either in a random or a block polymerization. The random copolymer is preferred. For this purpose, a randomizing agent is added to the polymerization reaction mixture. Suitable randomizers include: ethers, such as diethylether, dimethoxyethane, bis(2-methoxy-ethylether), 1,2 bis(methoxyethoxy)ethane and tetrahydrofuran. Other randomizing agents include the alkali metal salts of C_1 to C_{20} alcohols or phenols, e.g.: potassium *t*-butoxide or potassium *t*-amyloxide. Other agents are phosphite triesters, such as tributyl phosphite, tri-substituted triazines, dimethyl pyridine, potassium acetylonyl or potassium or sodium metals.

U.S. Patent No. 3,294,768 discloses a number of catalysts useful in forming random butadiene-styrene adducts are similar to the aforementioned initiators of the RM₁ formula.

Upon completion of the polymerization of the butadiene and styrene, since there are vinyl groups remaining in the molecule which could become oxidized or susceptible to other forms of deterioration during use, it is desirable to hydrogenate the copolymer. This can be carried out by terminating the initial copolymerization by adding a small amount of the polar compound of block B, such as ethylene oxide, followed by a small amount of a mineral acid or acetic acid and subjecting it to hydrogenation or by hydrogenating first and then acidifying the complete addition of the polar block, (such as that of ethylene oxide).

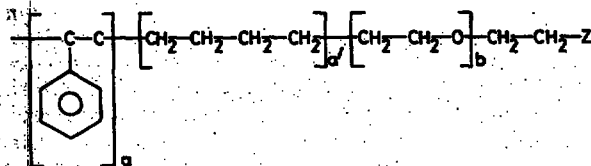
Hydrogenation is generally carried out in the presence of a heterogeneous or homogeneous hydrogenation catalyst. Heterogeneous catalysts include metals of the platinum series, e.g., platinum, palladium and the like, iron, cobalt, or nickel, particularly Raney nickel. The catalyst metals may be used alone or on a carrier, such as charcoal, silica or alumina. Homogeneous catalysts include organic salts of these metals, such as nickel acetylacetonate, nickel diisopropylsalicylate, nickel naphthenate, nickel octoate, and nickel ethyl hexanoate. Homogeneous catalysts also include tris(triphenyl)phosphine rhodium chloride and other group VIII metal compounds, particularly a compound obtained by reacting an aluminium trialkyl with a nickel or cobalt organic salt, such as aluminium triisobutyl with nickel naphthenate or 2-ethylhexanoate.

The units of butadiene and styrene in the first block may contain from 5 per

cent to 70 per cent styrene units based on the total number of units of butadiene and styrene together; most preferably between 20 per cent and 60 per cent styrene is present. The hydrogenation catalyst is preferably present in the amount of from about 0.0005 per cent to about 10 per cent by weight of the polymers, more preferably 0.005 per cent to about 5 per cent. The lower concentrations are desirable for homogeneous catalysts; the upper limits are for heterogeneous catalysts.

The next step in formation of the block copolymers of this invention is to react block A polymer, normally the hydrogenated butadiene-styrene copolymer (HBDS), with the polar compound; the hydrogenated reaction mass, although it may be separated therefrom and redissolved in a solvent. A catalyst for the alkylene oxide polymerization is added to the HBDS solution. Such catalysts include: potassium *t*-butoxide, potassium *t*-amyloxide, potassium hydroxide. The number of moles of catalyst would be approximately the same as that used for the anionic initiator. The alkylene oxide is then added to the polymer solution. The amount of alkylene oxide added to the solution is from 1 per cent to 50 per cent, and preferably from 5 per cent to 25 per cent, by weight of the polymer. Ethylene oxide is the most preferred monomer for reasons of cost, availability and performance characteristics. The carbon atoms attached to the oxygen atom are vicinal and each of these carbon atoms may be substituted by other carbon atoms, the total number of carbon atoms preferably ranging from 2 to 5. Therefore, also suitable would be 1,2-propylene oxide and 1,2-butylene or 2,3-butylene oxides and the like or their mixtures.

The diene-styrene copolymer reacts with the polar compound to add oxyalkylene or thioalkylene groups at the metaloxy or metalthio terminus, $-\text{CH}_2-\text{CH}_2-\text{OM}$ or $-\text{CH}_2-\text{CH}_2-\text{SM}$, to produce AB block copolymers preferably having at least 2 and up to 3,500 such polar groups. A structure may be illustrated as follows:



a, a' and b being integers of at least 2 and Z is the capping group. Thus, the block copolymers consist essentially of polymerized styrene-type block preferably having an average molecular weight of from 1,000 to 300,000 and a polar portion, preferably polyoxyalkylene, and preferably having from 2 up to 3,500 units, preferably 10 to 1,000 units. Preferred molecular weights of the copolymer of this invention may range from 1,000 to 3,000 and preferably from 10,000 to 200,000.

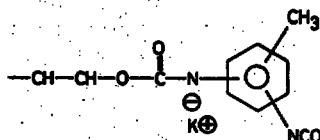
The polar block B may, if desired, be terminated either by precipitating the copolymer in a lower alkyl alcohol, i.e., from 1 to 5 carbon atoms, such as methanol, or by reacting with a compound containing a carbonyl group such as an organic acid, an isocyanate or a carbonyl halide, such as cyanuric chloride and phosgene, and then either precipitating the resulting reacted polymer or, by our preferred method of replacing the solvent (other than oil) with an oil including petroleum or synthetic oil, e.g. ester, ethers, polyolefins, etc. The end or capping group, Z above, may be hydroxy, metaloxy of the alkali metals, or $-\text{OR}''$ or



R'' being alkyl or aryl of from 1 to 10 carbon atoms or a heterocyclic nitrogen group of pyridines, pyrimidines or triazines. The preferred capping group is prepared by reacting the polymer with an isocyanate, alkyl isocyanate or preferably an aromatic diisocyanate, such as toluene diisocyanate (TDI), to form the mono- or the diisocyanate, or urethane-type, group



at the end of the block copolymer, wherein R''' may be alkyl or aryl and may contain an O=C=N— group, such as phenyl, tolyl, phenylene isocyanate or tolylene isocyanate. With the preferred diisocyanate, the second O=C=N— group may either remain unreacted or reacted with other compounds, such as anti-oxidants derived from phenol or aryl amines, or may even be used to cap a second copolymer chain, for example AB—TDI—BA. This cap provides unusually excellent thermal and oxidative stability to the polymer during use. It is usually in the form of an anion with the alkali metal of the initiator,



using potassium as the preferred example. Other capping groups consist of hydroxy or metaloxy derived from the metal of the anionic initiator, or another metal substituted by exchange reaction, or from cyanuric halide, dihalopyrimidine, halopyridine, and the like or halocarbonyl. These polyfunctional capping agents may also couple more than one AB polymer molecule, as TDI above.

The styrene polymerization reaction may be conducted at a temperature in the range of from $-80^{\circ}\text{C}.$ to $100^{\circ}\text{C}.$, but ordinarily room temperature is the desired maximum. The reaction may be terminated within a period of from 15 minutes to over about 4 hours. The second reaction with alkylene oxide or sulfide may be conducted at a temperature of from $0^{\circ}\text{C}.$ up to about $175^{\circ}\text{C}.$, and the time of reaction may range from about half an hour to about 24 hours. The products may be removed by filtering the precipitated copolymer from the solvent or as preferred by adding a hydrocarbon oil (in which the copolymer can be used) or a process oil and removing the volatile solvent by stripping or other known means. Should a capping group other than —OM be desired, the reactant providing the group is added to the reaction mixture prior to such separation and the mixture is heated. For example, as previously discussed, the addition of toluene diisocyanate to the reaction product would yield a TDIK end group (wherein M is potassium). Any metal halide or oxide side product resulting from the capping reaction may be removed by washing and/or filtration. In this invention, the retention of metals may be preferable.

The products of this invention are multifunctional additives for industrial organic fluids. Because of the high molecular weight and narrow molecular weight distribution of these copolymers, they provide high viscosity index and shear stable oil compositions which may perform as cross-graded lubricants, Diesel oils and greases. Thus, the oil compositions of this invention may be used both under high and low temperature conditions, since the higher the viscosity index the more stable the viscosity flow at extreme temperatures. One of the drawbacks of using certain polymers, such as polymethacrylates, as viscosity index improvers is that under the shearing conditions in an engine, the polymer chains may be destroyed resulting in lower viscosities, and possible breakdown of the additive package in oil. Serious viscosity loss may cause the engine to work inefficiently. It has been surprisingly discovered that the block copolymers of this invention have minimal loss in shear stability. It is preferred that the molecular weight distribution (M_w/M_n), wherein M_w is the weight average molecular weight and M_n is the number average molecular weight, be in the range of 1 to 5 and preferably 1 to 2. The block copolymers of this invention having such low M_w/M_n ratio may be readily prepared.

Another valuable function performed by copolymers of this invention, both high and low molecular weight copolymers, is their ability to disperse particles in the lubricant and to prevent them from becoming deposited on engine surfaces. It is believed that the combination of oil soluble and polar portions of the macromolecule permits the polymer both to remain dissolved in the oil and yet hold particles dispersed in the oil. These two characteristics are necessary to keep the oil free of deposits affecting engine performance. Mixed copolymers of different molecular weights or of different A blocks in the fluid medium may be used for a variety of functions.

(17) While these copolymer additives are useful as detergents in organic fluids, they also can thicken the base fluid medium. Of particular interest are gasoline and fuel oil which would have improved detergency as well as lower fuel consumption.

The additives of this invention may be used in conjunction with other additives normally used in lubricants and fuels, such as basic alkali or alkaline earth metal sulfonates and phenates, C_{20} —300 alkenylsuccinic acid imides of ethylene polyamines, such as tetraethylene pentamine, esters of mono and polyhydric alcohols, such as pentaerythritol, the polymethacrylates, sulfurized polyolefins such as polyisobutylene, and phosphites, dithiophosphates and carbamates.

The following examples illustrate the manner of preparing the block copolymers of this invention and the evaluation of such copolymers in organic industrial liquid compositions. The molecular weight measurements given in these examples were obtained by gel permeation chromatography in tetrahydrofuran.

Example 1.

(a) Into a 5 l. flask was added 3000 ml. of dry cyclohexane and 290 ml. of styrene. A quantity of 487 gms. of purified butadiene was distilled into the flask at -78°C . The reactor was warmed to room temperature and 0.20 gm. of potassium *t*-butoxide was added and dissolved, at which time 11.5 ml. of 1.31 N sec-butyllithium was added and the reaction allowed to proceed for about 4 hours at 100°F . and about 16 hours at ambient temperature. The polymerization was terminated by the addition of a small amount of gaseous ethylene oxide.

The resulting polymer solution was diluted with an additional 2000 ml. of cyclohexane and hydrogenated at 300 psi. and 40°C . for 24 hours using a nickel aceto-acetonate/triethylaluminum catalyst at a ratio of 2/1 Al/Ni. After the hydrogenation is complete, a quantity of 50 ml. of concentrated HCl in 25 ml. methanol was added to the cyclohexane solution and stirred for 2 hours. The polymer was then separated by precipitation into methanol and dried.

(b) A quantity of 99 gm. of the dried hydrogenated polymer was dissolved in 1100 ml. of benzene in a 2 l. reactor. About 700 ml. of benzene was distilled off and 0.32 gm. of potassium *t*-butoxide was added and dissolved. Fifty (50) additional ml. of benzene was then distilled off after heating at 70°C . for 1 hour. A quantity of 24.7 ml. of purified ethylene oxide was added and the reaction allowed to proceed for 5 hours at reflux temperature. The reactor was cooled to 100°F . and reaction was run for an additional 16 hours. At the end of this time, 3.0 ml. of toluene diisocyanate was added. The resulting polymer had the following properties:

$$M_n = 65,000$$

$$M_w = 114,000$$

$$M_w/M_n = 1.8$$

Example 2.

Into a 12 l. flask was charged 7200 ml. cyclohexane, 696 ml. of styrene and 1575 ml. of butadiene. A quantity of 14.4 ml. of tetrahydrofuran (THF) was added and the polymerization initiated with 31.3 ml. of 1.17 N sec-butyllithium and the reaction allowed to proceed for 2 hours at 120°F . The polymerization was terminated by the addition of 37 ml. of a 10% by weight ethylene oxide in cyclohexane solution. A quantity of 2.2 ml. of acetic acid was then added.

The resulting polymer solution was diluted with additional cyclohexane and hydrogenated using a nickel on Kieselguhr catalyst at a temperature of 310°F . and a pressure of 500 psi. for 10 hours. The catalyst was removed by filtration after the hydrogenation was complete.

The polymer solution was then returned to a 12 l. flask and 4 l. of cyclohexane was distilled off and replaced with 5 l. of benzene. A quantity of 14 ml. of a 17.8% by weight solution of potassium *t*-amyloxide in cyclohexane was added and 1 l. of solvent was removed by distillation. Ethyleneoxide (208 ml.) was added and the reaction allowed to proceed for 10 hours at reflux temperature. The reaction was terminated with 3.0 ml of toluene diisocyanate dissolved in 20 ml benzene. The resulting polymer had the following properties:

$$M_n = 65,030$$

$$M_w = 124,700$$

$$M_w/M_n = 1.9$$

Example 3.

Into a 2000-ml flask, 300 ml of hexane was added under a nitrogen blanket. Into the flask was distilled under vacuum at -78°C . 150 grams (2.5 moles) of purified butadiene followed by a solution of 50 grams (0.48 mole) of styrene in 800 ml of benzene. The reaction flask, still under a nitrogen blanket, was allowed to warm to room temperature. To the reaction flask was then added 100 ml of a 0.31 M solution of n-butyl lithium containing 0.384 grams of potassium t-butoxide. The reaction flask was maintained at room temperature for 16 hours following this addition during which time polymerisation occurred. The polymerisation was terminated by the addition of 0.6 gram of ethylene oxide and 2 ml of glacial acetic acid, and the polymer was removed by filtration.

A solution of 105 grams of the resulting polymer in 370 ml of benzene was subjected to hydrogenation by adding 15 grams of a catalyst consisting of 10 per cent by weight of palladium on charcoal and passing hydrogen gas through the reactor at 80°C and 400 psi for sixteen hours. The catalyst was filtered off from the polymer solution. To the filtrate was added 0.704 gram of potassium t-butoxide under a nitrogen blanket and the solution was heated to reflux; 40 ml of benzene was distilled off. To the resulting solution was added 18 grams (0.4 mole) of ethylene oxide by distilling in the ethylene oxide under vacuum. A nitrogen atmosphere was then applied, and the reaction allowed to proceed at 78°C for five hours. After polymerization of the ethylene oxide was completed, 70 grams of a process oil was added and the benzene stripped off under vacuum.

The resulting polymer now in the oil solution had the following properties:

$$M_n = 3,100$$

$$M_w = 19,100$$

$$M_w/M_n = 6.2$$

EVALUATION OF PRODUCTS.

The products of this invention evidence properties of viscosity index improvement accompanied by excellent shear stability and surprising detergency in both bench and engine testing. The tests used to demonstrate these properties are the shear stability test and measurement of thickening power and carbon removal tests and deposit formation tests. The base media are lubricating oils, Diesel oils and gasoline.

VISCOSITY CONTROL.

To indicate the shear stability of the oil compositions of this invention, oil formulations are subjected to a series of shearing forces and the viscosity is measured after each shearing period, or pass. A shear stable formulation will evidence little or no loss in viscosity.

The conditions of the shear stability test are as follows: About 250 cc. of the test oil formulation of known viscosity is passed through a standard Diesel engine fuel injector 10 times and the final viscosity is measured. The injector contains 7 orifices of 0.006-inch diameter each. The test is run at ambient temperature at about 40,000 to 50,000 psig.

The results of these tests on a solvent refined oil containing the block polymers of this invention are tabulated below. In these tables, the polymers are referred to by the following shortened terms: HBDS—EO hydrogenated butadiene-styrene/ethylene oxide copolymer; OK, oxypotassium end-group; TDIK, toluene diisocyanate-potassium end-group; OH, hydroxy end-group. Other terms referred to are: VI, viscosity index; MW, molecular weight; SSI, shear stability index (see Rohm and Haas Company Bulletin "Acryloid 700 Series," September, 1970) which is calculated by $[(v_1 - v_r)/(v_1 - v_0)] \times 100$, wherein v_1 is initial viscosity of the formulation, v_r is viscosity after the test, v_0 is viscosity of oil formulation without the viscosity improving additive, the lower the number the more effective the additive; and TP, thickening power or increase in viscosity at 210°F . per weight percent of additive.

TABLE I.

Test No.	Polymer/MW	Conc. % by wt.	VI	SSI%*	TP
1	none**/—	—	100	—	—
2	HBDS—EO—OK/100,000	5.0	169	0	8.66
3	HBDS—EO—TDIK/63,000	4.0	168	-7	6.3
comp.	Butadiene-Styrene Copolymer/70,000	3.5	148	6.2	3.4

* Negative numbers indicate 0% SSI.

** The base oil is a blend of solvent-refined lubricants used in producing 10W—50 oils. No other additives are present.

TABLE II.

Test No.	Polymer/MW	Conc. % by wt.	VI	SSI%*
1	Oil Formulation**/—	0	100	—
2	HBDS—EO—TDIK/100,000	4.0	170	-3
3	HBDS—EO—TDIK/74,000	5.0	158	3
4	Polymethacrylate Copolymer/about 100,000	8.8	184	36

* Negative number indicates 0% SSI.

** Oil contains about 6 per cent of other additives.

5 The products of Examples 1(a), the hydrogenated butadiene-styrene (HBDS) copolymer, and 1(b), the block copolymer terminating in TDIK (HBDS—EO—TDIK), were both tested for viscosity changes based on the temperature. Two samples of the oil formulation similar to that tested in Table II each containing 3% by weight of 1(a) copolymer and 1(b) copolymer were heated and the viscosity was measured at various temperature levels. The results were as follows:

TABLE III.

Temp., °F.	Oil Viscosity, cs with 1(a)	Oil Viscosity, cs with 1(b)	Percent Visc. Incr.**
0	16.3*	16.8*	3
40	768.0	1302.7	69
100	101.7	162.0	59
210	14.11	20.08	42

* Measured as poises.

** $[(1b-1a)/1a] \times 100$

Thus, the copolymers of this invention provide greater thickening power than the butadiene-styrene copolymer precursor at normal operating conditions encountered in engines, which is desirable for better engine performance and lubricant effectiveness. Yet, surprisingly, at the low temperature or "cold-crank" temperature range, the thickening by the copolymers of this invention actually decreases resulting in easier start-up whereas the butadiene-styrene copolymer causes increased thickening or more difficult start-up.

DETERGENT PROPERTIES.

One test to indicate the ability of an additive to pick up and disperse particles in oil is the carbon removal test:

A stainless steel cylindrical cell is mounted in a constant temperature bath of 100°C. Inside the cell is a 400-mesh nickel screen in which nickel powder has been placed as a porous bed. A dispersion of 250 ppm. of carbon black in white oil at 1 cc./min. followed by 5 cc. of white oil alone. A solution of a solvent-refined mineral oil containing 5% by weight of a block copolymer of this invention is passed through the bed at 1 cc./min. Light transmission measurements of the oil compositions before and after passage through the bed conform to Beer-Lambert, indicating the amount of carbon black removed from the bed. The following results were obtained using the block copolymers of this invention as detergent-dispersants:

TABLE IV.

Test No	Polymer	MW	Wt. %, EO	Percent Removal
1	Oil alone	—	—	0
2	HBDS—EO—TDIK	74,000	8.4	36
3	HBDS—EO—OK	100,000	15.0	20
4	HBDS—EO—TDIK	82,000	30.4	38

In our Patent Specification No. 34173/74 (Serial No. 1,485,155) we describe and claim block copolymers, their production, and their use in lubricant and petroleum compositions, in which the block copolymer has within its molecular structure at least two segments, segment A being a polymer of a nuclear-substituted alkylstyrene in which the alkyl group has at least three carbon atoms, segment B being a polymerized alkylene oxide or alkylene sulfide segment.

WHAT WE CLAIM IS:—

1. A block copolymer having within its molecular structure at least two segments, A and B, segment A being a hydrogenated copolymer of (i) a diene and (ii) styrene or a nuclear-substituted alkyl styrene or mixture thereof, segment B being a segment of polymerized alkylene oxide or alkylene sulfide and constituting from 1 to 50 per cent by weight of the block copolymer.

2. A copolymer according to Claim 1, in which segment A comprises a copolymerized *t*-butylstyrene.

3. A copolymer of Claim 1, where said segment A is a hydrogenated random butadiene-styrene copolymer prepared in the presence of a randomizing agent.

4. A copolymer according to Claim 3, in which the randomizing agent is selected from ethers and alkali metal salts of alcohols having from 1 to 20 carbon atoms and of phenols.

5. A copolymer according to any of Claims 1 to 4, in which segment B is polymerized ethylene oxide.

6. A copolymer according to any of Claims 1 to 5, which includes a terminating group $-\text{CH}_2-\text{CH}_2-\text{Z}$ where Z is hydroxy; $-\text{OM}$ where M is an alkali metal; OR^+ or



1,487,823

Thus, the copolymers of this invention provide greater thickening power than the butadiene-styrene copolymer precursor at normal operating conditions encountered in engines, which is desirable for better engine performance and lubricant effectiveness. Yet, surprisingly, at the low temperature or "cold-crank" temperature range, the thickening by the copolymers of this invention actually decreases resulting in easier start-up whereas the butadiene-styrene copolymer causes increased thickening or more difficult start-up.

DETERGENT PROPERTIES.

One test to indicate the ability of an additive to pick up and disperse particles in oil is the carbon removal test:

A stainless steel cylindrical cell is mounted in a constant temperature bath of 100°C. Inside the cell is a 400-mesh nickel screen in which nickel powder has been placed as a porous bed of a dispersion of 250 ppm. of carbon black in white oil at 1 cc./min. followed by 5 cc. of white oil alone. A solution of a solvent-refined mineral oil containing 5% by weight of a block copolymer of this invention is passed through the bed at 1 cc./min. Light transmission measurements of the oil compositions before and after passage through the bed conform to Beer-Lambert, indicating the amount of carbon black removed from the bed. The following results were obtained using the block copolymers of this invention as detergent-dispersants:

TABLE IV.

Test No	Polymer	MW	Wt. %, EO	Percent Removal
1	Oil alone	—	—	0
2	HBDS—EO—TDIK	74,000	8.4	36
3	HBDS—EO—OK	100,000	15.0	20
4	HBDS—EO—TDIK	82,000	30.4	38

In our Patent Specification No. 34173/74 (Serial No. 1,485,155) we describe and claim block copolymers, their production, and their use in lubricant and petroleum compositions, in which the block copolymer has within its molecular structure at least two segments, segment A being a polymer of a nuclear-substituted alkylstyrene in which the alkyl group has at least three carbon atoms, segment B being a polymerized alkylene oxide or alkylene sulfide segment.

WHAT WE CLAIM IS:—

1. A block copolymer having within its molecular structure at least two segments, A and B, segment A being a hydrogenated copolymer of (i) a diene and (ii) styrene or a nuclear-substituted alkyl styrene or mixture thereof, segment B being a segment of polymerized alkylene oxide or alkylene sulfide and constituting from 1 to 50 per cent by weight of the block copolymer.

2. A copolymer according to Claim 1, in which segment A comprises a copolymerized *n*-butylstyrene.

3. A copolymer of Claim 1, where said segment A is a hydrogenated random butadiene-styrene copolymer prepared in the presence of a randomizing agent.

4. A copolymer according to Claim 3, in which the randomizing agent is selected from ethers and alkali metal salts of alcohols having from 1 to 20 carbon atoms and of phenols.

5. A copolymer according to any of Claims 1 to 4, in which segment B is polymerized ethylene oxide.

6. A copolymer according to any of Claims 1 to 5, which includes a terminating group $-\text{CH}_2-\text{CH}_2-\text{Z}$ where Z is hydroxy; $-\text{OM}$ where M is an alkali metal; OR' or

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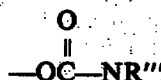
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where R'' is alkyl of from 1 to 10 carbon atoms;



where R''' is phenyl, tolyl, phenylene isocyanate, tolylene isocyanate and ionic forms thereof with M; or a heterocyclic group.

7. A copolymer according to Claim 6, in which Z is derived from toluene diisocyanate in ionic bond with a metal.

8. A copolymer according to Claim 6 or 7, in which M is sodium, lithium or potassium.

9. A copolymer according to Claim 6, in which the heterocyclic group is a pyridine, diazine or triazine.

10. A copolymer according to any of Claims 1 to 9, in which the molecular weight of the copolymer is in the range of from 1,000 to 300,000.

11. A lubricant or fuel composition comprising a major proportion by weight of a lubricant base vehicle or a petroleum base fuel and a minor amount of a copolymer as claimed in any of Claims 1 to 10.

12. A composition according to Claim 11, in which the petroleum base fuel is gasoline.

13. A composition according to Claim 11, in which the petroleum base fuel is fuel oil.

14. A method of making a hydrogenated block copolymer, which comprises: (a) copolymerising a mixture of (i) a diene and (ii) styrene or a nuclear-substituted alkylstyrene under anionic polymerization conditions to form an intermediate copolymer, (b) polymerising an alkylene oxide or alkylene sulfide in the presence of a catalyst therefor and in the presence of the intermediate copolymer to form a block copolymer of the intermediate copolymer to form a block copolymer of the intermediate copolymer with segments of the alkylene oxide or alkylene sulfide blocked on to the intermediate copolymer, and (c) hydrogenating the intermediate copolymer or the block copolymer.

15. A method according to Claim 14, in which the diene is copolymerized with styrene.

16. A method according to Claim 15, in which units of ethylene oxide are blocked on to the diene/styrene polymer.

17. A method according to any of Claims 14 to 16, in which the diene is butadiene.

18. A method according to any of Claims 14 to 17, in which the diene/styrene copolymer is hydrogenated prior to the formation of alkylene oxide or alkylene sulfide blocks.

19. A method according to any of Claims 14 to 17, in which the final block copolymer is hydrogenated.

20. A method according to any of Claims 14 to 19, in which the block copolymer is terminated with a terminating agent selected from lower alkanols (C₁-C₃), a carboxylic acid, an isocyanate or a carbonyl halide.

21. A method according to Claim 20, in which the terminating agent is tolylene diisocyanate.

22. A copolymer as claimed in Claim 1 and substantially as herein described with reference to the Examples.

23. A composition according to Claim 11, comprising a liquid base and a copolymer, substantially as herein described with reference to any of the Examples.

24. A method of making a copolymer according to Claim 14, substantially as herein described with reference to any of the Examples.



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