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(54) Title: AMORPHOUS OLEFIN POLYMERS, COPOLYMERS, METHODS OF PREPARATION AND DERIVATIVES THEREOF		
(57) Abstract The present invention is directed to amorphous olefin polymers and their preparation using cationic polymerization and the functionalization and derivatization of such polymers. The invention includes a polymer composition comprising amorphous polymer derived from a monomer having the formula H_2C-CHR ; and optionally at least one monomer of the formula $R^1HC-CHR^2$; or $H^2C-CR^2R^3$, wherein R is a hydrocarbon or substituted hydrocarbon having from 2 to 22 carbon atoms, and R^1 , R^2 and R^3 are the same or different hydrocarbons or substituted hydrocarbons having 1 to 22 carbon atoms. R is preferably an ethyl group ($-CH_2-CH_3$) and R^1 , R^2 and R^3 are preferably methyl groups ($-CH_3$).		

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AMORPHOUS OLEFIN POLYMERS, COPOLYMERS, METHODS OF
PREPARATION AND DERIVATIVES THEREOF

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FIELD OF THE INVENTION

The present invention relates to the preparation of amorphous olefinic polymers, preferably poly-n-butenes, using cationic polymerization, and the functionalization and derivatization of such polymers.

10

BACKGROUND OF INVENTION

Feedstreams containing C₄ to C₂₄ hydrocarbons are fractionated during the processing of crude oil. In particular, C₄ feedstreams containing butadiene, isobutylene, 1-butene, cis- and trans-2-butene, butane and isobutane, are often processed to extract the butadiene leaving behind a mixture commonly referred to as Raffinate I, which typically contains isobutylene, 1-butene, cis- and trans-2-butene, n-butane and isobutane.

The Raffinate I stream is commonly used to produce polyisobutylene. Processes to produce isobutylene polymers use Lewis acid catalysts such as aluminum chloride in the presence of a number of cocatalysts, also referred to as catalyst promoters, which can include hydrogen chloride, and hydrocarbon chlorides such as isopropyl chloride, t-butyl chloride and water. Isobutylene has been polymerized using a BF₃ catalyst and a cocatalyst such as water.

The remaining feedstream, after removal of the isobutylene, is commonly referred to as Raffinate II. While the specific compositions may vary, Raffinate II typically contains n-butane, isobutane, and greater than 50% by weight of a mixture of n-butene-1, and cis- and trans-2-butene, as well as minor amounts, typically less than 5%, of isobutylene. There can also be minor amounts, i.e. less than 3%, of C₃ compounds. The amount of polymerizable butenes in purified Raffinate II is typically 70% or greater. The ready supply of the Raffinate II feedstream makes it desirable to convert the Raffinate II, and particularly the 1- and 2-butenes in the Raffinate II, to useful products.

While attempts have been made over the years to generate polymers from n-butenes, limitations in the ability to process and polymerize n-butenes have limited their use. Generally, n-butenes have been polymerized using Ziegler-Natta type catalysts as well as Friedel-Crafts catalysts. Polymers made by using Ziegler-Natta catalysts are generally stereoregular. In particular, polymers such as poly(1-butene)

are known to be polymerized using Ziegler-Natta catalysts to form stereoregular structures which leads to a crystalline polymer.

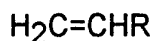
In contrast, cationic polymerization results in a head to tail addition of monomer in a random or atactic configuration which leads to an amorphous polymer.

5 Disclosed Lewis acid and Friedel-Crafts catalysts include AlCl_3 , AlBr_3 , BF_3 , SnCl_4 , H_2SO_4 and other strong acids.

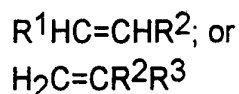
Fontana et al., Catalyzed Polymerization of Monoalkylethylenes, Industrial and Engineering Chemistry, Volume 44, No. 7, pp. 1688 - 1695 describes the continuous polymerization of 1-butene at polymerization temperatures of from -50°C to 0°C , with optimum results obtained at -35°C . The reference reports a molecular weight of poly(1-butene) of 1,120,000 obtained by light scattering.

EP-A-337737 discloses the polymerization of olefins in a Raffinate II composition containing 1-butene and trans-2-butene with BF_3 or alkyl aluminum chlorides in the presence of HCl , HF or organic compounds with a reactive chlorine or fluorine bonded to a tertiary-, benzyl- or allyl carbon atom as co-initiators. The method is conducted in the presence of at least 20% 1-butene and at least 15% 2-butene at from -70°C to $+100^\circ\text{C}$. The resulting polymer has a number average molecular weight of 300 to 1,200.

The invention provides a polymer composition comprising amorphous copolymer derived from at least one monomer having the formula:

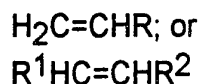


wherein R is a hydrocarbon having from 2 to 22 carbon atoms, and at least one comonomer of the formula:



30 wherein R^1 , R^2 and R^3 are the same or different hydrocarbon groups or substituted hydrocarbon groups having from 1 to 22 carbon atoms, the copolymer comprising at least 50 mole% of repeating units derived from $\text{H}_2\text{C}=\text{CHR}$, and up to 5 mole% of the repeating units derived from $\text{H}_2\text{C}=\text{CR}^2\text{R}^3$, being at least 95% amorphous and having a number average molecular weight of greater than 1,300.

35 It also provides a cationically polymerized polymer composition derived from at least one monomer of the formula:



wherein R is a hydrocarbon having from 2 to 22 carbon atoms and R¹ and R² are the same or different hydrocarbon groups or substituted hydrocarbon groups having from 1 to 22 carbon atoms.

The polymer composition comprises at least 50 mole % of repeating units derived from H₂C=CHR; is at least 95% amorphous; and has a number average molecular weight (M_n) of from 1,200,000 to 15,000,000. R is preferably an ethyl group (-CH₂CH₃) and R¹ and R² are preferably methyl groups (-CH₃).

The amorphous polymer and copolymers of the present invention preferably have at least one unsaturated group, preferably at least one carbon-carbon double bond at an internal or terminal position.

The method of the present invention comprises an improved process of polymerization conducted in the presence of a strong Lewis acid catalyst and preferably a reaction promoter also referred to as a cocatalyst or initiator. Strong Lewis acids can be classified as having Hammett Acidity Scale Value (H_o) of less than -10 when dissolved in a non-reactive aprotic solvent. The concentration of the monomer relative to the catalyst can be controlled during the polymerization to minimize competing reactions of isomerization, cracking, alkylation and dimerization. These competing reactions can result from the formation of chain transfer agents which can reduce the molecular weight of the polymer. The amount of monomer being reacted can also be controlled to control polymer chain length. For higher molecular weight polymers, lower concentration of monomers in the reactor are maintained to drive the reaction to form longer polymer chains.

A preferred process of polymerization comprises the steps of: (1) forming a catalyst solution of an acid catalyst having a Hammett Acidity Scale Value of less than -10 in a non-reactive aprotic solvent; and (2) polymerizing at least one monomer having the formula H₂C=CHR and at least one comonomer selected from the group consisting of monomers having the formula R¹HC=CHR² and H₂C=CR²R³, wherein R, R¹, R² and R³ are as defined above, in the presence of the catalyst solution, said polymerization being conducted in a manner and under conditions sufficient to form copolymer comprising at least 50 mole% of units derived from H₂C=CHR, and less than 5 mole% of units derived from H₂C=CR²R³, being at least 95% amorphous and having a number average molecular weight of greater than 1,300.

Another embodiment of the process comprises the steps of forming a catalyst solution of an acid catalyst having a Hammett Acidity Scale Value of less than about

-10 in a non-reactive aprotic solvent; and combining the catalyst solution with at least one monomer selected from the group consisting of monomers having the formula $H_2C=CHR$ and $R^1HC=CHR^2$, wherein R, R^1 , and R^2 are as defined above, polymerizing at least one monomer in the presence of the acid catalyst, said
5 polymerization being conducted in a manner and under conditions sufficient to form polymer comprising at least 50 mole% $H_2C=CHR$, there being from 0.5 to 1.0 carbon-carbon double bond per polymer chain, and at least 95% amorphous and having a number average molecular weight of from 1,200,000 to 15,000,000.

The polymers and copolymers of the present invention can be "functionalized",
10 e.g. chemically modified, with a functional group as described hereinafter. Preferred functional groups are selected from acid, ester, anhydride, acid-ester, oxycarbonyl, carbonyl, formyl, formylcarbonyl, hydroxyl, and acetyl halides.

The functionalized polymer can in turn be derivatized with a derivatizing compound. The derivatizing compound can react with the functional groups of the
15 functionalized polymer by means such as nucleophilic substitution, Mannich Base condensation, and the like. The derivatizing compound can be polar and/or contain reactive derivative groups. Preferred derivatizing compounds are selected from hydroxy containing compounds, amines, metal salts, anhydride containing compounds and acetyl halide containing compounds.

20 The polymers, functionalized polymers and/or derivatized polymers have uses as lubricating additives which can act as dispersants, viscosity index improvers, or multifunctional viscosity index improvers.

BRIEF DESCRIPTION OF THE DRAWINGS

25 Figure 1 shows a flow chart of an embodiment of the process of the present invention.

Figure 2 shows a laboratory reactor useful for the present invention.

Figure 3 is a plot of concentration vs. time (M_n) based on gel permeation chromatography (GPC) for polymer made in Example 1.

30 Figures 4A to 4E are a series of plots of concentration vs. time (M_n) based on GPC of Examples 2 - 6.

Figure 5 illustrates the GPC of concentration vs. time (M_n) for poly-n-butene prepared in Example 7.

Figure 6 shows a pilot plant system used to prepare polymer in Example 8.

35 Figures 7A to 7C are GPC plots of concentration vs. time (M_n) with varying temperature based on polymers produced in Examples 9 - 11.

Figure 8 shows the GPC as a plot of concentration vs. time for polymer made in Example 8, RUN 9.

Figures 9 and 10 are a GPC trace, having a curve (related to the right axis), showing cumulated % of sample concentration vs. number average weight for Example 8, runs 3 and 6 respectively.

Figure 11 shows M_n , temperature and monomer cation ratio in a continuous process with a 1.5 cocatalyst-catalyst ratio.

Polymers

Preferred embodiments of the present invention relate to amorphous polymers and copolymers derived from at least one monomer having the formula (1) $H_2C=CHR$, or (2) $R^1HC=CHR^2$ where R is a hydrocarbon having from 2 to 22 carbon atoms, R^1 and R^2 are the same or different hydrocarbons or substituted hydrocarbons having from 1 to 22 carbon atoms. A preferred homopolymer is derived from 1-butene.

Preferred homopolymer has a number average molecular weight which includes polymer molecules of from greater than 1,200,000 up to 15,000,000. The homopolymer composition comprises up to 1, preferably 0.5 to 1.0, more preferably 0.75 to 1.0 and most preferably 0.9 to 1.0 carbon-carbon double bonds per polymer chain.

A further preferred embodiment of the present invention is a composition comprising an amorphous copolymer having present within its structure at least 50 and preferably at least 75 mole% of monomer units derived from at least one monomer having the formula (1) $H_2C=CHR$ (e.g. butene-1), and at least 5, but not greater than 60, preferably not greater than 40, and most preferably not greater than 25 mole% of monomer units derived from at least one comonomer selected from the group of monomers represented by the formulas (2) $R^1HC=CHR^2$ (e.g. cis or trans butene-2) and (3) $H_2C=CR^2R^3$ (e.g. isobutylene), with the proviso that the copolymer contains monomer units derived from monomers of formula (3) in amounts not greater than 5, preferably not greater than 4 and most preferably not greater than 3 mole%. R, R^1 and R^2 are as defined above; R^3 has the same definition as R^1 and R^2 . Preferably, R is an ethyl group, and R^1 , R^2 and R^3 are methyl groups. The copolymer comprises up to 1, preferably 0.5 to 1.0, more preferably 0.75 to 1.0 and most preferably 0.9 to 1.0 carbon-carbon double bonds per polymer chain.

Useful formula (1) monomers include C_4 - C_{24} linear α -olefins (e.g., butene-1, pentene-1, hexene-1, etc.). C_4 - C_{24} branched α -olefins are also useful, with the proviso that there be at least one $-CH_2-$ group between the olefinic bond and the

branch. R groups include ethyl, butyl, pentyl, cyclohexyl, and methylcyclohexyl, and preferably ethyl. Useful formula (2) 1,2-disubstituted comonomers include cis-butene-2 and trans-butene-2, which is preferred. R¹, R² and R³ groups include methyl, ethyl, cyclohexyl, and methylcyclohexyl, and preferably methyl.

5 Limits are placed on the monomer content derived from formula (3) such as isobutylene derived monomer units. This stems from the fact that isoolefins such as isobutylene more readily polymerize, while the present invention is directed to the discovery of how to polymerize or copolymerize monomers of feed streams containing α -olefins, e.g., butene-1, and also olefin-2, e.g. butene-2, monomer which are much
10 more difficult to polymerize cationically. α -Olefins polymerize cationically at a faster rate than olefin-2 monomers, resulting in polymer with a maximized α -olefin content. However, it is an advantage of the process of the present invention that it is possible to incorporate olefin-2 monomers into the polymer since many commercial feeds also contain such monomers to varying degrees.

15 Copolymers of the present invention will typically comprise from 40 to 95 (e.g. 50 - 90), preferably 50 to 95, (e.g. 60 - 85) and more preferably 60 to 95 (e.g. 65 - 85) mole% of α -olefin derived monomer units and typically from 60 to 5 (e.g. 50 - 10), preferably from 50 to 5 (e.g. 40 - 15) and most preferably from 40 to 5 (e.g. 45 - 15) mole% olefin-2 derived monomer units of formula 2.

20 The polymers typically have a number average molecular weight of greater than 1,300, preferably 1,300 to 15,000,000. Specific embodiments of the polymers and copolymers of the present invention have number average molecular weight ranges of from 1,500 to 15,000,000; 2,000 to 15,000,000; 2,500 to 15,000,000; 3,000 to 15,000,000; 3,500 to 15,000,000; 5,000 to 15,000,000; 1,300 to 200,000; 3,500 to
25 20,000; 1,500 to 10,000; 10,000 to 100,000; 1,200,000 to 15,000,000; 1,500,000 to 15,000,000; 1,500 to 2,000,000; and 3,500 to 2,000,00.

Dispersant range molecular weight polymers are low molecular weight polymers having a number average molecular weight of typically less than 20,000, preferably less than 10,000 and most preferably less than 8,000 and typically can
30 range from 500 to 10,000 (e.g. 500 to 5,000), preferably from 1,000 to 8,000 (e.g. 1,000 to 5,000) and most preferably from 1,500 to 6,000 (e.g. 1,500 to 3,000). Other embodiments include 3,500 to 19,000. The low molecular weights are number average molecular weights which may be measured by well known techniques such as vapor phase osmometry or by gel permeation chromatography. Low molecular
35 weight polymers are useful per se as synthetic base oils and in forming dispersants for lubricant additives through the functionalization and derivatization techniques described hereinafter.

Viscosity modifier range polymers are medium molecular weight polymers having number average molecular weights of typically greater than 20,000 and typically can range from 20,000 to 200,000. The polymers are useful for viscosity index improvers for lubricating oil compositions, adhesive coatings, tackifiers and sealants. The medium number average molecular weights can be determined by well known techniques such as membrane osmometry. The polymers may be functionalized and derivatized to make multifunctional viscosity index improvers which also possess dispersant properties.

The higher molecular weight materials have a number average molecular weights of typically greater than 200,000 and typically range from 210,000 to 15,000,000. These polymers are useful in polymeric compositions and blends including elastomeric compositions.

Molecular weight materials having M_n 's of from 20,000 to 15,000,000 can be measured by well known techniques such as gel permeation chromatography or light scattering. A convenient method for such determination is by gel permeation chromatography which additionally provides molecular weight distribution information; see W. W. Yau, J. J. Kirkland and D. D. Bly, Modern Size Exclusion Liquid Chromatography, John Wiley, (1979).

The molecular weight distribution (MWD) depends on polymerization conditions. MWD can be controlled depending on the desired polymer. Useful polymers have narrow molecular weight distributions of less than 4 and ranging from 1.1 to 4.0, 1.2 to 2.0 and 1.3 to 1.5. Such polymers include those useful as lubrication and viscosity index improvers. Other polymers can have large MWD's of 10 or greater. Polymers can also be prepared with multiple distribution.

The preferred copolymers contain monomer units derived from monomer comprising 1-butene, 2-butene and up to 5 wt.%, typically 0 to 4 wt.%, isobutylene. This enables feedstreams such as Raffinate II to be polymerized to form higher molecular weight polymers which are oil soluble. Raffinate II feedstreams typically contain a mixture of 1-butene, cis-2-butene and trans-2-butene. The Raffinate II feedstock typically comprises less than 5%, preferably less than 4% and most preferably less than 3% by weight of isobutylene, and typically at least 12, preferably at least 30% and most preferably at least 45 mole% of 1-butene and 2-butenes.

The copolymer derived from Raffinate II, comprises up to 95 mole% and typically up to 75% (e.g., 50 to 95 mole%) of monomer units derived from 1-butene and up to 50 mole% (e.g., 5 to 50 mole%) of at least one 2-butene. The mole ratio monomer units derived from 1-butene and 2-butene in the copolymer, ranges typically from 1:1 to 20:1, preferably from 5:1 to 15:1 and most preferably from 8:1 to 15:1.

The copolymer can additionally include from up to 50, typically up to 40 mole% and more typically up to 10 mole% of other repeating units including units derived from styrenic comonomers selected from the group consisting of styrene and substituted styrene including α -methylstyrene and paramethylstyrene.

5 The polymers or copolymers of the present invention are preferably at least 99% amorphous, and most preferably 100% amorphous. In accordance with the method of polymerization as recited below, polymers and copolymers result which are substantially, and preferably completely amorphous. By amorphous is meant that the monomer units have side chains randomly located along the polymer backbone. The
10 polymer chains form substantially no crystallinity and substantially no stereoregularity. Hence they are oil soluble even at extremely high molecular weights. More particularly, polymers are produced which form substantially no crystals when dissolved or suspended in oleaginous liquids, typically hydrocarbon liquids such as oil base stock or gasoline. The amorphous polymers are formed by
15 the random polymerization of at least one monomer recited above. During formation the monomers and comonomers polymerize randomly in a head-to-tail fashion. The random nature of the substituents on the backbone precludes packing which results in crystal formation.

20 The degree of crystallinity (inversely the % amorphous) can be determined by well known techniques such as 1) specific volume measurement, 2) X-ray diffraction, 3) infrared spectroscopy, 4) heat content as a function of temperature through fusion range, 5) differential scanning calorimetric measurements or 6) NMR spectroscopy.

25 The polymers of the present invention are made by cationic polymerization based on the use of a strong Lewis acid. This type of polymerization typically results in the polymer having a carbon-carbon double bond, i.e., an olefinic unsaturation at the end of the polymer chain. However, unsaturation can also be present near the chain end or intermediate in the chain depending on the condition of polymerization.

30 The polymers of the present invention preferably comprise a high degree of terminal unsaturation. Terminal olefinic groups include vinylidene unsaturation, $R^aR^bC=CH_2$; trisubstituted olefin unsaturation, $R^aR^bC=CR^cH$; vinyl unsaturation, $R^aHC=CH_2$; 1,2-disubstituted terminal unsaturation, $R^aHC=CHR^b$; and tetra-substituted terminal unsaturation, $R^aR^bC=CR^cR^d$. At least one of R^a and R^b is a polymeric group of the present invention, and the remaining R^b , R^c and R^d are hydrocarbon groups as defined with respect to R , R^1 , R^2 and R^3 above. Ranges of
35 terminal unsaturation of polymers of the present invention are 1 to 50 mole% of vinylidene termination; 5 to 90 mole% of trisubstituted termination; 0 to 20 mole% vinyl termination; 0 to 40 mole% 1,2-disubstituted terminal unsaturation; and 0 to 60

mole% tetra-substituted terminal unsaturation. Terminal unsaturation of copolymer made from Raffinate II is typically from 10 to 20 mole% vinylidene (typically ethylvinylidene); 20 to 80 mole% tri-substituted; 1 to 10 mole% vinyl; 5 to 20 mole% of 1,2-disubstituted; and 5 to 50 mole% tetra-substituted terminal unsaturation.

5

Method of Polymerization

The method of the present invention is an improved process of cationic polymerization conducted in the presence of a strong Lewis acid catalyst and a reaction promoter. Strong Lewis acids are defined herein as having Hammett Acidity
10 Scale Value (H_o) less than -10, when dissolved in a non-reactive aprotic solvent. The cationic polymerization results in an amorphous polymer.

The polymer chain length is a function of monomer concentration in the reactor. For higher molecular weight polymers, the monomer concentration in the reactor is controlled to be relatively low so that the minimum of competing reaction of
15 the monomer takes place. Additionally, feedstreams containing compounds such as isobutylene result in low molecular weight polymers. By controlling the amount of isobutylene and other chain transfer agents, the effects of these types of materials is reduced. However, small amounts (i.e., <5 wt.%) of isobutylene can be tolerated and even copolymerized into the forming polymer chains.

20 The method of the present invention has a particular advantage of being capable of polymerizing petroleum feedstreams such as those disclosed in US-A-4952739. Such feedstreams can be characterized as dilute, preferably liquified, olefin feedstreams comprising at least 1, preferably at least 2, olefin reactant(s) and diluent. The amount of diluent in the feedstream will typically be at least 10,
25 preferably at least 15, and most preferably at least 20 wt.% thereof, and will typically range from 10 to 80, preferably from 15 to 70, and most preferably from 20 to 55 wt.% thereof. Moreover, typically at least 10, preferably at least 20, and most preferably at least 30 wt.%, typically from 10 to 100, preferably from 20 to 95, and most preferably from 30 to 90 wt.% of the diluent constituents possess a boiling point under reaction
30 conditions within 5°C to 10°C of the average boiling point of the reactive constituents at the same temperature.

The preferred copolymers can be prepared from Raffinate II feedstreams, which are typically derived from either butane/butene catalytic cracking refinery streams (BB-streams) or from Raffinate I which can be derived from butadiene crude
35 produced by steam cracking plants. Typical Raffinate II feedstock useful in the process of this invention comprises a mixture of pressure liquefied C₄ hydrocarbons which comprise less than 5 wt.% isobutylene, and at least 12 wt.% butene-1 and cis-

and trans-butene-2, together with 10 to 70% n-butane and isobutane and preferably less than 0.8 wt.% butadiene. More typically, Raffinate II is 20 to 55% of 1-butene and 5 to 35% of 2-butene.

5 The C₄ feedstream is preferably substantially free of H₂ and sulfur contaminants (e.g., mercaptans), e.g. <20 wppm H₂ and <5 wppm S. The C₄ feedstream is also preferably substantially anhydrous; i.e., it contains less than 0.05 wt.% water, more preferably less than 300 wppm water, based on the C₄ monomers in the feedstream.

10 The C₄ feedstream is maintained at a sufficient pressure to be in liquid form both at the reactor inlet and in the reaction mixture at the reaction temperature, which is generally from -50°C to +20°C. Reaction pressures are generally from 250 to 1,000 kPa, and more typically from 300 to 700 kPa. Conventional cooling means can be used in view of the exothermic nature of the reaction. Preferred reaction temperatures are -20°C to +10°C, and most preferred -15°C to +10°C. Generally,
15 higher temperatures tend to produce lower molecular weight polymer.

The polymer or copolymer of the present invention is polymerized in the presence of a strong Lewis acid catalyst. The catalyst is a Lewis acid having a Hammett Scale Value acidity H_o of less than -10, and preferably less than -15 when dissolved in a non-reactive aprotic solvent. Hammett acidity is defined in March,
20 Advanced Organic Chemistry, 3d Ed., p. 223 - 225 which refers to Hammett and Deyrup, J. Am. Chem. Soc., 54, 2721 (1932). Useful strong Lewis acids are disclosed in US-A-4229611.

Preferably, the strong Lewis acids comprise the formula MX_n wherein M is selected from the Group IIIA elements of the Periodic Table described in
25 Encyclopedia of Chemistry, 2d Ed., Reinhold (1966) at page 790. X is a halogen, with at least one X representing bromine, and n is the ratio of halogen atoms to atoms of M and varies from 1 to 8. The preferred Lewis acids are the bromides of aluminum and gallium, e.g., AlBr₃, AlBr₂Cl, AlBrCl₂, GaBr₃, GaBr₂Cl and GaBrCl₂. The most preferred strong Lewis acid for use in the present invention is aluminum bromide.
30 The aluminum bromide can be added directly to a monomer stream, or, more preferably, dissolved in a suitable solvent.

Organo aluminum bromide catalyst is also useful in the process of this invention and comprises at least one compound of the formula:



wherein M is defined as above and is preferably Al, R⁴ is C₁ to C₂₀ hydrocarbyl and x is 1 or 2. R⁴ can comprise branched or straight chain alkyl, cycloalkyl, aryl, alkaryl, aralkyl, alkynyl, alkenyl, and hydrocarbyl substituted derivatives thereof. When R⁴ is alkyl, the alkyl group is a C₁-C₂₀, preferably a C₁-C₁₀, and most preferably a C₁-C₄ alkyl group (e.g., methyl, ethyl, propyl, n-butyl, isobutyl, etc.). Useful organo-
5 aluminum bromides include (CH₃)AlBr₂, (CH₃)₂AlBr, C₂H₅AlBr₂, (C₂H₅)₂AlBr, (CH₃)₂CHAlBr₂, [(CH₃)₂CH]₂AlBr, (C₃H₇)AlBr₂, (C₃H₇)₂AlBr, CH₃CH(CH₃)AlBr₂, [CH₃CH(CH₃)]₂AlBr, (CH₃)₃CAI Br, [(CH₃)₃C]₂AlBr, C₆H₁₃AlBr₂, C₅H₁₁AlBr₂, C₁₀H₂₁AlBr₂, and mixtures thereof. Especially preferred are C₂H₅AlBr₂,
10 (C₂H₅)₂AlBr and mixtures thereof. Preferred organo-aluminum bromide catalysts are liquids under reaction conditions.

The high acidity of the catalyst can cause reactions with the solvent and/or the monomer present in the reacting mixture. The concentration of the monomer relative to the catalyst can be controlled during the polymerization to minimize competing
15 reaction of isomerization, cracking, alkylation and dimerization. These competing reactions can result from the formation of chain transfer agents which can reduce the molecular weight of the polymer. The method must be carefully controlled since the Lewis acid catalyst can also react with the catalyst solvent as well as the monomer to form compounds which are deleterious to the polymerization process. The amount of
20 monomer being reacted can be controlled to control polymer chain length. For higher molecular polymers, lower concentration of monomers in the reactor are maintained to drive the reaction to form longer polymer chains.

The strong Lewis acid is preferably dissolved in a nonreactive aprotic solvent. The term "non-reactive" includes compounds which do not undergo an elimination
25 reaction, cracking, alkylation, dimerization or an isomerization or reduce the acidity of the Lewis acid by acting as a Lewis base. Non-reactive solvents include hydrocarbons such as C₃-C₂₄ alkanes, the halogenated C₁-C₃ alkanes, halogenated cyclopropane or halogenated C₂-C₃ alkenes (wherein the C₂-C₃ compounds contain 2 or more halogen atoms per mole and the halogens are preferably chlorine, bromine
30 or fluorine). Saturated hydrocarbons are useful solvents, preferably methane, propane, n-butane, pentane, hexane, cyclohexane and octane. The most preferred solvents include n-butane, n-hexane and cyclohexane.

When using a strong acid in a solvent, it is preferred that the solution be prepared immediately prior to use to minimize the recited undesirable side reactions
35 of the solvent. The catalyst solution is typically prepared within 2 hours of the reaction, preferably within 1 hour, more preferably within 30 minutes, and most preferably immediately.

A preferred method of the present invention employs a reaction promoter, also referred to as cocatalyst or initiator, in addition to the catalyst. Useful reaction promoters include hydrogen halides with hydrogen bromide most preferred. Other useful promoters include alkyl halides such as alkyl bromide and alkyl chloride (e.g., t-butyl bromide, 2-bromobutane). Most preferably, the promoter is hydrogen bromide which is added to the monomer prior to contact with the catalyst. The hydrogen bromide is believed to interact with at least some of the monomer to form alkyl bromides in situ. The catalyst alone or in solution is then combined with the monomers and cocatalyst.

The addition of HBr cocatalyst to the feedstream in the absence of aluminum bromide to form a pre-reacted feedstream offers the further advantage of substantially reducing the presence of brominated poly-n-butene in the finished product. The use of a pre-reacted feedstream also avoids the presence of free HBr in the reactor, which has the potential of corrosion of the reactor. The HBr injected into the feedstream reacts quickly with normal-butenes to produce 2-bromobutane which, upon entering the reactor, functions as a cocatalyst with the aluminum bromide to initiate the polymerization, the aluminum bromide reacting with the 2-bromobutane to form AlBr_4 anion and a butyl cation, thereby initiating polymerization. Other organo bromides can also be formed, principally t-butyl bromide from reaction with the isobutylene content of the monomer feedstream.

The combination of monomer plus cocatalyst is contacted with the catalyst in a tank or tube-type reactor for a period of time sufficient to polymerize the monomer to desired amount of polymerization. In a preferred method of polymerization the concentration of monomer relative to catalyst is controlled to control the polymerization and minimize competing reactions of isomerization, cracking, alkylation and dimerization of the monomer and catalyst solvent.

Useful polymerization conditions include temperatures ranging from -50°C to $+20^\circ\text{C}$, more preferably -30°C to $+20^\circ\text{C}$, pressures ranging from 345 to 1035 kPa (50 to 150 psig), monomer to catalyst mole ratio of up to 250 and typically from 25 to 250; monomer to cocatalyst molar ratio of up to 500 and typically from 20 to 500; cocatalyst to catalyst mole ratio of from 0.25 to 3.00; reaction time of up to 2 hours, and typically from 20 to 45 minutes.

A preferred process uses either a tubular reactor or a stirred reactor (preferably a continuous-type stirred reactor) having two separate inlet means for introduction of C_4 feedstream and the organo-aluminum chloride catalyst. The latter are added alone or in admixture with a diluent or solvent which is substantially inert under the premixing and polymerization conditions.

The HBr should be introduced into the C₄ feedstream sufficiently in advance of the reactor entry to permit substantially complete reaction of the HBr in the feedstream prior to the polymerization reaction zone. The concentration of free HBr in the treated feedstream mixture at the point of reactor entry is preferably less than 1.0 ppm (parts per million). The treated feedstream mixture, containing the C₄ monomers and the pre-reacted HBr, is added to the reactor. The aluminum bromide catalyst is preferably introduced into the reaction mixture through a separate inlet.

The process of this invention can be practiced in a batchwise, semi-continuous or preferably in a continuous manner. Preferably, the treated feedstream mixture, containing the C₄ monomers and the pre-reacted HBr, and the aluminum bromide catalyst streams are added to the reaction zone substantially simultaneously, at a rate sufficient to maintain the selected ratio of the monomers and aluminum bromide catalyst in the liquid reaction mixture. However, it is also possible to add these streams in a stagewise manner to a liquid reaction mixture.

Polymerization occurs in an exothermic reaction in the reaction zone of the reactor upon contacting the two incoming streams. The reactor temperature is preferably maintained at -50°C to +20°C. For a continuous-type stirred reactor, average reactant residence time is generally 20 to 60 minutes and preferably 20 to 50 minutes. There is generally a mole ratio of up to 250 and preferably 25 to 250 of monomer to aluminum bromide catalyst, a mole ratio of up to 500 and preferably from 20 to 500 of monomer to HBr cocatalyst, and mole ratio of cocatalyst, i.e., HBr cocatalyst, to catalyst, i.e., aluminum bromide catalyst, of from 0.1 to 3.0, preferably from 1.0 to 20 parts.

FIG. 1 illustrates one embodiment of the process of the present invention. A liquid monomer feed 4 (i.e., Raffinate I) comprising 1-butene, 2-butene, isobutylene, and saturates (butanes), and generally containing at least 6 wt.% isobutylene, and a polymerization catalyst 6 are introduced into first polymerization reaction zone 10 wherein the isobutylene monomer is selectively polymerized to form a polyisobutylene (PIB) polymer mixture 18 containing PIB and unreacted monomers. The temperature in the first polymerization reaction 10 is typically from -10°C to +10°C. Mixture 18 is passed to catalyst removal zone 20 wherein the polymerization catalyst 22 is separated from the remaining components of the polymerization mixture. The resulting liquid PIB/monomer mixture 24 is passed to a polymer recovery zone 30 for separation of monomer stream 32 from liquid PIB stream 34. Typically, monomer stream 24 is removed from zone 30 as a gas. Stream 32 comprises a crude spent C₄ stream (i.e., Raffinate II) which can include 1-butene, 2-butene, unreacted isobutylene, and butanes. The catalysts and polymerization conditions, and the

methods of catalyst separation and polymer recovery, employed in zones 10, 20 and 30, respectively, are conventional.

The crude spent monomer stream 32 is passed to drying zone 40 wherein water is removed, to provide a C₄ monomer feedstream 42 containing less than about 200 wppm, preferably less than about 100 wppm, water (e.g., 5 to 100 wppm, more preferably from about 5 to 50 wppm water). The C₄ monomer feedstream 42 is then contacted with HBr 44 in a portion 46 of conduit 42 to form the treated feedstream mixture containing not greater than about 1 wppm free HBr which is then charged to polymerization reaction zone 50, along with a separately charged aluminum bromide catalyst stream 52, for polymerization as described above to form the poly-n-butene polymers of this invention. The resulting poly-n-butene polymerization reaction mixture 54 can be withdrawn from zone 50 and treated as described above for recovery of the polymer product, including the steps of catalyst removal and stripping to remove low molecular weight polymer fractions, as desired.

The drying of the crude spent C₄ monomer stream in zone 40 can be accomplished by contacting the stream with a desiccant which is substantially nonreactive with any organic component of the stream, such as CaCl₂, molecular sieves, and the like. Drying zone 40 can comprise one or more vessels containing a solid desiccant through which stream 32 is passed.

Because of the olefin-2 monomer, e.g. butene-2, present in conventional Raffinate feeds, the resulting polymer will be a copolymer. Homopolymers can be obtained by using pure α -olefin feeds. Accordingly, the term "poly-n-butenes" as used herein includes homopolymers of butene-1 and copolymers of butene-1 and butene-2. The polymers, particularly poly-n-butenes, prepared by the process of this invention preferably contain an average of about 1 double bond per polymer chain. Up to about 20% of the polymer chains may be saturated.

The poly-n-butene of the present invention offers a number of advantages over poly-n-butenes prepared by prior art techniques with respect to properties which are important for use in making lubricating oil additives such as dispersants. There is a significant reduction in the quantity of so called "light ends"; i.e., poly-n-butenes of M_n less than 300, typically from about 110 to 250. Products of this invention generally contain less than about 5 wt.% of light ends in the reaction mixture prior to product finishing. After stripping, the finished polymer preferably contains less than about 2 wt.% of poly-n-butenes having M_n below 250.

Polymers of the present invention have a variety of uses. The polymers, particularly poly-n-butene, which are useful for dispersants have a number average molecular weight of from 1,300 to 20,000, preferably 1,300 to 10,000, more preferably

1,500 to 10,000, and most preferably 1,500 to 5,000. Polymers useful for lubricating oil viscosity index improvers preferably have a number average molecular weight of 20,000 to 100,000, preferably 20,000 to 100,000 and more preferably 20,000 to 65,000.

5

Functionalized Polymers

The polymers produced in accordance with the present invention can be functionalized; i.e., chemically modified to have at least one functional group present within its structure, which functional group is capable of (1) undergoing further
10 chemical reaction (e.g. derivatization) with other material or (b) imparting desirable properties, not otherwise possessed by the polymer alone, absent such chemical modification.

The functional group typically will be polar and contain hetero atoms such as P, O, S, N, halogen and/or boron. It can be attached to the saturated hydrocarbon
15 part of the polymer via substitution reactions or to an olefinic portion via addition or cycloaddition reactions. The functional group can also be incorporated into the polymer during polymerization via a functional group containing comonomer or by oxidation or cleavage of a small portion of the end of the polymer (e.g. as in ozonolysis). Functionalization of the polymer backbone with substituent functional
20 groups typically relies on an ethylenic unsaturation, preferably a terminal ethylenic unsaturation, present in the polymer for reaction with a functional compound containing or constituting the functional group. Useful and preferred functional groups include halogen, carboxyl materials present as acids, esters, salts, anhydrides, alcohols, amines, ketones, aldehydes and the like.

25 Useful functionalization reactions include maleation, which is the reaction of the polymer at the point of unsaturation with maleic acid or anhydride; halogenation of the polymer at the olefinic bond and subsequent reaction of the halogenated polymer with an ethylenically unsaturated functional compound; the "ene" reaction of the polymer with an unsaturated functional compound; reaction of the polymer with at
30 least one phenol group; a Koch-type reaction of the polymer at its point of unsaturation with carbon monoxide to form an iso or neo or other acid group; free radical reaction of the polymer with the functional compound via a free radical catalyst; and reaction of the polymer by air oxidation methods, epoxidation, chloroamination or ozonolysis.

35 Suitable functional comonomers which can be incorporated into polymer backbone include vinyl monomers (e.g., $>C=C<$) with pendant functional groups, such as carboxyl, ester, carbonyl, aryl, heteroaryl, i.e., at least one aromatic ring

containing one or more heteroatoms such as oxygen, nitrogen or sulfur within the ring structures (e.g., pyridine). Representative examples of suitable vinyl comonomer type compounds include vinylacetate, styrene, p-alkyl styrene, e.g., p-methyl styrene, vinyl carbonate, acrylic acid, and vinyl alcohol.

Characterization of the degree to which the polymer has been functionalized is referred to as functionality, which relates to the average number of functional groups present within the polymer structure per polymer chain. Functionality can be expressed as the average number of moles of functional groups per mole of polymer. When the "mole of polymer" in the functionality ratio includes both functionalized and unfunctionalized polymer, functionality is referred to as F. When the "mole of polymer" includes only functionalized polymer, functionality is referred to as F*. The distinction between F and F* arises in non-copolymerization methods of functionalization, when all the polymer chains do not undergo reaction with the functional compound. Analytical techniques employed to determine F* will normally require identification of the Active Ingredient (or A.I.), which is the weight fraction of functionalized polymer, based on the total weight of polymer (functionalized + unfunctionalized) in the sample.

F and F* values can be related by the A.I. which for polymers of the present invention typically are at least .50, preferably from .65 to .99, more preferably from .75 to .99, yet more preferably .85 to .99. However, the upper limit of A.I. is typically from 0.90 to 0.99, and more typically 0.90 to 0.95. Where A.I. is 1, $F = F^*$.

For dispersant end uses, F* is typically not greater than 3, preferably not greater than 2, and typically can range from 1 to 3, preferably from 1.5 to 2.5, and most preferably from 1.1 to 2 (e.g. 1.2 to 1.3). F* for viscosity modifier end uses of derivatized polymer are contemplated to be typically greater than 3, preferably greater than 5, and most preferably greater than 10, and typically will range from 4 to 20, preferably from 5 to 15, and most preferably from 8 to 15.

Acyl Functionalized Polymer

The most preferred functionalization technique in the present invention is to chemically modify the polymer to have chemical moieties present within its structure which contain or constitute at least one acyl functional group, i.e. $-C(=O)-X$ wherein X is hydrogen, nitrogen, hydroxy, oxyhydrocarbyl (e.g. ester), oxygen, the salt moiety - OM wherein M is a metal, e.g. alkali, alkaline earth, transition metal, copper, zinc and the like, oxyhetero, e.g. $-O-Z$ wherein Z represents a hetero atom such as phosphorus boron, sulfur, which hetero atom may be substituted with hydrocarbyl or oxyhydrocarbyl groups, or two acyl groups may be joined through (X).

Within this broad class of compounds the most preferred are acyl groups derived from monounsaturated mono- or dicarboxylic acids and their derivatives, e.g. esters and salts. More specifically, polymer functionalized with mono- or dicarboxylic acid material, i.e., acid, anhydride, salt or acid ester, suitable for use in this invention, includes the reaction product of the polymer with a monounsaturated carboxylic reactant comprising at least one member selected from the group consisting of (i) monounsaturated C₄ to C₁₀ dicarboxylic acid (preferably wherein (a) the carboxyl groups are vicinyl, (i.e. located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said monounsaturation); (ii) derivatives of (i) such as anhydrides or C₁ to C₅ alcohol derived mono- or diesters of (i); (iii) monounsaturated C₃ to C₁₀ monocarboxylic acid wherein the carbon-carbon double bond is conjugated to the carboxyl group, i.e., of the structure —C=C—C(=O)— and (iv) derivatives of (iii) such as C₁ to C₅ alcohol derived monoesters of (iii). Upon reaction with the polymer, the double bond of the monounsaturated carboxylic reactant becomes saturated. Thus, for example, maleic anhydride reacted with the polymer becomes succinic anhydride, and acrylic acid becomes a propionic acid.

Suitable unsaturated acid materials which are useful functional compounds, include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, and the like. Particularly preferred are the unsaturated dicarboxylic acids and their derivatives, especially maleic acid, fumaric acid and maleic anhydride.

Normally, not all of the polymer reacts with the monounsaturated carboxylic reactant and the reaction mixture will contain unfunctionalized polymer. The mono- or dicarboxylic acid functionalized polymer, non-functionalized polymer, and any other polymeric by-products, e.g. chlorinated polyolefin (also included within "unfunctionalized" polymer), are collectively referred to as "product residue" or "product mixture". The unfunctionalized polymer is typically not removed from the reaction mixture (because such removal is difficult and would be commercially infeasible) and the product mixture, stripped of any monounsaturated carboxylic reactant, can be used in further derivatization reactions to make, for example, dispersant.

The functionality (F) of the polymer can be based upon (i) a determination of the saponification number (SAP) of the reaction mixture; i.e., mg of potassium hydroxide consumed in the neutralization of 1 g of product mixture, and (ii) the number average molecular weight of the polymer charged (M_n). For the case where maleic anhydride is the monounsaturated carboxylic reactant, $F = (\text{SAP} * M_n) / [112,200 - (\text{SAP} * 98)]$. Alternatively, functionality (F^*) for polymer functionalized

with maleic anhydride is determined by the following equation: $F^* = [(SAP/A.I.) * M_n] / [112,200 - (SAP/A.I.) * 98]$ wherein A.I., SAP and M_n are as described above.

The polymer of the present invention can be functionalized with the monounsaturated carboxylic reactant by a variety of methods. Such methods include halogen assisted functionalization, the "ene" reaction, and free radical grafting. For halogen assisted polymer functionalization, the polymer can be first halogenated, to 1 to 8 wt.% based on the weight of polymer, by passing the halogen (e.g., chlorine) through the polymer at a temperature of 60°C to 250°C for 0.5 to 10 hours. The halogenated polymer may then be reacted with sufficient monounsaturated carboxylic reactant at 100°C to 250°C for 0.5 to 10 hours so the product obtained will contain the desired number of moles of the monounsaturated carboxylic reactant per mole of the halogenated polymer. Processes of this general type are taught in US 3087436; 3172892; and 3272746. Alternatively, the polymer and the monounsaturated carboxylic reactant are mixed and heated while adding chlorine to the hot material. Processes of this type are disclosed in US 3215707; 3231587; 3912764; 4110349; 4234435 and UK 1440219.

The polymer and the aforescribed monounsaturated carboxylic reactant can be contacted at elevated temperature to cause a thermal "ene" reaction to take place. Thermal "ene" reactions are described in US 3361673 and 3401118. Functionalized polymer can be prepared using a thermal "ene" type reactor or by chlorination as disclosed in EP-A-0441548.

An ethylenically unsaturated carboxylic acid or derivative thereof may be grafted onto saturated or unsaturated polymer backbone in solution or in solid form using a radical initiator. The free radical-induced grafting of ethylenically unsaturated carboxylic acid materials is preferably done using a mechanical or thermal shearing technique. It is carried out at an elevated temperature in the range of 100°C to 250°C. Suitable unsaturated acids include those described above.

Free radical grafting is particularly suited for functionalizing intermediate molecular weight polymers in preparing multifunctional viscosity index improvers. This functionalization technique can also be employed to functionalize polymer intended to make dispersants, but the functionality typically will be limited, and/or derivatization and/or post-treatment controlled, to avoid gellation of the dispersant as described in commonly assigned US Applications 992516 and 991837, both filed December 17, 1992.

Hydroxy Aromatic Compounds

A further suitable functionalization technique involves the reaction of hydroxy aromatic functional compounds with the polymer. Hydroxy aromatic compounds useful in the preparation of the functionalized polymer of this invention include those compounds having the formula $H-Ar-(OH)_c$ wherein Ar represents aryl groups such as phenylene, biphenylene, naphthylene and the like, containing from 0 to 2 halogen substituents; c is 1 or 2.

The polymer, i.e. poly-n-butene, having at least one olefinic unsaturation and hydroxy aromatic compound are contacted in the presence of a catalytically effective amount of at least one acidic alkylation catalyst under conditions effective to alkylate the aromatic group of the hydroxy aromatic compound. The alkylation catalyst is conventional and can comprise inorganic acids such as H_3PO_4 , H_2SO_4 , HF, BF_3 , $HF-BF_3$ and the like or complexes of the foregoing with ethers, alcohols, ketones, phenols, and the like.

The hydroxy aromatic compound and polymer will be generally contacted in a ratio of from 0.1 to 10 moles of the aromatic compound per mole of the polymer. The selected acid catalyst can be employed in widely varying concentrations. Generally, when the acid catalyst comprises an inorganic catalyst, the acid catalyst will be charged to provide at least 0.001 moles of catalyst per mole of hydroxy aromatic compound charged to the alkylation reaction zone. The temperature for alkylation will usually range from 20°C to 250°C. The alkylation reaction time will generally be from 1 to 5 hours, although longer or shorter times can also be employed. The alkylation process can be batchwise, continuous or semicontinuous.

Koch Functionalized Polymer

Yet another method to functionalize the polymer of the present invention is by a Koch-type reaction as disclosed in commonly assigned US Application 992403, filed December 17, 1972. The polymer of the present invention having unsaturation, preferably terminal unsaturation, can be reacted via the Koch mechanism to be functionalized with an acid or an ester. The polymer is contacted with carbon monoxide or a suitable carbon monoxide source such as formic acid, in the presence of an acidic catalyst. The catalyst preferably has a Hammett Scale Value acidity (H_o) of less than -7 in order to be sufficiently active, particularly to form neo structures. Useful catalysts include H_2SO_4 , BF_3 , and HF. The catalyst is believed to cause a carbenium ion to form at the point of unsaturation. The carbon monoxide reacts with the carbenium ion forming an acylium ion. Water or a hydroxy-containing compound or a thiol containing compound can be added to react with the acylium cation to form

a carboxylic acid or a carboxylic ester/or a thiol ester. Preferably, the hydroxy-containing compound or water is added in combination with the catalyst as a catalyst complex. Preferred catalyst complexes include ($\text{BF}_3 \cdot \text{H}_2\text{O}$) and (BF_3 -substituted phenols) with a most preferred catalyst complex being $\text{BF}_3 \cdot 2,4$ dichlorophenol.

5 In accordance with the Koch process, carboxyl groups, including carboxylic acid or carboxylic esters, can be formed at moderate temperatures and pressures at the point of unsaturation of the polymer of the present invention. The polymer is heated to a desired temperature range which is typically between -20°C to 200°C and preferably from 0°C to 80°C . The pressure in the reactor can be maintained based
10 on the carbon monoxide source, with pressures ranging up to 34,500 kPa (5,000 psig) with a preferred range of from 3,450 to 20,700 kPa (500 to 3,000 psig).

Other Functionalizations

The polymers of the present invention can be functionalized by oxidation
15 including air oxidation, ozonolysis, and hydroperoxidation to form a polymer containing at least one oxygen containing functional group, such as carboxyl, oxycarboxyl (esterbond), formyl, carbonyl and hydroxyl groups. The oxidatively modified polymer of the present invention can be prepared by oxidizing the above recited polymers with a gas containing molecular oxygen and/or ozone, optionally in
20 an inert hydrocarbon medium (e.g., pentane, hexane, benzene, toluene, and the like). Oxidation is effected at a temperature in the range of from 100°C to 250°C and a time from 10 minutes to 20 hours at either atmospheric pressure or applied pressure and optionally in the presence of a radical initiator or an oxidative catalyst. Useful air oxidation processes are described in US 4925579 and US 4943658.

25 Useful methods of ozonolysis are disclosed in a US 4076738, EP-A-0389722, and WO90/09371. A method of hydroperoxidation is disclosed in US 4925579.

The polymer of the present invention can be functionalized by hydroformylation methods of the type disclosed in US 4832702; 4859210 and UK 1049291. Hydroformylation can be carried out using a conventional rhodium or cobalt catalyst
30 at from 80°C to 200°C under a CO/H_2 pressure of up to 60,000 kPa (600 bar). The oxygen-containing polymer resulting from the hydroformylation process are formed by addition of carbon monoxide and hydrogen to a double bond. Reactive double bonds are predominantly converted to aldehydes and ketones. Isomerization can cause a mixture of aldehydes to be obtained.

35 The polymers of the present invention can be functionalized by epoxidation as disclosed in US 4981605, JP H01-132605, PCT WO90/10022 and EP-A- 461744.

Other functionalized polymers include those suitable for use as intermediates in making ash-producing detergents as described hereinbelow including sulfurized alkylphenols, alkyl sulfonic acids, alkyl salicylates, alkyl naphthanates wherein the alkyl group is derived from the polymer of the present invention.

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Derivatized Polymers

A derivatized polymer is one which has been chemically modified to perform one or more functions in a significantly improved way relative to the unfunctionalized polymer and/or the functionalized polymer. The functionalized polymer can be
10 derivatized by reaction with at least one derivatizing compound to form derivatized polymers. The derivatizing compound typically contains at least one reactive derivatizing group, selected to react with the functional groups of the functionalized polymers by the various reactions described below. Representative of such reactions are nucleophilic substitution, Mannich Base condensation, transesterification, salt
15 formation, and the like. The derivatizing compound preferably also contains at least one additional group suitable for imparting the desired properties to the derivatized polymer, e.g., polar groups. Thus, such derivatizing compounds typically will contain one or more groups including amine, hydroxy, ester, amide, imide, thio, thioamido, oxazoline or salt groups derived from reactive metal or reactive metal compounds.

20 The derivatized polymers include the reaction product of the above recited functionalized polymer with a nucleophilic reactant which include amines, alcohols, amino-alcohols and mixtures thereof to form oil soluble salts, amides, imides, oxazoline, reactive metal compounds and esters of mono- and dicarboxylic acids, esters or anhydrides.

25 Suitable properties sought to be imparted to the derivatized polymer include one or more of dispersancy, multifunctional viscosity modification, antioxidancy, friction modification, antiwear, antirust, seal swell, and the like. The preferred properties sought to be imparted include dispersancy and multifunctional viscosity modification. It is contemplated that a multifunctional viscosity improver (MFVI)
30 derived from functionalized polymer will typically have at least one functional group for each 7,000, preferably for each 5,000, M_n molecular weight segment in the backbone polymer. Thus, a functionalized polymer having M_n of 30,000 will typically have a functionality (F^*) of 6.

35 Dispersants

Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid thus preventing sludge flocculation and precipitation. Suitable

dispersants include, for example, dispersants of the ash-producing (also known as detergents) and of the ashless type, the latter type being preferred.

The ash-producing detergents which can be made using the functionalized polymers of the present invention are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with alkyl phenols, alkyl sulfonic acids, carboxylic acids, or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage such as those prepared from the functionalized olefin polymer of the present invention with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus trichloride and sulfur, or the like.

10 The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium. The alkyl groups of the above acids or compounds constitute the polymer of the present invention. The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the derivatized polymer.

15 Preferred ash-producing detergents which can be derived from the functionalized polymers of the present invention include the metal salts of alkyl sulfonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates, alkyl naphthenates and other oil soluble mono- and dicarboxylic acids. Highly basic (viz, overbased) metal salts, such as highly basic alkaline earth metal alkyl sulfonates (especially Ca and Mg salts) are frequently used as detergents.

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The alkaline earth metal compounds which may be used in neutralizing these acids to provide the compounding metal salts include the oxides and hydroxides, alkoxides, carbonates, carboxylate, sulfide, hydrosulfide, nitrate, borates and ethers of magnesium, calcium, and barium.

25 Various types of ashless dispersants suitable for use in the lubricant compositions can be made by derivatizing the polymer of the present invention. The following are illustrative:

1. Reaction products of functionalized polymer of the present invention derivatized with nucleophilic reagents such as amine compounds, e.g. nitrogen-containing compounds, organic hydroxy compounds such as phenols and alcohols, and/or basic inorganic materials. More specifically, nitrogen- or ester-containing ashless dispersants comprise members selected from the group consisting of oil-soluble salts, amides, imides, oxazolines and esters, or mixtures thereof, of the polymer of the present invention, functionalized with mono- and dicarboxylic acids or anhydride or ester derivatives thereof, said polymer having dispersant range molecular weights as defined hereinabove. One class of particularly preferred dispersants includes those derived from the polymer of the present invention

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functionalized mono- or dicarboxylic acid material, e.g. succinic anhydride, and reacted with (i) a hydroxy compound, e.g. pentaerythritol, (ii) a polyoxyalkylene polyamine, e.g. polyoxypropylene diamine, and/or (iii) a polyalkylene polyamine, e.g., polyethylene diamine or tetraethylene pentamine. Another preferred dispersant class
5 includes those derived from functionalized polymer reacted with (i) a polyalkylene polyamine, e.g. tetraethylene pentamine and/or (ii) a polyhydric alcohol or polyhydroxy-substituted aliphatic primary amine, e.g., pentaerythritol or trismethylolaminomethane.

2. Reaction products of the polymer of the present invention functionalized
10 with an aromatic hydroxy group and derivatized with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines), through the Mannich reaction, which may be characterized as "Mannich dispersants".

3. Reaction products of the polymer of the present invention functionalized by reaction with halogen and then derivatized by reaction with amines (e.g. direct
15 amination), preferably polyalkylene polyamines. These may be characterized as "amine dispersants", examples of which are described in US 3275554; 3438757; 3454555; 3565804; 3755433; 3822209 and 5084197.

Derivatized Polymer From Amine Compounds

20 Useful amine compounds for derivatizing functionalized polymers comprise at least one amine and can comprise one or more additional amines or other reactive or polar groups. Where the functional group is a carboxylic acid, ester or derivative thereof, it reacts with the amine to form an amide. Where the functional group is an epoxy it reacts with the amine to form an amino alcohol. Where the functional group
25 is a halide the amine reacts to displace the halide. Where the functional group is a carbonyl group it reacts with the amine to form an imine.

Preferred amines are aliphatic saturated amines. Non-limiting examples of suitable amine compounds include 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene
30 triamine; triethylene tetramine; tetraethylene pentamine; etc.

Other useful amine compounds include alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane; heterocyclic nitrogen compounds such as imidazolines; commercial mixtures of amine compounds, e.g., poly(ethyleneamine), compounds averaging 5 to 7 nitrogen atoms per molecule available under trade
35 names such as "Polyamine H", "Polyamine 400", etc.; polyoxyalkylene polyamines; and the polyamido and related amines disclosed in US 4857217, 4963275, and 4956107.

Derivatization Polymer From Alcohols

The functionalized polymers, particularly acid functionalized polymers, of the present invention can be reacted with alcohols, e.g. to form esters. The alcohols may
5 be aliphatic compounds such as monohydric and polyhydric alcohols or aromatic compounds such as phenol, beta-naphthol, alpha-naphthol, cresol, resorcinol, catechol, etc.

The alcohols from which the esters may be derived preferably contain up to 40 aliphatic carbon atoms. They may be monohydric alcohols such as methanols,
10 ethanol, isooctanol, etc. The polyhydric alcohols preferably contain from 2 to 10 hydroxy radicals, such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, etc. The esters may also be derived from unsaturated alcohols such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexene-3-ol, an oleyl alcohol. Still another class of useful alcohols comprise the ether-alcohols and
15 amino-alcohols.

The functionalized polymer of this invention are reacted with the alcohols according to conventional esterification techniques. This normally involves heating the functionalized polymer with the alcohol, optionally in the presence of a normally liquid, substantially inert, organic liquid solvent/diluent and/or in the presence of
20 esterification catalyst.

Derivatized Polymer From Mannich Base Condensation

The hydroxy aromatic functionalized polymer aldehyde/amino condensates useful as ashless dispersants in the compositions of this invention include those
25 generally referred to as Mannich condensates. Generally they are made by reacting simultaneously or sequentially at least one active hydrogen compound such as a hydrocarbon-substituted phenol (e.g., hydroxy aromatic functionalized polymer of the present invention), having at least one hydrogen atom bonded to an aromatic carbon, with at least one aldehyde or aldehyde-producing material (typically formaldehyde precursor) and at least one amino or polyamino compound having at least one NH
30 group. Preferred phenolic compounds include the hydroxy aromatic functionalized polymer recited above. Useful amine compounds can be selected from those recited above. The aldehyde reactants will generally comprise formaldehyde or paraformaldehyde, although other aldehyde group-containing compounds, such as butyraldehyde, acetaldehyde, propionaldehyde, and the like can be employed.
35

The Mannich Base condensate dispersants are prepared by condensing at least one of the above-described hydroxy/aromatic functionalized polymers with an

amine, which can include amines as described, in the presence of an aldehyde. The reactants are contacted for a time and under conditions sufficient to form the desired dispersant product. The process employed in the condensation reaction can be any of those disclosed in US 3634515; 3649229; 3442808; 3798165; 3798247 and
5 3539633.

A useful group of Mannich Base ashless dispersants are those formed by condensing phenol functionalized polymer with formaldehyde and polyethylene amines, e.g., tetraethylene pentamine, pentaethylene hexamine, polyoxyethylene and polyoxypropylene amines, e.g., polyoxypropylene diamine and combinations thereof.

Derivatized Polymer From Reactive Metals/Metal Compounds

Useful reactive metals or reactive metal compounds are those which will form metal salts or metal-containing complexes with the functionalized polymer. Metal complexes are typically achieved by reacting the functionalized polymers with amines
15 and/or alcohols as discussed above and also with complex forming reactants either during or subsequent to amination. Complex-forming metal reactants include the nitrates, nitrites, halides, carboxylates, etc.

Post Treatment

Another aspect of this invention involves the post treatment of derivatized polymer. The processes for post-treating derivatized polymer are analogous to the post-treating processes used with respect to conventional dispersants and MFVI's of the prior art. Accordingly, the same reaction conditions, ratio of reactants and the like can be used. For example, the amine derivatized polymers can be treated with a
25 boron compound selected from the class consisting of boron oxide, boron halides, boron acids and esters of boron acids in an amount to provide from 0.1 atomic proportion of boron for each mole of said nitrogen composition to 20 atomic proportions of boron for each atomic proportion of nitrogen of said nitrogen composition. Borated derivatized polymer useful as dispersants can contain from
30 0.05 to 2.0 wt.%, e.g. 0.05 to 0.7 wt.% boron based on the total weight of said borated nitrogen-containing dispersant compound.

Treating is readily carried out by adding from 0.05 to 4, e.g. 1 to 3 wt.% (based on the weight of the said derivatized polymer) of the boron compound, preferably boric acid, which is usually added as a slurry to the nitrogen compound and heating
35 with stirring at from 135°C to 190°C, e.g. 140°C to 170°C, for from 1 to 5 hours followed by nitrogen stripping at said temperature ranges.

Lubricating Compositions

The polymer per se has a variety of utilities depending on its molecular weight including synthetic base oil (for lower molecular weights), adhesive coatings for intermediate molecular weights, and as elastomeric compositions for high molecular weights, e.g. films, composites, and the like. The functionalized polymer, in addition to acting as intermediates for dispersant and MFVI manufacture, can be used as molding release agents, molding agents, metal working lubricants, point thickeners and the like. The primary utility for all the above-described material, from polymer all the way through post-treated derivatized polymer, is as an additive for oleaginous compositions. These materials are collectively and individually referred to herein as additives. The additives of the present invention may be used by incorporation and dissolution into an oleaginous material such as fuels and lubricating oils. When the additives of this invention are used in normally liquid petroleum fuels such as middle distillates boiling from 65°C to 430°C, including kerosene, diesel fuels, home heating fuel oil, jet fuels, etc., a concentration of the additives in the fuel in the range of typically from 0.001 to 0.5, and preferably 0.005 to 0.15 wt.%, based on the total weight of the composition, will usually be employed.

The additives of the present invention, particularly those adapted for use as dispersants or viscosity modifiers, can be incorporated into a lubricating oil in any convenient way. Thus, they can be added directly to the oil by dispersing or dissolving the same in the oil at the desired level of concentrations of the additive. Such blending into the additional lube oil can occur at room temperature or elevated temperatures. Alternatively, the additives can be blended with a suitable oil-soluble solvent and base oil to form a concentrate, and then blending the concentrate with a lubricating oil basestock to obtain the final formulation. Such dispersant concentrates will typically contain (on an A.I. basis) from 10 to 80 wt.%, typically 20 to 60 wt.%, and preferably from 40 to 50 wt.%, additive, and typically from 40 to 80 wt.%, preferably from 40 to 60 wt.%, base oil, i.e., hydrocarbon oil based on the concentrate weight.

The additives of the present invention will be generally used in admixture with a lube oil basestock, comprising an oil of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. Natural oils include animal oils and vegetable oils, liquid petroleum oils and hydrotreated, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Synthetic lubricating oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized olefins (e.g., polybutylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, etc.); alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have

been modified by esterification, etherification, etc.; esters of dicarboxylic acids (e.g., di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, etc.); esters made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers; and silicon-based oils.

5 The additives of the present invention may be mixed with other types of conventional additives, each selected to perform at least one desired function. Among the other additives which may be in the lubricating oil formulation are metal containing detergent/inhibitors, viscosity index improvers, and anti-wear agents. The metal detergent/inhibitors are generally basic (viz, overbased) alkali or alkaline earth metal salts (or mixtures thereof, e.g., Ca and Mg salts) of one or more organic acids
10 (e.g., sulfonic acids, petroleum naphthenic acids, alkyl phenols, and the like). Viscosity index improvers are generally hydrocarbon polymers or polyesters, optionally derivatized to impart dispersancy or some other property, having number average molecular weights of from 10³ to 10⁶. The antiwear agents are typically oil-soluble zinc dihydrocarbyl dithiophosphates.

15 Compositions, when containing one or more of these additives, typically are blended into the base oil in amounts which are effective to provide their normal attendant function. In such compositions, the additives of the present invention are generally employed (e.g., as a dispersant additive) in an amount of 0.1 to 20 wt.%, preferably 0.1 to 6 wt.%, based upon the total weight of the composition.

20 The invention is described in more detail, though only by way of illustration, in the following examples.

EXAMPLES 1 - 7

In a series of runs, liquefied anhydrous feedstream composed of isobutene, 1-
25 butene, 2-butene, n-butane and isobutane were mixed for pre-reaction with the selected amount of gaseous anhydrous HBr. Referring to Figure 2, the reaction was conducted in a laboratory reactor 60 having cooling coils 62, pressure regulator 64, and stirrer 66. Aluminum bromide solution was prepared immediately before each example and placed in catalyst reservoir 68. Cocatalyst HBr was added through
30 cocatalyst line 70. N-butane was added from n-butane reservoir 72. C₄ feed was added from C₄ reservoir 74. There were heptane wash reservoirs 76 and 78 and also nitrogen lines 80 and 82 to maintain the reaction under a blanket of nitrogen. The resulting product was fed to product tank 84.

The apparatus was used to polymerize 1-butene in Example 1, using the
35 compositions and conditions summarized in Table I below. C₄= represents the C₄ feed having an unsaturated double bond (i.e. 1-butene in Example 1). Figure 3 is a

gel permeation chromatography plot of concentration vs. minutes. Molecular weight peaks were observed at 16,860 and 15,000,000.

EXAMPLES 2-6

- 5 Examples 2 through 6 were conducted according to the same procedure as Example 1 with reaction temperatures of -30°C in Example 2, -15°C in Example 3, -10°C in Example 4, -5°C in Example 5 and 0°C in Example 6. Figures 4A, 4B, 4C, 4D, and 4E are gel permeation chromatography plots. Based on Figures 4A to 4E, it was determined that at -30°C the molecular weight ranged up to 1,000,000. As the
10 temperature increased, the molecular weight decreased. At -30°C there was a molecular weight concentration peak at 280,000 while at 0°C the high molecular weight peak was at 79,000.

EXAMPLE 7

- 15 Using a reactor as shown in Figure 2, a simulated Raffinate II feedstream was added to reactor from C₄ reservoir 74. Cocatalyst HBr gas was added through cocatalyst line 70 to premix with feedstream through a series of gas-liquid mixers before adding to reactor. The simulated Raffinate II composition comprised (in wt.%) 16.12 isobutane; 50.49 n-butane; 7.59 trans-2-butene; 20.66 1-butene; 1.05
20 isobutylene; and 4.08 cis-2-butene. The polymerization conditions listed in Table I were used. The resulting PNB polymer mol. wt. was measured by GPC with peak mol. wt. 5,992, M_n of 2,899, and weight average molecular weight 7,134 as shown in Figure 5.

EXAMPLE 8

- 25 Example 8 was conducted in a pilot plant reactor, a schematic diagram of which is shown in Figure 6. The reactor system included a continuous feed stirred tank reactor 100. A simulated Raffinate II feedstream as described in Example 7 was fed through line 102 to the continuous stirred reactor 100. A catalyst solution was fed
30 to the reactor through catalyst feedline 104.

- The Raffinate II feedstream was mixed with a cocatalyst HBr gas fed through cocatalyst line 106. The reactor had a suitable stirring means 108. The reactor was a sealed reactor which had means to provide an inert atmosphere such as nitrogen as well as a means to control the temperature of the incoming fluids and the
35 temperature in the reactor. The reactants were fed at or near the bottom of the reactor with product removed at reactor outlet 110 and reactor outlet 112. The pressure was 600 Kpa. The reactor was run continuously with variations in

temperature T°C), monomer (M) to catalyst (CAT) molar ratio, monomer to catalyst molar ratio, cocatalyst (COCAT) to catalyst molar ratio with reaction time (min) peak molecular weight(s) of product, and percent monomer conversion measured. Results are summarized in Table II for runs 1 through 21. The results of run 9 are shown in
5 Figure 8, with molecular weights at various peaks indicated. The results for runs 3 and 6 are shown in Figures 9 and 10 respectively.

EXAMPLES 9-11

Examples 9 through 11 were conducted according to the similar procedure as
10 Example 8. Poly-n-butene was prepared with the reactor at 0°C in Example 9, -15°C in Example 10, and -30°C in Example 11. Results of gel permeation chromatography are shown on Figures 7A to 7C. At lower temperatures the molecular weight increased.

A correlation analysis was conducted based on the results in Table II with the
15 analysis results summarized in Figure 11. The analysis used a preferred cocatalyst to catalyst mole ratio of 1.5. The molecular weight of the polymers was estimated from the equation: Molecular Weight = 30918 - 227.6 (Temperature) - 137.1 (M/CAT) with R-square = 0.76. The temperature is the reactor temperature (RC), and M/CAT is the mole ratio of monomer to catalyst.

20

Table I

Semi Batch Reactor	<u>Example 1</u>	<u>Example 7</u>
Volume of Feed, ml ¹	120.0	120.0
Wt% C ₄ =	20.5	33.5
Moles C ₄ =	0.264	0.423
C ₄ = delivery time, min	60	60
C ₄ = flow rate, ml/min	2.00	2.00
Mole ratio per minute C ₄ =/AlBr ₃ /min	0.83	0.83
Mole ratio n-butane/C ₄ =	6.63	3.71
Conc AlBr ₃ , g/ml in n-butane ²	0.0500	0.0500
AlBr ₃ /C ₄ = ratio	0.020	0.020
Vol AlBr ₃ , ml	28.1	45.1
AlBr ₃ delivery time, min	5	5
AlBr ₃ rate, ml/min	5.62	9.02
HBr/C ₄ = ratio	0.0080	0.0080
HBr delivery time, min	10	10
HBr rate, g/min	0.01706	0.02737
Initial n-butane charge, ml	50	50
total reactor charge, ml	198	215
Reactor temp, °C	-30	-30

- 1 - Example 1: The feed was 1-butene and n-butane. The feed was prepared by mixing 102.5 g 1-butene with 397.5 g n-butane.
 Example 2: The feed was 50% dil Raff-2. About 300 g of dilute feed was prepared by mixing equivalents of simulated Raff-2 and n-butane.
- 2 - 38 g AlBr₃ was dissolved in 440 g n-butane.

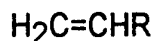
Table II

PNB CONTINUOUS RUNS SUMMARYCFST REACTOR, CAT=AIBR₃, COCAT=HBR

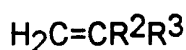
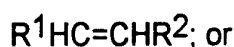
<u>RUN</u>	<u>TEMP</u>	<u>M/CAT MOLE RATIO</u>	<u>M/COCAT MOLE RATIO</u>	<u>COCAT/CAT MOLE RATIO</u>	<u>TIME</u>	<u>GPC PEAK MW</u>	<u>%CONV</u>
1	-10.6	175	100.2	1.75	22.9	1634	99.2
2	7.8	50.0	185.0	0.27	44.2	2315	100.0
3	-6.1	116.2	125.0	0.93	34.7	3533	100.0
4	-23.2	202.3	185.0	1.09	55.1	2271	99.9
5	7.5	197.0	100.0	1.97	55.0	1635	99.3
6	10.1	54.6	33.3	1.64	23.1	47000 21000 1300	99.9
7	7.5	184.6	443.6	0.42	22.3	1578	97.5
8	-20.5	53.0	500.0	0.11	22.6	2119	100.0
9	-15.5	60.2	33.3	1.80	44.2	60000 0 72000 37000 2000	100.0
10	-16.0	50.0	50.0	1.00	40.8	65000 25000 2000	100.0
11	-4.7	50.0	50.0	1.00	40.8	76000 24000 1200	100.0
12	-3.0	120.6	140.6	0.86	25.9	3045	100.0
13	-1.0	150.0	150.0	1.00	27.1	1632	97.5
14	-20.0	217.0	75.0	2.89	27.6	2004	97.5
15	-1.2	217.0	75.0	2.89	27.6	1716	98.3
16	-10.7	92.0	67.0	1.37	29.7	4528	99.9
17	-10.5	45.0	20.0	2.25	31.6		99.1
18	-20.5	44.0	50.0	0.88	31.4		100.0
19	-1.0	39.0	50.0	0.79	30.9	64000	99.9
20	-1.0	39.0	20.0	1.96	30.9		100.0
21	-15.0	134.0	189.0	0.71	27.0	2447	99.9

CLAIMS:

1. A polymer composition comprising amorphous copolymer derived from at least one monomer having the formula:



wherein R is a hydrocarbon having from 2 to 22 carbon atoms, and at least one comonomer of the formula:



wherein R^1 , R^2 and R^3 are the same or different hydrocarbon groups or substituted hydrocarbon groups having from 1 to 22 carbon atoms, the copolymer comprising at least 50 mole % of repeating units derived from $\text{H}_2\text{C}=\text{CHR}$, and up to 5 mole % of the repeating units derived from $\text{H}_2\text{C}=\text{CR}^2\text{R}^3$, being at least 95% amorphous and having a number average molecular weight of greater than 1,300.

2. The polymer composition as claimed in claim 1 wherein the monomer is 1-butene, and the comonomer comprises at least one monomer selected from the group consisting of cis-2-butene, trans-2-butene, and isobutylene.

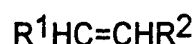
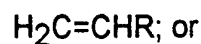
3. The polymer composition as claimed in claim 1 or claim 2, the amorphous copolymer having a number average molecular weight of 1,300 to 20,000.

4. The polymer composition as claimed in any of claims 1 to 3, in which the amorphous copolymer is functionalized with at least one functional group selected from the group consisting of an alkyl phenol, a substituted alkyl phenol, C_3 to C_{10} monocarboxylic acid, C_1 to C_5 alcohol derived mono- or diester, derivatives of said C_3 to C_{10} monocarboxylic acid, C_4 to C_{10} dicarboxylic acid, anhydride or C_1 to C_5 alcohol derived mono- or diester derivatives of said C_4 to C_{10} dicarboxylic acid, oxycarboxyl, carbonyl, formylcarbonyl, epoxy and hydroxyl groups.

5. The polymer composition as claimed in claim 4, in which the functionalized copolymer is further reacted with a derivatizing compound containing

at least one reactive derivatizing group selected to react with the functional group of the functionalized copolymer.

6. A cationically polymerized polymer composition derived from at least one monomer of the formula:



wherein R is a hydrocarbon having from 2 to 22 carbon atoms and R¹ and R² are the same or different hydrocarbon groups or substituted hydrocarbon groups having from 1 to 22 carbon atoms, the polymer comprising at least 50 mole % of repeating units derived from H₂C=CHR, being at least 95% amorphous and having a number average molecular weight of from 1,200,000 to 15,000,000.

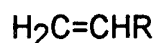
7. A lubricating oil concentrate containing from 10 to 80 wt. % of the polymer composition as claimed in any of claims 1-6.

8. A lubricating oil composition containing from 0.1 to 20 wt. % of the polymer composition as claimed in any of claims 1-6.

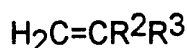
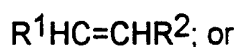
9. A process for preparing the polymer composition of claim 1, which process comprises the steps of:

(1) forming a catalyst solution of an acid catalyst having a Hammett Acidity Scale Value of less than -10 in a non-reactive aprotic solvent; and

(2) polymerizing at least one monomer having the formula:



and at least one comonomer of the formula:

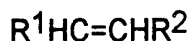
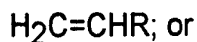


in the presence of the catalyst to form the amorphous copolymer of the composition of claim 1.

10. A process for preparing polymer compositions of claim 6, which process comprises:

forming a catalyst solution of an acid catalyst having a Hammett Acidity Scale Value of less than -10 in a non-reactive aprotic solvent; and

combining the catalyst solution with at least one monomer of the formula:



and polymerizing the monomer in the presence of the acid catalyst to form the polymer composition of claim 6 in which the polymer has from 0.5 to 1.0 carbon-carbon double bond per polymer chain.

11. The process as recited in claim 9 or 10 wherein the monomer of the formula $\text{H}_2\text{C}=\text{CHR}$ is 1-butene; the monomer of the formula $\text{H}_2\text{C}=\text{CR}^2\text{R}^3$ is isobutylene; and the monomer of the formula $\text{R}^1\text{HC}=\text{CHR}^2$ is 2-butene.

12. The process as recited in any of claims 9-11 further comprising:

the step of forming a catalyst solution of the catalyst in a saturated hydrocarbon solvent immediately prior to use in the process so as to minimize undesirable side reactions of the solvent; or

the step of controlling the concentration of at least one monomer relative to the catalyst to minimize the competing reactions of isomerization, cracking and/or dimerization of the monomer; or

the step of controlling the concentration of catalyst relative to the monomer to from 0.05 to 1.5 wt. % of catalyst based on the weight of the monomer feed; or

the step of premixing hydrogen halide as a reaction cocatalyst with the monomer composition to form an alkyl halide in situ; or

the step of maintaining the polymerization temperature at from -50°C to +20°C; or

the step of maintaining the polymerization pressure at from 345 to 1035 kPa (50 to 150 psig); or

the step of functionalizing the polymer; or

the steps of functionalizing the polymer; and then derivatizing the functionalized polymer.

FIG. 1

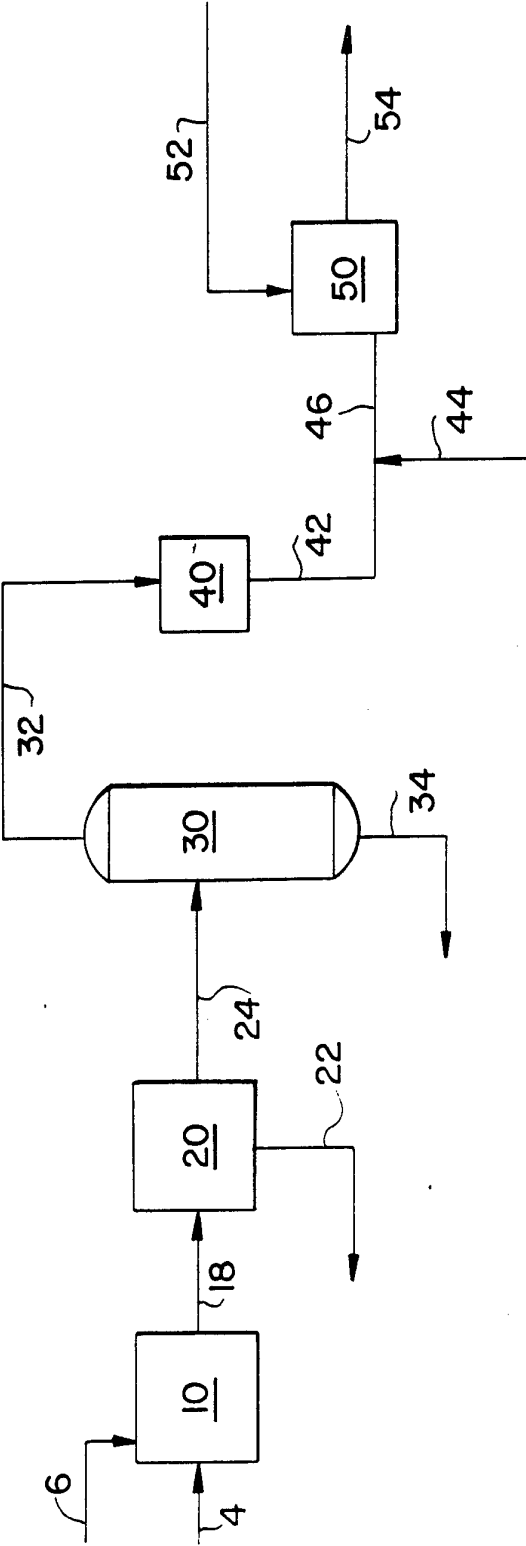


FIG. 2

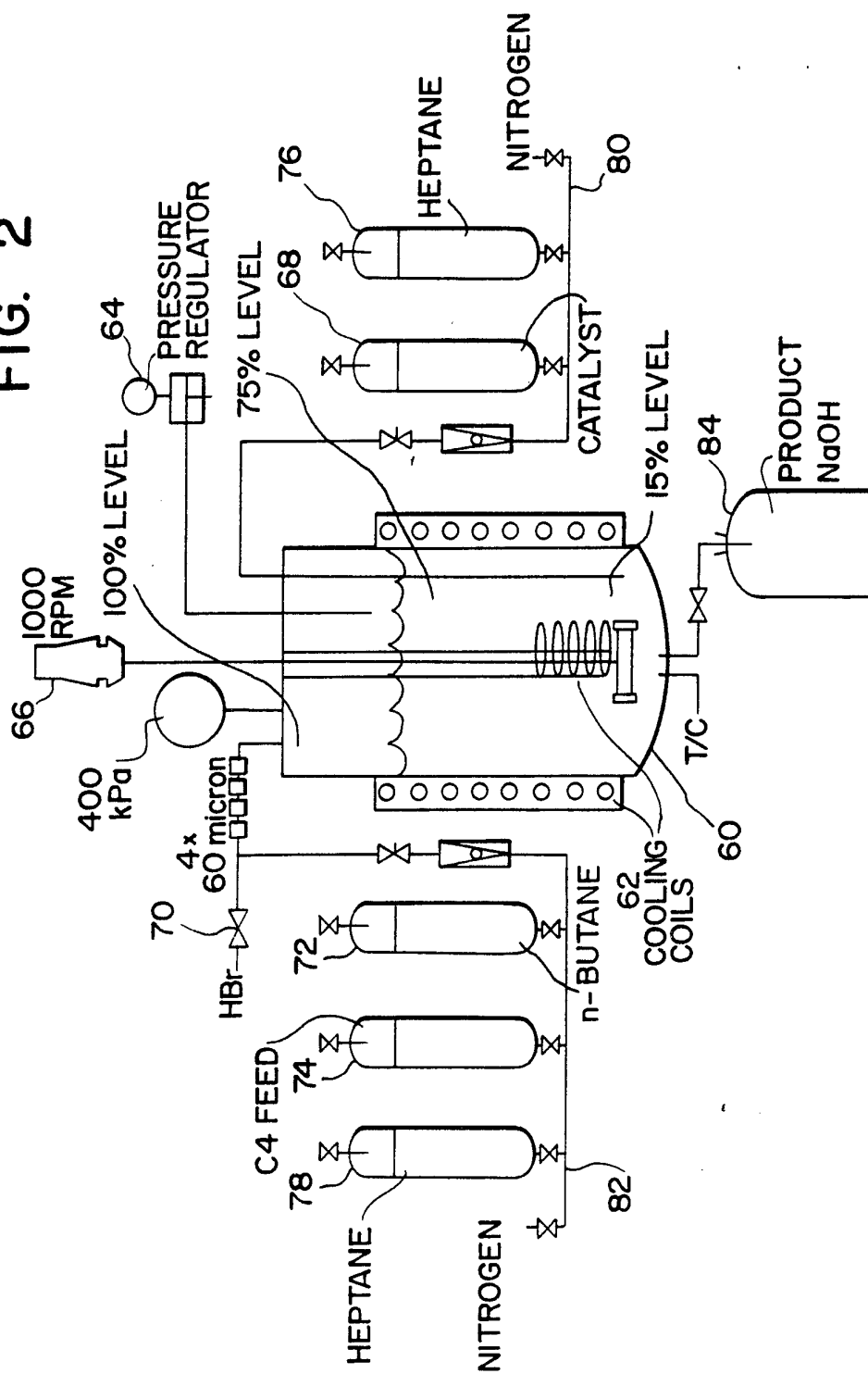
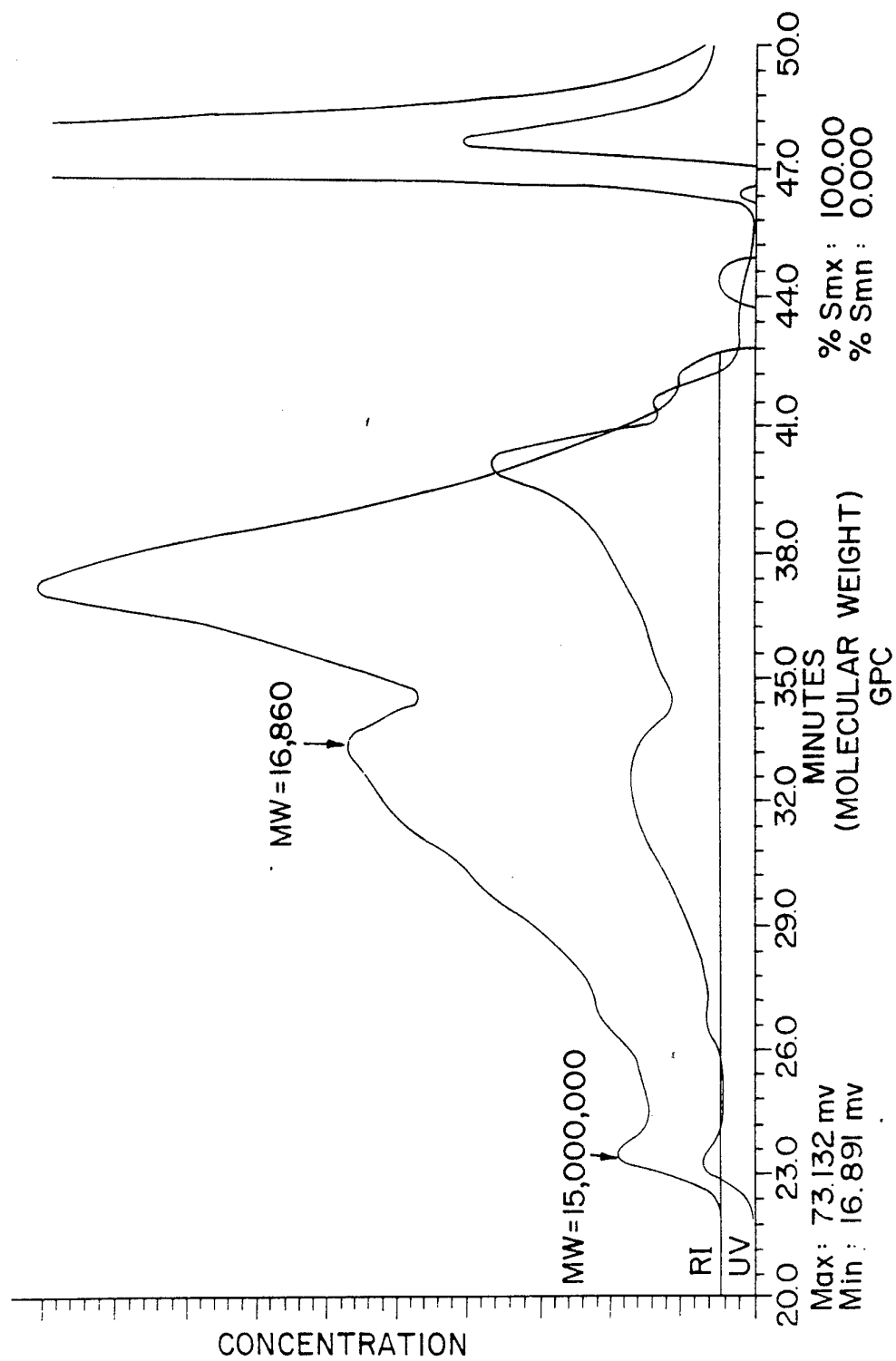
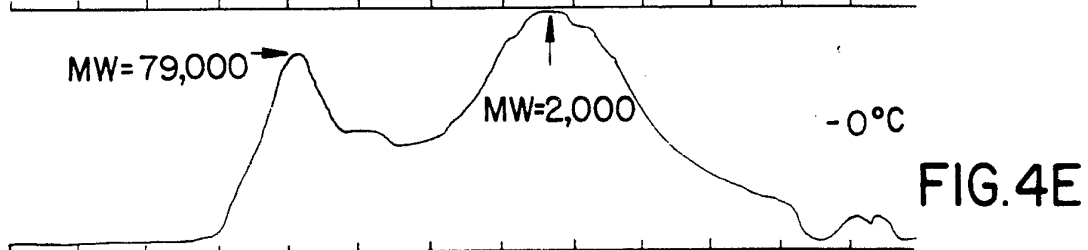
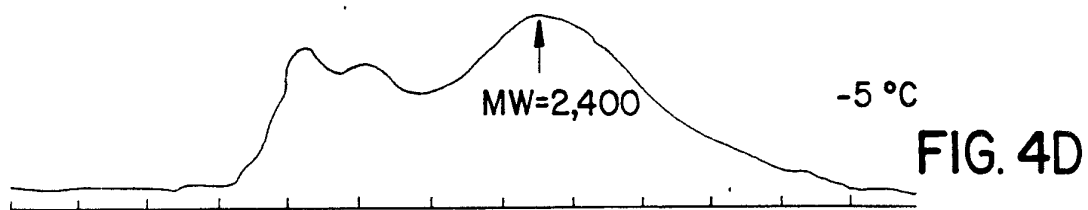
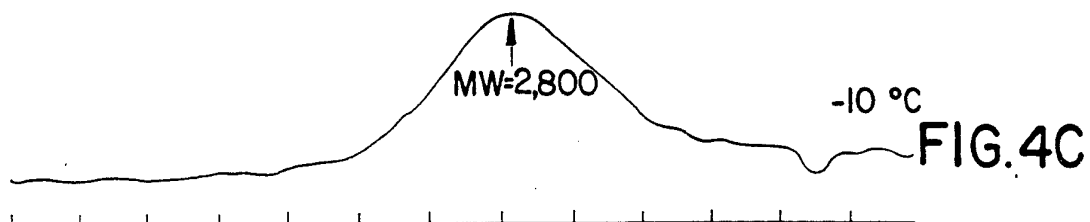
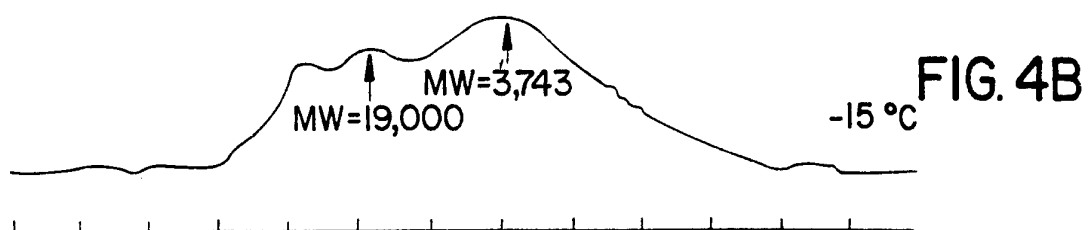
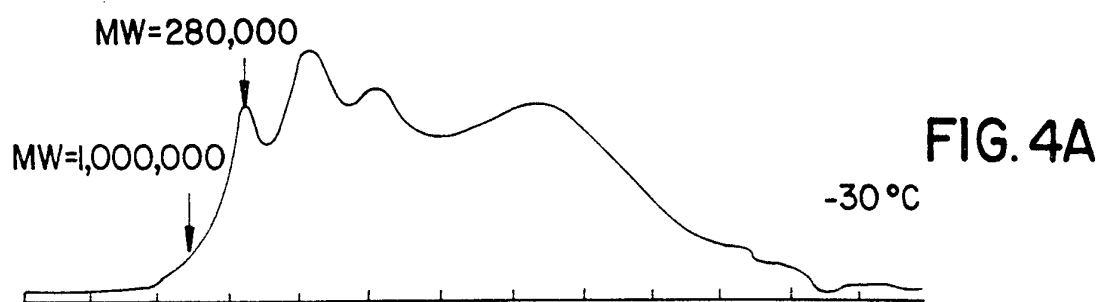


FIG. 3

SEMI-BATCH REACTOR PRODUCES VERY HIGH MW H-PNB
AT -30 C, MW > 15 MILLIONS





5 / 11

FIG. 5

H-PNB PREPARED FROM SIMULATED RAFF -2 FEED

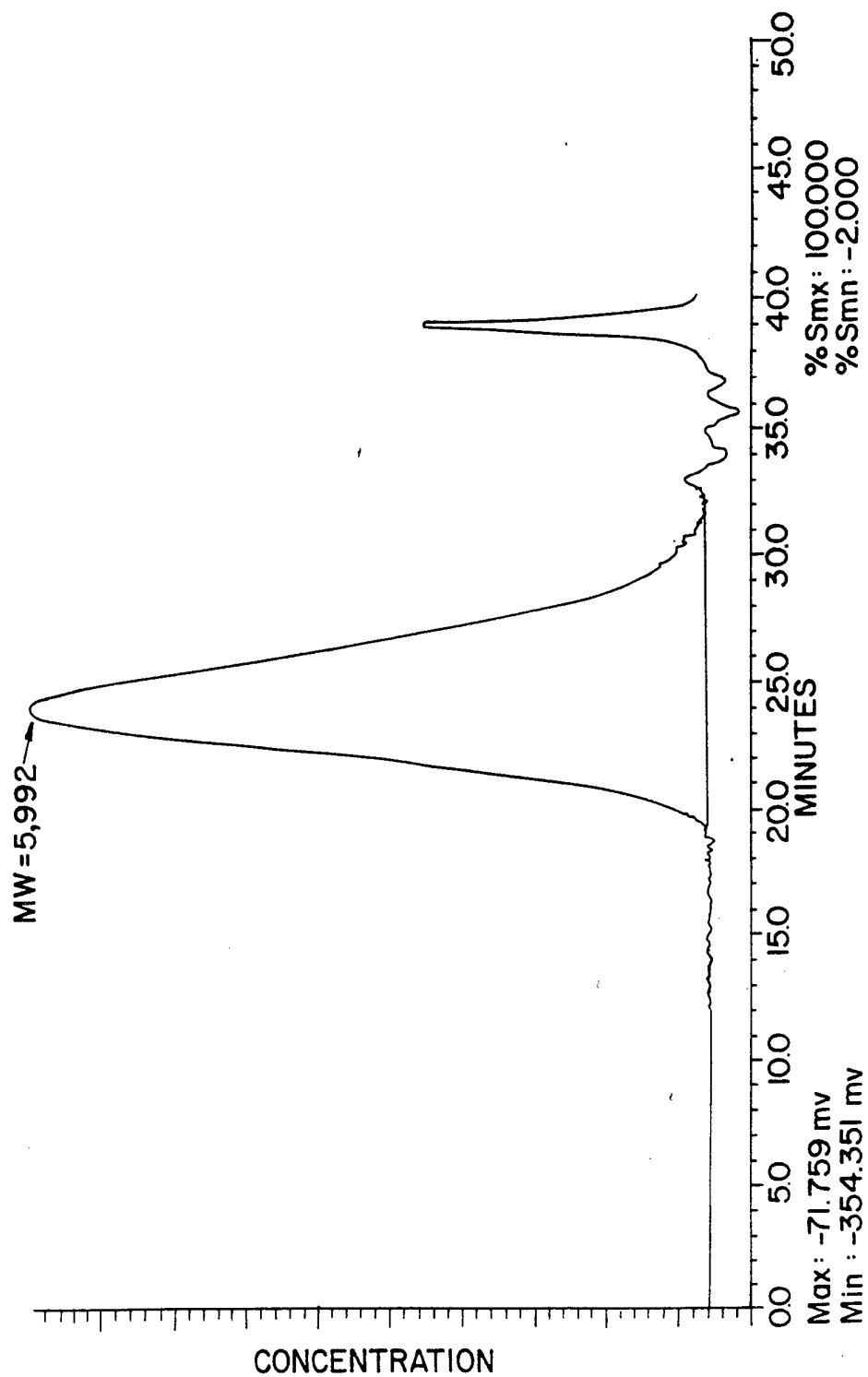


FIG. 6

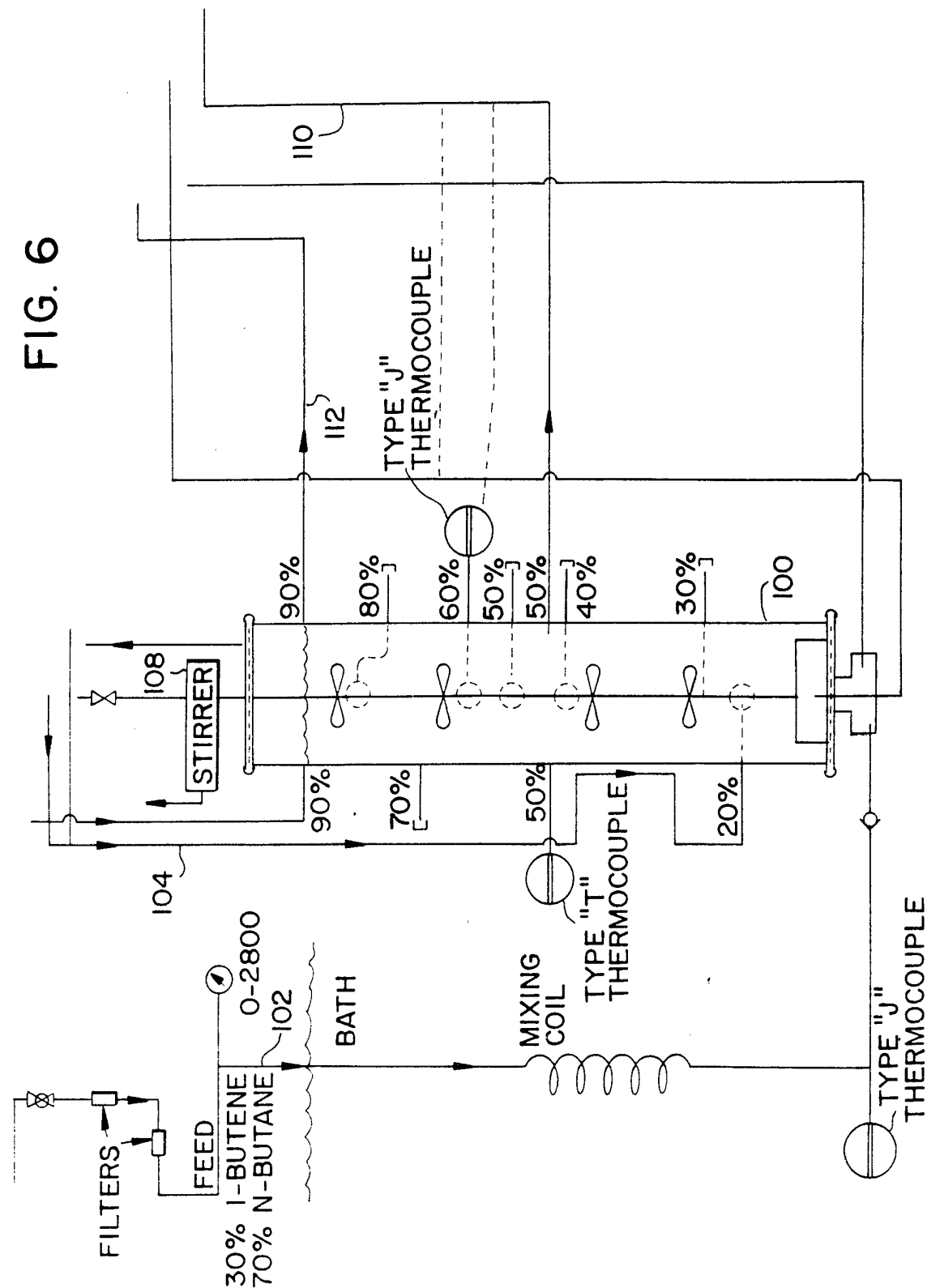


FIG. 7A

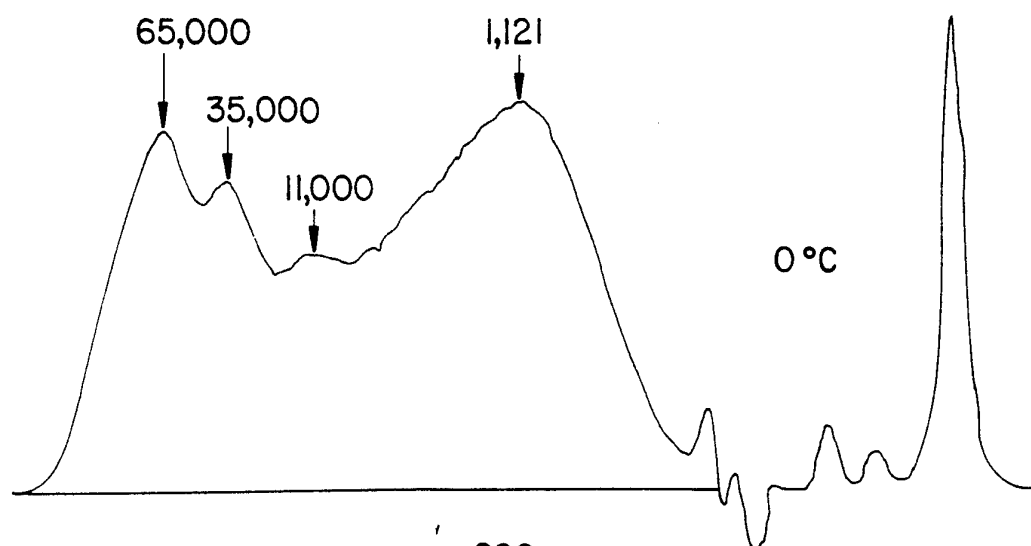


FIG. 7B

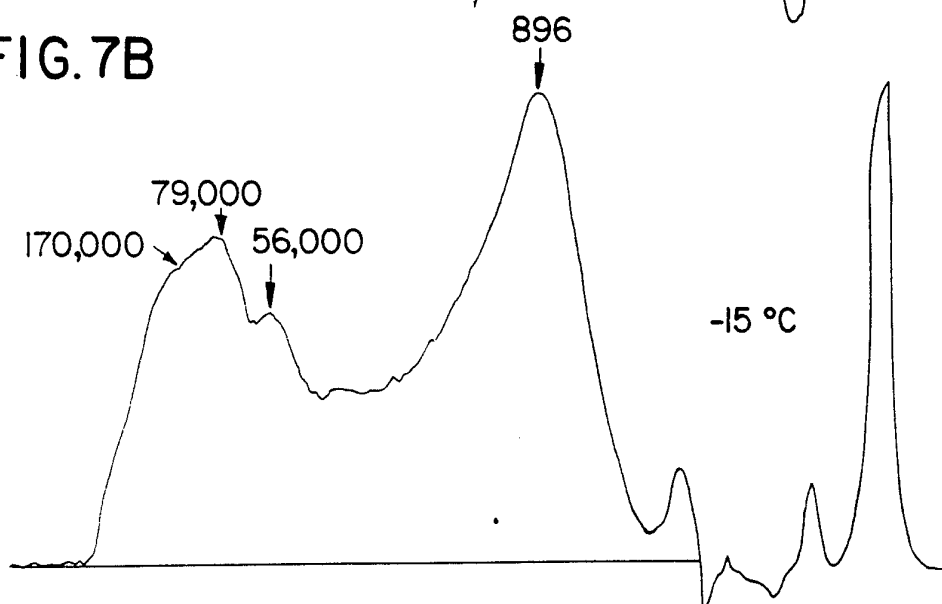


FIG. 7C

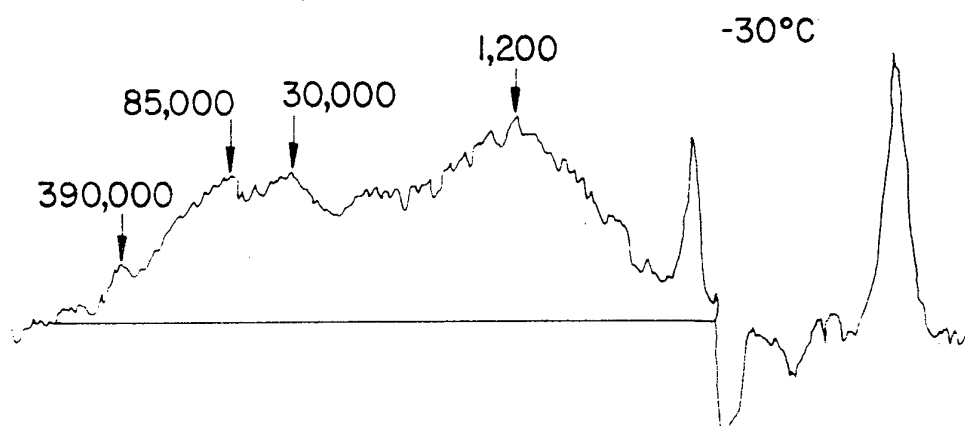


FIG. 8

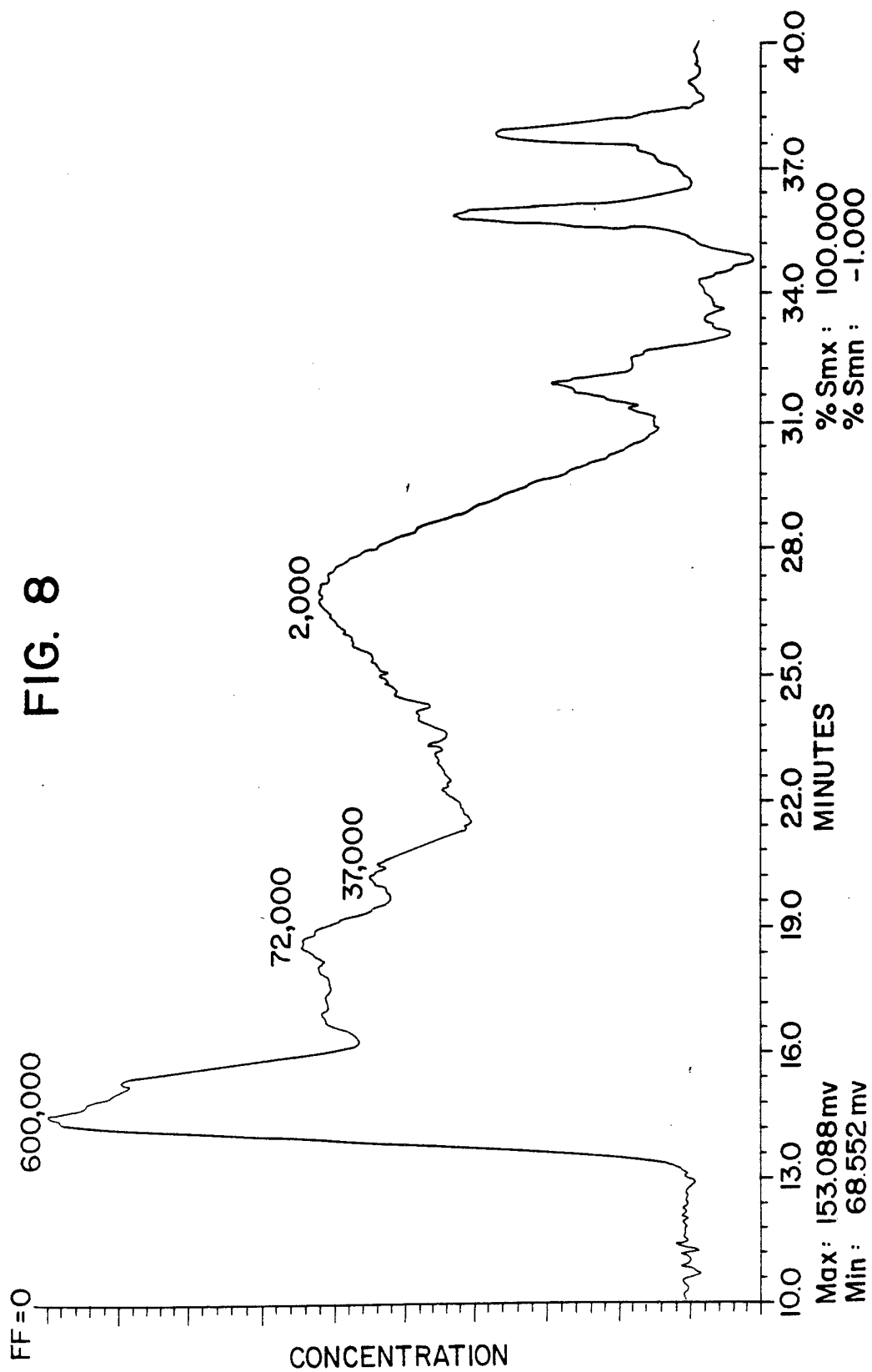


FIG. 9

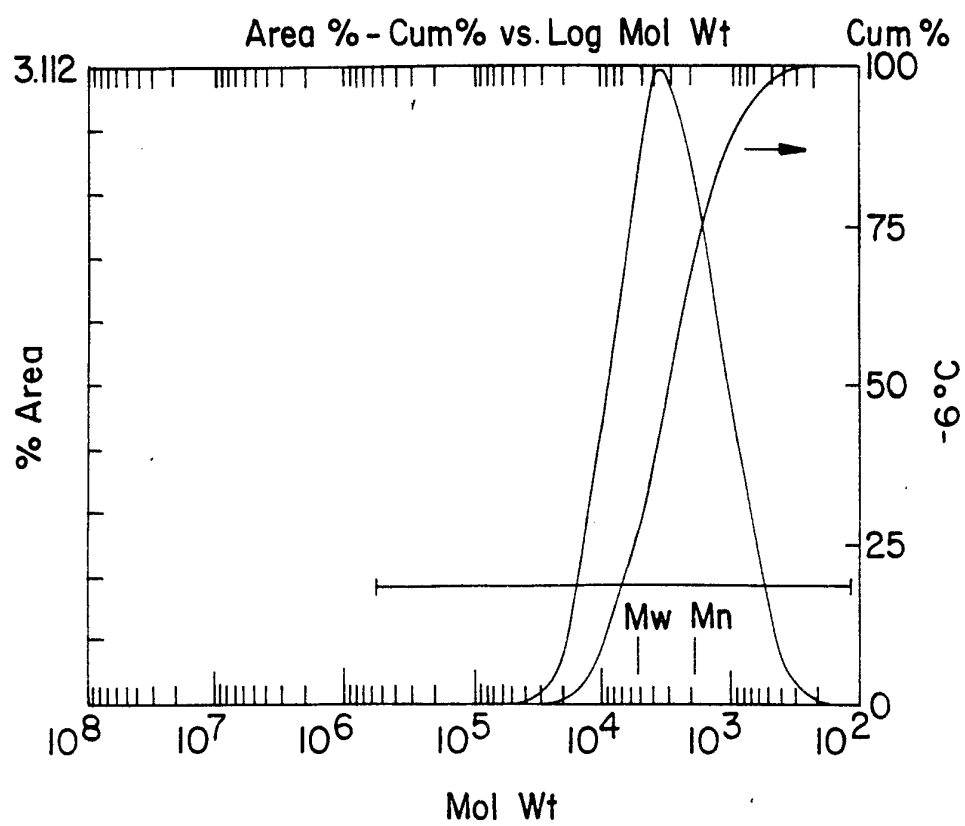


FIG. 10

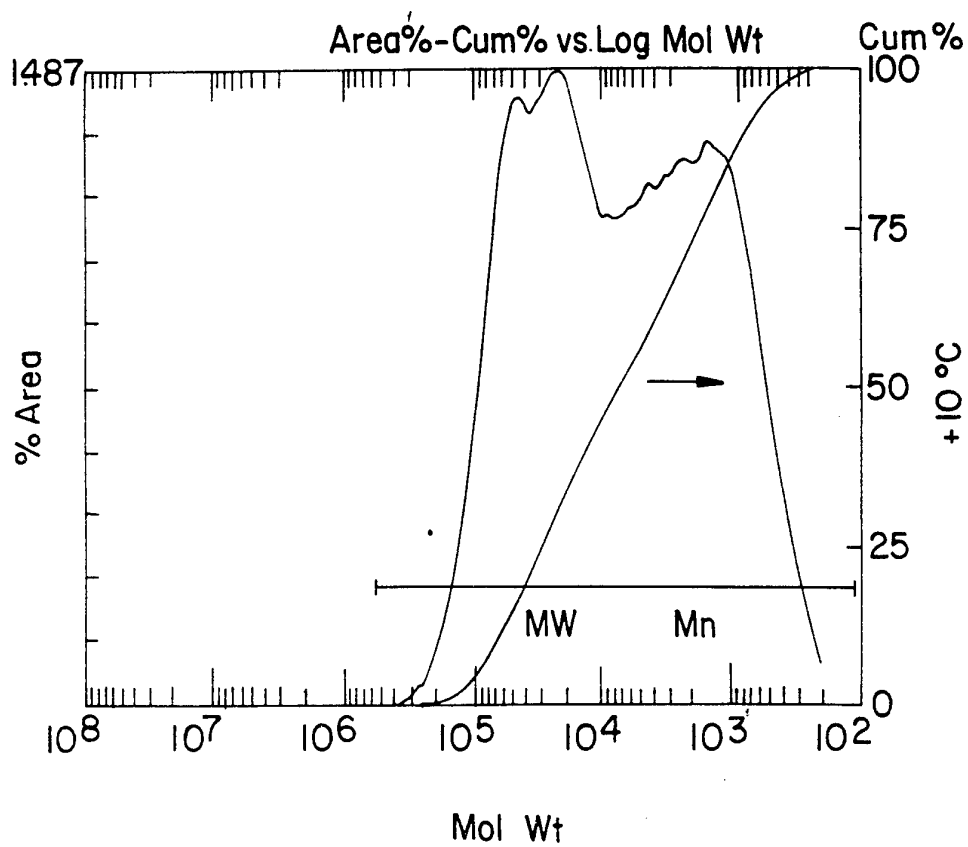
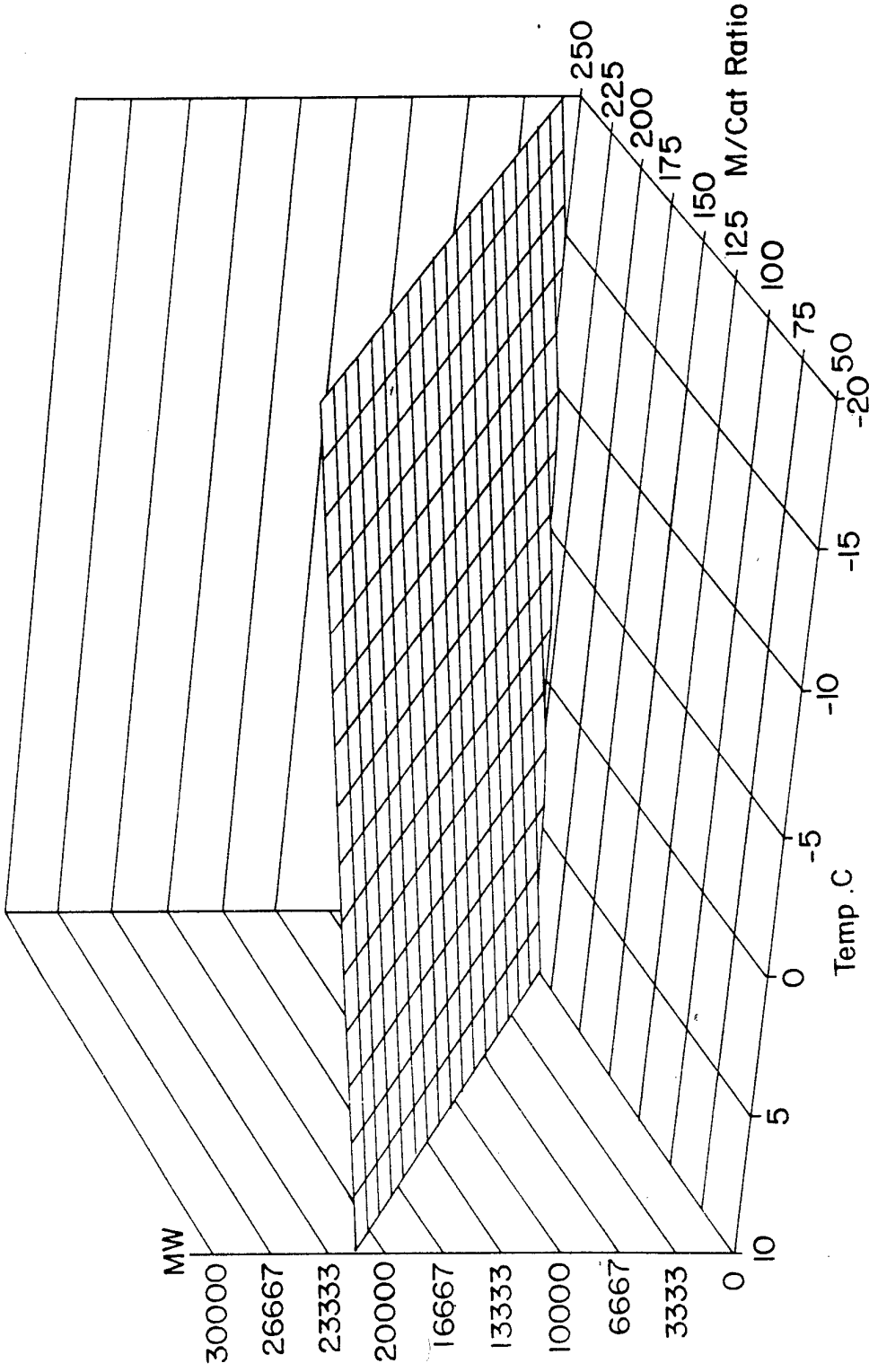


FIG. II

3D GRAPH OF MW - TEMP - MONOMER/CAT RATIO
H-PNB CONTINUOUS PROCESS Cocat/Cat = 1.5



MW = 30918 - 227.6 (Temp) - 137.1(M/CAT) R-square = 0.76