

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 polymerisation using n-butyl lithium as the initiator. Polymerisation 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 polymerisation. 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. According to the invention we provide a block copolymer having 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 polymerised alkylene oxide or alkylene sulfide segment. The B block usually constitutes at least 1 per cent, generally 1 per cent to 50 per cent by weight of the copolymer.

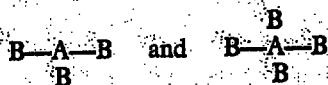
These copolymers may contain end groups, Z, derived from an organic or inorganic compound capable of reacting with an alkoxide or alcohol. For example Z may be hydroxy, alkoxy, metaloxy of the alkali metal series, carboxylate, sulfonate, carbamate, isocyanate, diisocyanate, halocarbonyl or heterocyclic 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 oil, 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 block copolymer, which comprises (a) polymerising a nuclear-substituted alkyl styrene in which the alkyl group has at least three carbon atoms under anionic polymerisation conditions to form an intermediate polymer, and (b) polymerising an alkylene oxide or alkylene sulfide in the presence of the intermediate polymer to form a block copolymer of the intermediate polymer with segments of the alkylene oxide of alkylene sulfide blocked on to the intermediate polymer, an initiator being used in step (a) which is effective to bring about the polymerization in step (b). In the first step of producing the copolymers (of this invention), an alkyl styrene is polymerised by anionic polymerisation 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 RM_y , 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-diphenylethylene 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-trithiocyclohexane and 1,4,7,10-tetrapotassio-decane. In anionic polymerization of this type each molecule of the initiator starts one anionic polymer chain; 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 poly(alkylstyrene), block A, the alkylstyrene 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 alkylstyrene. The alkylstyrenes useful in this phase of the invention include propylstyrene, n-butylstyrene, i-butylstyrene, t-butylstyrene, n-amylstyrene, i-amylstyrene, hexylstyrenes, heptylstyrenes, methylpropylstyrene, and methylbutylstyrene. The butylstyrenes are most preferred. Mixtures of different alkylstyrenes or an alkylstyrene with styrene may also be used, preferably in a ratio to provide an average of at least 2 carbon atoms of the alkyl substituent per nucleus. Polymerization is carried out for sufficient period of time to provide a block of poly(alkylstyrene) 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 alkylstyrene 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.

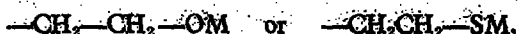
The presence of the alkyl group on the styrene is believed to permit adequate solubility of the final resulting copolymer in petroleum-base or hydrocarbon or non-hydrocarbon or synthetic fuels and lubricants.

The next step in formation of the block copolymers is to react block A polymer with the polar compound. The alkylene oxide or sulfide may be added directly to the poly(alkylstyrene) solution.

The amount of alkylene oxide added to the solution is generally from 1 per cent to 50 per cent, and preferably from 5 per cent to 25 per cent, by weight of the poly(alkylstyrene). 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

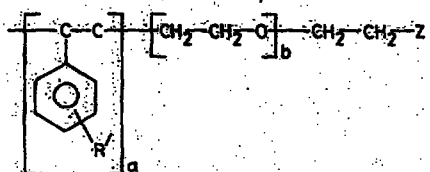
carbon atoms preferably ranging from 2 to 5. Therefore, also suitable would be 1,2-propylene oxide and 1,2-butylene or 2,3-butylene oxides or their mixtures.

- 5 The polar compound adds oxyalkylene or thioalkylene groups at the metaloxy or metalthio terminus,



- 10 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:



- 15 R' being an alkyl group of at least 3 carbon atoms and preferably from 3 to 20, a and b are 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.

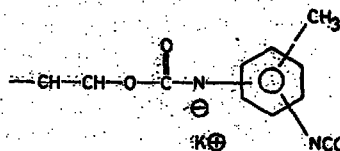
- 20 The polar block B may, if desired, be terminated either by precipitating the copolymer in a lower alkyl alcohol, i.e. from 1 to 5 carbon atoms, such as methanol, or by reacting with a compound containing a carbonyl group, such as an organic acid, an isocyanate or a carbonyl halide, such as cyanuric 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



- 45 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-
50 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 or 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, dithalopyrimidine, halopyridine, and the like or halocarbonyl. These polyfunctional capping agents may also couple more than one AB polymer molecule, as TDI above.

The alkylstyrene polymerization reaction may be conducted at a temperature in the range of from -80°C. to 100°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°C. up to about 175°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 more 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 multi-

functional 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.

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 co-

polymers in organic industrial liquid compositions. The molecular weight measurements given in these examples were obtained by gel permeation chromatography in tetrahydrofuran.

EXAMPLES.

Example 1.

Into a 2000-ml 4-necked flask was distilled 1000 ml of dried tetrahydrofuran (THF) under a vacuum at -78°C . Nitrogen gas was passed through the reactor. The THF was treated with about 30 drops of 0.5 M solution of cumyl potassium in THF. Then 6.6 ml of the 0.5 M cumyl potassium solution were added to the reactor. To the solution was added 80 grams (0.5 mole) of t-butylstyrene through a dropping funnel at -78°C . The polymerization was allowed to proceed at this temperature for approximately one hour. To the resulting reaction mixture was added 20 grams (0.45 mole) of ethylene oxide which had been dried over calcium hydride. The reaction mixture was allowed to react without temperature control and proceed at room temperature for sixteen hours. The reaction was terminated by adding to the resulting copolymer 2 ml of methanol and the solvent was replaced by a process oil. The product is an AB block polymer having the following characteristics:

$$\begin{aligned} M_n &= 20,850 \\ M_w &= 28,040 \\ M_w/M_n &= 1.35 \end{aligned}$$

Example 2.

Using a procedure similar to that of Example 1, t-butylstyrene and ethylene oxide were copolymerized to form an AB block polymer, except that 40 grams (0.25 mole) of t-butylstyrene was polymerized in the presence of 8.5 ml of 0.6 M cumyl potassium solution in THF and 10 grams (0.227 mole) of ethylene oxide was copolymerized with it. The block copolymer has the following characteristics:

$$\begin{aligned} M_n &= 5,700 \\ M_w &= 6,800 \\ M_w/M_n &= 1.2 \end{aligned}$$

It should be noted that the difference in molecular weights between the copolymer of Example 1 and that of Example 2 is due to the higher ratio of monomer to initiator in the first example. The lower ratio copolymer would indicate the formation of more short chains and hence, the lower molecular weight. Copolymers having specific desired properties may be produced by controlling this ratio and the ratio between the oleophilic and polar monomers.

Example 3.

Using a procedure similar to that of Example 1, except that the amount of ethylene oxide added was only 10% of total monomers in-

stead of 20%, the final copolymer product was reacted with 2 ml of acetic acid. The end group of the copolymer is understood to be $-\text{CH}_2\text{CH}_2\text{OH}$, while those for Examples 1 and 2 have end groups of $-\text{CH}_2\text{CH}_2\text{OK}$. The molecular weight analysis is as follows:

$$\begin{aligned}M_n &= 5,800 \\M_w &= 6,600 \\M_w/M_n &= 1.1\end{aligned}$$

Example 4.

A copolymer was prepared using the same procedure as in Example 1, except that only 10% of the ethylene oxide based on total monomers was used. To the resulting polymer solution was added 0.9 gram (6×10^{-3} mole) of toluene diisocyanate (TDI) at a temperature of 25°C . The end group in this polymer consists of diisocyanate-potassium group having a free isocyanate group. The molecular weight analysis of the product is as follows:

$$\begin{aligned}M_n &= 9,300 \\M_w &= 15,800 \\M_w/M_n &= 1.7\end{aligned}$$

Example 5.

A copolymer prepared by using the procedure of Example 1 (with 10% oxide) was reacted with 0.93 gram (5×10^{-3} mole) of cyanuric chloride, leaving a triazinyl end group. The molecular weight analysis is as follows:

$$\begin{aligned}M_n &= 7,600 \\M_w &= 10,100 \\M_w/M_n &= 1.3\end{aligned}$$

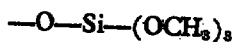
Example 6.

A copolymer prepared as in the method of Example 1 having an OK end group was reacted with amino dichloropyrimidine leaving an amino-pyrimidinyl end group. The molecular weight analysis is as follows:

$$\begin{aligned}M_n &= 6,500 \\M_w &= 9,700 \\M_w/M_n &= 1.5\end{aligned}$$

Example 7.

Another copolymer prepared as in the process of Example 1 was reacted with trimethoxysilane, leaving the following end group:



The molecular weight analysis is as follows:

$$\begin{aligned}M_n &= 7,100 \\M_w &= 10,700 \\M_w/M_n &= 1.5\end{aligned}$$

Example 8.

In this example, t-butylstyrene is polymerized as in Example 1, except 6 ml. of 1.0 M dipotassium alpha-methylstyrene tetramer solution in THF is the initiator. After one hour, 20 grams (0.90 mole) of ethylene oxide is added to the reaction mixture, and the reaction is allowed to proceed. About 98 grams of polymeric product is precipitated in methanol and separated by filtration. This product is a block copolymer of the BAB type.

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: TBS—EO, t-butyl styrene/ethylene oxide copolymer; OK, oxy-potassium 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

$$[(v_i - v_t)/(V_i - v_o)] \times 100,$$

wherein v_i is initial viscosity of the formulation, v_t is viscosity after the test, v_o 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	TBS-EO-TDIK/28,000	5.0	178	5 to 10	1.43
3	TBS-EO-OH/60,000	5.0	220	-9	6.03
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	TBS-EO-OH/60,000	6.0	240	18
3	TBS-EO-TDIK/30,000	3.0	132	1
4	Polymethacrylate Copolymer/about 100,000	8.8	184	36

* Negative number indicates 0% SSI.

** Oil contains about 6% of other additives.

DETERGENT PROPERTIES.

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

10 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 10 c.c. 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:

15

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oxide (20% EO) was used to form the B-portion of the copolymer. The amount of THF was 3000 ml. and the amount of cumyl potassium solution was 120 ml. in a 0.415N solution. The resulting copolymer had the following characteristics:

$$\begin{aligned} M_n &= 9,000 \\ M_w &= 11,200 \\ M_w/M_n &= 1.25 \end{aligned}$$

(2) 50 pounds per 1000 barrels of gasoline of (1) above.

(3) 35 pounds per 1000 barrels of gasoline of a copolymer of TBS—EO—TDIK prepared as in Example 1 and Example 4, the resulting copolymer having an M_n of 29,000, M_w of 46,000, M_w/M_n of 1.6 and % EO of 11.9.

(4) 35 pounds per 1000 barrels of gasoline of the commercial complex polyamine additive. The engine test was operated as follows: The engine was started and allowed to warm

up, set at 700 ± 50 rpm. Fuel flow is set to 2.9 lbs./hr. on individual flowmeters. A heater attached to each deposit tube in the "Y" section is set to 350°F . and air heater set to provide preheated air at 150°F . Cooling water out is set at 180°F . oil temperature out at 170°F . Then the engine is set to 2500 ± 50 rpm, then back to 700 ± 50 . These speeds are alternatively changed as follows:

8.5 minutes at 700 ± 50 rpm.
0.5 minutes at 2500 ± 50 rpm.

for a total of 12 hours, the engine is shut down at the end of the 80th cycle. The deposit tubes and carburetor sleeves are removed, heated in an oven at 230°F . for at least 15 minutes, then weighed. The initial weight is subtracted from the new weight and the difference reported as deposits. The sleeves are then washed in normal heptane, again heated and dried and weighed again. The results of deposits on the sleeves and tubes are as follows:

Sleeve Deposit, mg.

Run	Treated	Base Fuel	% Red.
(1)	14.1	22.6	38
(2)	13.9	20.7	33
(3)	8.5	15.7	46
(4)	—	—	44

Tube Deposit, mg.

	Unwashed			Washed		
	Treated	Base Fuel	% Red.	Treated	Base Fuel	% Red.
(1)	14.7	23.1	26	5.7	22.1	74
(2)	19.6	23.3	16	1.8	22.1	92
(3)	112.6	24.6	—(358)	5.1	23.8	79
(4)	—	—	—	—	—	83

Thus, the copolymers of this invention provide gasoline detergency, even as high as 92 per cent reduction in carburetor deposits, equivalent to commercial fuel detergents.

WHAT WE CLAIM IS:—

1. A block copolymer having within its molecular structure at least two segments, segment A being a polymer of a nuclear-sub-

oxide (20% EO) was used to form the B-portion of the copolymer. The amount of THF was 3000 ml. and the amount of cumyl potassium solution was 120 ml. in a 0.415N solution. The resulting copolymer had the following characteristics:

$$\begin{aligned}M_n &= 9,000 \\M_w &= 11,200 \\M_w/M_n &= 1.25\end{aligned}$$

(2) 50 pounds per 1000 barrels of gasoline of (1) above.

(3) 35 pounds per 1000 barrels of gasoline of a copolymer of TBS—EO—TDIK prepared as in Example 1 and Example 4, the resulting copolymer having an M_n of 29,000, M_w of 46,000, M_w/M_n of 1.6 and % EO of 11.9.

(4) 35 pounds per 1000 barrels of gasoline of the commercial complex polyamine additive.

The engine test was operated as follows: The engine was started and allowed to warm

up, set at 700 ± 50 rpm. Fuel flow is set to 2.9 lbs./hr. on individual flowmeters. A heater attached to each deposit tube in the "Y" section is set to 350°F . and air heater set to provide preheated air at 150°F . Cooling water out is set at 180°F . oil temperature out at 170°F . Then the engine is set to 2500 ± 50 rpm, then back to 700 ± 50 . These speeds are alternatively changed as follows:

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Thus, the copolymers of this invention provide gasoline detergency, even as high as 92 per cent reduction in carburetor deposits, equivalent to commercial fuel detergents.

WHAT WE CLAIM IS:—

1. A block copolymer having within its molecular structure at least two segments, segment A being a polymer of a nuclear-sub-



1,485,155

TABLE IV

Test No.	Polymer	MW	Wt. %, EO	Percent Removal
1	Oil alone	—	—	0
2	TBS-EO-OK	10,000	20.0	37
3	TBS-EO-TDIK	101,000	19.2	36
4	TBS-EO-OH	10,000	10.0	52
5	TBS-EO-TDIK	30,000	20.0	39
6	TBS-EO-pyrimidine	10,000	10.0	9
7	TBS-EO-trichloro triazine	10,000	10.0	27

Two of the copolymers of this invention were tested in a "Caterpillar" (registered Trade Mark) engine as a lubricant additive. The lubricant formulation consisted of 9.75% by weight of other additives including a substantially ashless dispersant, an overbased calcium phenate, a zinc dialkyl phosphorodithioate and an amine and a phenol antioxidants. In the lubricant formulation was present 1.5% by weight of a mixture of copolymers of *t*-butylstyrene and ethylene oxide capped with TDIK. Both copolymers were prepared in the manner of Examples 1 and 4. The mixture was prepared by mixing 554 grams of copolymer having the following characteristics:

$M_n = 43,000$
 $M_w = 72,000$
EO, % wt. = 16.8

with 56 grams of a copolymer of the following characteristics:

$M_w/M_n = 1.5$
 $M_n = 58,000$
 $M_w = 86,000$
EO, % wt. = 10.0

The engine used was a single cylinder, 4-cycle engine operating under the following conditions:

Speed, rpm. = 1000
Brake load, HP = 19.8
Oil Temperature, °F = 150
Jacket Temperature, °F = 150
Fuel = Diesel fuel containing 1% sulfur

The engine was operated for 240 hours. At the completion of the test, the engine piston and cylinder were examined and rated as follows (on the basis of 0 to 100): piston rating, 100 is perfectly clean; lacquer demerits,

0 means no lacquer; top groove carbon packing, 0 is clean. The results of the test using the above oil formulation are as follows:

	Oil With Copolymers
Piston Rating	93.8
Lacquer Demerits	3.8
Top Groove Carbon Packing	less than 1

The copolymers of this invention have equally effective detergent characteristics for gasolines and other fuels. Three products were tested along with a commercial complexed polyamine detergent in a carburetor detergency test. A gasoline formulation containing the detergent is used to operate a standard 302 CID "Ford" (registered Trade Mark) V/8 engine containing a modified intake system.

Essentially, the standard air system is replaced by a "Y" manifold fitted with thermocouples and two aluminum deposit tubes. On each leg of the "Y" manifold is mounted a single-barrel carburetor fitted with an aluminum sleeve near the throttle plate in the carburetor base. The tubes and sleeves are preweighed. The air inlet is divided to permit the inlet air into each leg of the "Y". The inlet air is preheated to 150°F.

The fuel system consists of two 15-gallon tanks, one for each carburetor. The neat or base gasoline is run through one carburetor; the gasoline containing the test additives is run through the second carburetor. In the following runs the treated formulations consist of the base gasoline containing:

(1) 35 pounds per 1000 barrels of a copolymer prepared as in Example 1, except that 400 grams of *t*-butylstyrene was used to form the A-polymer and 100 grams of ethylene



88

stituted alkylstyrene in which the alkyl group has at least three carbon atoms, segment B being a polymerized alkylene oxide or alkylene sulfide segment.

5 2. A copolymer according to Claim 1, in which segment B is at least 1 per cent by weight of the total copolymer.

10 3. A copolymer according to Claim 2, in which segment B is 1 to 50 per cent by weight of the total copolymer.

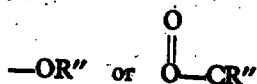
4. A copolymer according to any of Claims 1 to 3, in which segment A is a polymerized *t*-butylstyrene.

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

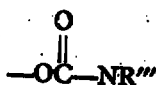
6. A copolymer according to any of Claims 1 or 5, which includes a terminating group



20 where Z is hydroxy; $-\text{OM}$ where M is an alkali metal;



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



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

30 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.

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

40 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 com-

prising a major proportion by weight of a lubricant base vehicle or a petroleum base fuel and a minor amount of the copolymer as claimed in any of Claims 1 to 10. 45

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. 50

14. A method of making a block copolymer, which comprises (a) polymerising a nuclear-substituted alkyl styrene in which the alkyl group has at least three carbon atoms under anionic polymerisation conditions to form an intermediate polymer, and (b) polymerising an alkylene oxide or alkylene sulfide in the presence of the intermediate polymer to form a block copolymer of the intermediate polymer with segments of the alkylene oxide or alkylene sulfide blocked on to the intermediate polymer, an initiator being used in step (a) which is effective to bring about the polymerization in step (b). 55

15. A method according to Claim 14, in which the alkyl styrene is *t*-butylstyrene. 60

16. A method according to Claim 14 or 15, in which units of ethylene oxide are blocked onto the alkyl styrene polymer. 65

17. A method according to any of Claims 14 to 16, in which the block copolymer is terminated with a terminating agent selected from lower alkanols (C_1-C_6), a carboxylic acid, an isocyanate or a carbonyl halide. 70

18. A method according to Claim 17, in which the terminating agent is tolylene diisocyanate. 75

19. A copolymer as claimed in Claim 1, and substantially as herein described with reference to any of the Examples. 80

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

21. A method of making a copolymer according to Claim 14, substantially as herein described with reference to any of the Examples. 85

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