Innovation, Sciences et Développement économique Canada
Office de la Propriété Intellectuelle du Canada

Innovation, Science and Economic Development Canada
Canadian Intellectual Property Office

CA 2714797 C 2020/01/28

(11)(21) 2 714 797

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 2010/09/13

(41) Mise à la disp. pub./Open to Public Insp.: 2011/03/22

(45) Date de délivrance/Issue Date: 2020/01/28

(30) Priorité/Priority: 2009/09/22 (MX MX/A/2009/010135)

(51) Cl.Int./Int.Cl. *C08L 25/02* (2006.01), *C08L 31/04* (2006.01), *C08L 33/06* (2006.01), *F17D 1/16* (2006.01), *F17D 3/16* (2006.01)

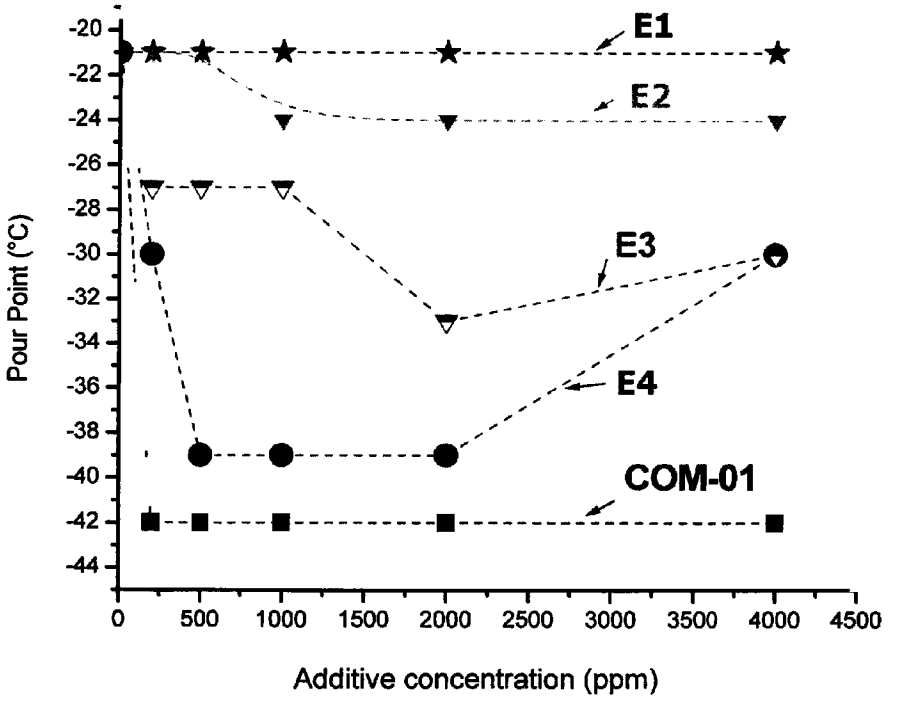
(72) Inventeurs/Inventors:
CASTRO SOTELO, LAURA VERONICA, MX;
FLORES OROPEZA, EUGENIO ALEJANDRO, MX;
CENDEJAS SANTANA, GABRIEL, MX;
LOZADA Y CASSOU, MARCELO, MX;
VAZQUEZ MORENO, FLAVIO SALVADOR, MX

(73) Propriétaire/Owner:
INSTITUTO MEXICANO DEL PETROLEO, MX

(74) Agent: GOWLING WLG (CANADA) LLP

(54) Titre : FORMULATIONS DE POLYMERES ALEATOIRES POUR AMELIORER L'ECOULEMENT DU PETROLE BRUT

(54) Title: FORMULATIONS OF RANDOM POLYMERS FOR IMPROVING CRUDE PETROLEUM FLOW



(57) Abrégé/Abstract:
The present invention is related to the use of formulations of new random copolymers and terpolymers, synthesized by a method of semi continuous emulsion polymerization, and that function as flow improvers, lowering the pour point and reducing the viscosity of Mexicans crude oils, which have gravities within the range of 9 to 30° API.

ABSTRACT

The present invention is related to the use of formulations of new random copolymers and terpolymers, synthesized by a method of semi continuous emulsion polymerization, and that function as flow improvers, lowering the pour point and reducing the viscosity of Mexicans crude oils, which have gravities within the range of 9 to 30° API.

FORMULATIONS OF RANDOM POLYMERS FOR IMPROVING CRUDE PETROLEUM FLOW

DESCRIPTION

TECHNICAL FIELD OF INVENTION

This invention is related to the synthesis of random polymers, their formulation and application as flow improvers of crude petroleum with API densities between 9 and 30° API. These flow improvers decrease petroleum pour point and viscosity.

The random polymers considered in this invention were synthesized by semi continuous emulsion polymerization making react two or three commercial monomers and were added as a formulation in Mexican crude oils at concentrations between 250 and 4000 parts per million.

ANTECEDENTS OF THE INVENTION

Crude oil and any of their distillates, such as diesel, gasoil, naphtha and kerosene, contain different percentages of paraffins, which precipitate when temperature decrease and crystallize very often coating the hydrocarbon.

The crystallization and agglomeration of paraffins degrade the flow properties of the oil or their distillates and break off the extraction procedure, processing, transport, storage and the use of the hydrocarbon.

This paraffin agglomeration is often observed during winter, when the environmental temperature falls and approaches to the pour point, producing the obstruction and even the complete plugging of pipelines in refineries, storage centers and other installations for petroleum processing.

Paraffin agglomeration takes place also in some crude distillates, in example diesel, producing obstructions in the filters of internal combustion motors, plugging heating pipes, which results in a bad operation.

When there is a cooling, paraffins disaggregate and form small crystals which interact forming a tridimensional network able to trap the liquid and increasing the viscosity. If this one happens in distillates like diesel, filter and valve stoppages are observed, but, when this phenomenon occurs in crude oil, the petroleum suffers gelling and deposits are formed on pipelines ant storage tanks, provoking great damages to the production and storage capacity.

There are two kinds of flow improvers: nucleation and Crystal growing modifiers (Odriozola *et al*, 2008). The first promote the formation of tiny paraffin crystals, whereas the second kind facilitates the appearance of great crystal groups. In both cases the formation of a tridimensional crystal network is hindered. Nucleation modifiers are applied in gas and diesel transport and processing because paraffin crystals are so tiny that can traverse trough filters. In contrast, growing modifiers are specially employed in crude oils (Tomassen HPM *et al*, 1998).

Most common flow modifiers are polymers, some of them homopolymers and the most copolymers. Homopolymers are obtained making react a single monomer while copolymers are synthesized from a combination of two different copolymers (M1 and M2). Monomers forming a copolymer chain may be arranged following an alternate sequence (alternate copolymer $M_1M_2M_1M_2M_1M_2$), or a succession of first monomers followed by a succession of the second monomer (block copolymers M_1 M_1 M_1 M_1 M_2 M_2 M_2 M_2) or a random sequence of monomers (M_1 M_2 M_1 M_1 M_2 M_2 M_2 M_1). This last kind of copolymers is specially characterized by their high homogeneous composition. The monomer sequence arrangement in copolymer chains, just that composition homogeneity, has a strong influence on their application properties. The employ of single terpolymers as petroleum flow improvers has not yet been reported.

In the specific case of polymers employed as petroleum flow improvers, branched polyoleffins, alphaoleffin and esters of unsaturated carboxylic acids copolymers, ethylene and vinyl esters of fat acid copolymers, vinyl acetate and alpha olefin copolymers, styrene maleic anhydride copolymers, fat acid amides and polyalkylacrylates, (Castro LV *et al*, 2008).

More specifically, ethylene-vinyl acetate copolymers (EVA) are produced by BASF under the trade mark Keroflux (Eisenbeis A et al., 2005).

Some examples of petroleum flow improvers given by the international literature are the following: European patent EP0931825 B1depicts a process for improving flow properties of oils with a sulfur content lower than 500 ppm and a minimal paraffin content around 8 % weight, using mixtures of copolymers and terpolymers, at a rate of 15% to 50% by weight of copolymers consisting of: polyethylene from 87% to 92% mol; polyvinyl acetate from 6.5% to 12% mol and 4-methyl-polypentene from 0.5% to 6% mol and terpolymers made of ethylene, vinyl esters and vinyl acrylates, at a composition between 50 and 85 % (Krull M *et al*, 2003).

US patent 4362533 describes the synthesis and use of terpolymers as pour point depressors crude oil middle distillates, made of polyethylene (45 -75% wt.), at least 5 % weight of polyvinyl acetate and 5 % weight of polystyrene. These polymers present a homogeneous distribution and composition of each monomer (Kidd, N.A., 1982).

European patent 4362533 describes as a new flow improver a polymer with content between 50 and 90 % weight of ethylene, 10 to 40 % weight of esters of polyvinyl, 0.2 to 10 % weight of olefins and since 2% until 25 % weight of aromatic vinyl, its molecular masse vary from 1000 to 50000, more preferential 2000 until 10 000 Dalton. The polymer is added at concentrations between 0.03 and 0.10 % wt., being very effective to decrease the pour point of oils and middle distillates of petroleum (Chen JCS, 1985).

US patent 20040092665 describes the employ of copolymers constituted by a butylic fraction (isoprene, butadiene, 2-4dimethyl-butadiene, 2,4-hexadiene and halogenated derivatives, among others) and styrenic fraction (alfa-methyl-styrene and styrene)(Pazur R et al, 2004).

Copolymer synthesized from vinyl esters, alkyl acrylate and styrene were added (200 to 4000 ppm) into Mexican crude oils and diminished viscosity and pour point (Castro LV et al, 2008). These additives were synthesized semi continuous emulsion polymerization and, afterwards, characterized by spectroscopic and calorimetric techniques, in order to ensure a random distribution in the chains and a homogeneous composition. The synthesis procedure showed their efficiency to avoid the formation of homopolymers mixtures. The performance of these products depends strongly on this molecular feature and on the inexistence of long sequences of a single monomer.

In Mexico, the reserves of light crude oil diminishes very fast and, in consequence, only heavy and extra-heavy crude oils will be processed in the future by the national system of refineries. This situation represents a challenge because of the technical and economical difficulties related to this problem. Therefore, it is very important to find a solution to the problem of the low API gravity and high viscosity of the Mexican crude oils (Camacho-Bragado *et a*, 2002).

Taking in account the great importance of these technical and economical requirements, a series of formulations of new random copolymers and terpolymers dissolved in different solvents was prepared. All these polymers were prepared by emulsion polymerization and showed a considerable performance as pour point and viscosity decrease agents in some Mexican crude oils. It is important to remark that none of the references mentioned above neither disclose nor claim the application of polymers and/or formulations whose main characteristic is that polymers are

composed of combinations of two or three acrylic, vinylic and styrenic monomers together at random which main component are styrenic type.

Bibliographic references

Ahlers W. *et al* .US Patent Application *20070094920* (2007).

Bharambe Dinakar P. and Soni Hemant P. Synthesis and Evaluation of Polymeric Additives as Flow Improvers for Indian Crude Oil. *Iranian Polymer Journal* 15 943-954 (2006).

Borthakur A., Chanda D., Dutta Choudhury S. R., Alkyl fumarate-vinyl acetate copolymer as flow improver for high wxy Indian crude oils. *Energy & Fuels* 10 844-848 (1996).

Camacho-Bragado G. A., Santiago P, Marin-Almazo M, Espinoza M, Romero E. T., Murgich J, Rodríguez-Lugo V, Lozada-Cassou M and Jose-Yacaman M, Fullerenic structures derived from oil asphaltenes. *Carbon* 40 2761-2766 (2002).

Castro LV and Vazquez F. Copolymers as flow improvers for mexican crude oils. *Energy and Fuel.* 22 4006-4011 (2008).

Castro Laura V. and Vazquez Flavio, Fractionation and characterization of Mexican Crude oils. *Energy and Fuels.* 23 1603-1609 (2009).

Charles Adams, Emulsion Polymerization process and reactor for such a process. US Patent 6569961 B1. (2003).

Chen JCS. Cold flow improver. EP0136698 (1985).

Eisenbeis A, Ahlers W, Troetsch-Schaller I, Fechtenkoetter A and Maehling FO. Fuel oil compositions with improved cold flow properties. CA 2 548 008 A1 (2005).

Jimenez-Angeles F, Duda Y, Odriozola G, and Lozada-Cassou M. Population inversion of a NAHS Mixture Absorbed into a cylindrical pore. *J. Phys. Chem. C.* 112 18028-18033 (2008).

Kidd, N.A. Terpolymer of ethylene, vinyl acetate, and styrene as pour point depressants for distillate fuel US4362533 (1982).

Krull M and Reimann W. Process and product to improve cold flow properties of fuel oils. EP0931825 B1 (2003).

Nuñez S. Ma. Del Carmen. *Introducción a la reología*, D. R. Instituto Politécnico Nacional, 2001.

Odriozola G, Jimenez-Angeles F and Lozada-Cassou M,Entropy driven key-lock assembly. *J. Chem. Phys.* 129 101-111 (2008).

Pazur R and Sumner AJ. Butyl polymer composition having improved cold flow properties US 20040092665 (2004).

Reyes-Mercado Y., Vazquez F., Rodriguez-Gomez F. J., Duda Y. Effect of the acrylic acid content on the permeability and water uptake of poly(styrene-co-butyl acrylate) latex films. *Colloid Polym Sci.* 286 603-609 (2008).

Ronningsen Hans Petter and BjØrndal. Wax precipitation from North Sea crude oils: 1. Crystallization and dissolution temperatures, and Newtonian and non-newtonian flow properties. *Energy & Fuels* 5 895-908 (1991).

Tomassen HPM, Van de KCC, Reynhout MJ and Lin J. Polymeric flow improver additives US Patent 5721201 (1998).

Torres E, Dutta N, Roy C.N. and Matisons J. Effect of composition on the solution rheology of Stearyl Methacrylate-co-styrene-co-vinyl pyrrolidinone in paraffinic base oil. *Polymer Engin. Sci.* 44 736-748 (2004).

SHORT DESCRIPTION OF THE INVENTION DRAWS

The following figures are given in order to understand clearly the performance of the formulation of random polymers for improving crude petroleum flow and are used as reference of the application examples.

Figure 1 shows the effect of the pour point decrease activity in light crude oil of examples E1-E4, evaluated between 200 and 4000 ppm, and compared to the commercial product COM-01.

Figure 2 shows the effect of the pour point decrease activity in middle crude oils, evaluated from 250 to 4000 ppm.

Figure 3 exhibits the effect of the reducing viscosity activity at 20 °C in heavy crude oil in examples 6, 7, 8, 9 and 10, evaluated at 1000 ppm.

Figure 4 presents the effect of the viscosity decrease activity at 20 °C in heavy crude oil of examples 11, 14 and 16 evaluated at 1000 ppm.

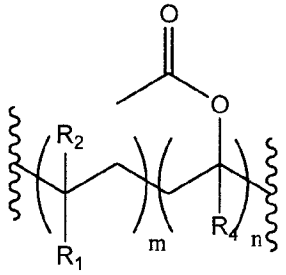
Figure 5 exposes the effect of the viscosity decrease activity in heavy crude oil at different temperatures of examples 11, 12 and 16 evaluated at 500 and 1000 ppm.

Figure 6 shows the effect of the decrease activity of the activity in heavy crude oil at different temperatures of examples 12, COM-01 and COM-02, evaluated at 1000 ppm.

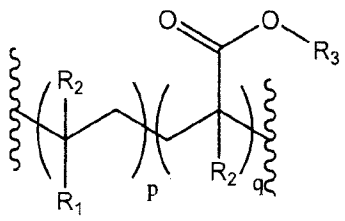
DETAILED DESCRIPTION OF THE INVENTION

The present invention consists of the synthesis of new random copolymers and terpolymers by semicontinuous emulsion polymerization and the preparation of formulations (random copolymers and terpolymers combined with organic solvents) and their application as flow improvers and viscosity reducers. In schemes 1 to 3 the copolymers structure (random combination of a couple of monomers) are shown and in scheme 4 the terpolymer structure obtained from three monomers combination are shown:

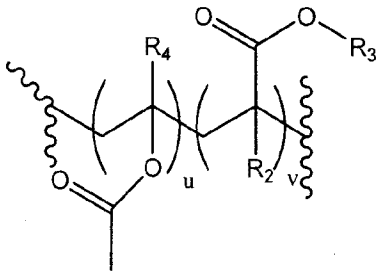
Copolymers



Scheme 1

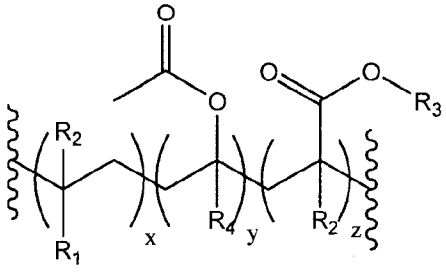


Scheme 2



Scheme 3

Terpolymers



Scheme 4

Where:

R_1, R_2, R_3 y R_4 are represented by independent radical groups listed below:

R_1= C_6H_5, $CH_3C_6H_4$, $(CH_3)_2C_6H_3$, $(CH_3)_3C_6H_2$, $(CH_3)_3CC_6H_4$.

R_2= H, CH_3.

R_3= CH_3, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{18}H_{37}$.

R_4= H, CN.

Where in addition:

x, y, z, m, n, p, q, u and v are numbers within the following ranges:

x = from 2 to 900, preferably from 20 to 850, even more preferably from 25 to 700.

z = from 1 to 300, preferably from 10 to 235, still more preferably from 20 to 220.

y = from 1 to 226, preferably from 10 to 210, still more preferably from 20 to 200.

m = from 10 to 700, preferably from 20 to 650, still more preferably from 40 to 620.

n = from 1 to 220, preferably from 10 to 200, still more preferably from 20 to 170.

p = from 1 to 700, preferably from 25 to 650, still more preferably from 60 to 620.

q = desde1 to 50, preferably from 5 to 45, even more preferably from 10 to 40.

u = from 1 to 220, preferably from 10 to 200, more preferably from 30 to 170.

v = from 1 to 50, preferably from 10 to 40, more preferably from 15 to 30.

Besides the molecular weights are in the following ranges, from 1000 to 100,000 Daltons, preferably between 5000 and 90000 g / mol for the case of copolymers and from 1000 to 140000, preferably from 2000 to 100,000 g / mol in the case of random terpolymers.

The combination of styrene and vinyl monomers to prepare combinations of two monomers (copolymers) or three monomers (terpolymers) as flow improvers of petroleum is based on the physical interactions between the polymer chains and the petroleum components which provokes the high viscosity of the crude oil, mainly paraffins. The vinyl sequences in the polymer backbone are compatible to paraffins and allow the molecule to approach to these petroleum components. In contrast, the styrene units in the polymer chain hinder the paraffin crystallization, which provokes the viscosity rise of petroleum. A good a homogeneous distribution in the polymer chain of the styrene and vinyl monomers (random structure) allows stablishing a good

balance between the compatibility with paraffins and the bulk effect which hinder the paraffin crystallization. An adequate molecular weight of the random copolymers or terpolymers is also required. Too short polymer chains cannot diffuse trough petroleum. Too long polymer chains tangle and form agglomerates. An effective diffusion trough the paraffins agglomerates for a subsequent dispersion is ensured by random copolymers or terpolymers with an adequate molecular weight.

The copolymers and terpolymers of the present invention are prepared by emulsion polymerization technique, which presents ecological advantages when using water as dispersion medium avoiding the use of large amounts of organic solvents during the synthesis stage. Emulsion polymerization is widely used for the synthesis of adhesives, paints and varnishes, but has not reported used as improvers in crudes oil (Charles Ad 2003). This procedure of synthesis allows obtaining random copolymers and terpolymers with a homogeneous distribution of styrene and vinyl monomers in the polymer chain, which ensures an optimal interaction with paraffins. These last ones are responsible of the high viscosity of petroleum.

The following describes by way of example, it does not imply any limitation, the monomers used in the synthesis of polymers object of this invention: methyl acrylate, *tert*-butyl methacrylate, butyl acrylate, butyl methacrylate, hexyl acrilate, hexyl methacrylate, *iso*-butyl acrylate, *iso*-butyl methacrylate, ethyl acrylate, ethyl methacrylate, *tert*-butyl acrylate, 3,5,5-trimethyl-hexyl acrylate, *iso*-decyl acrylate, *iso*-decyl methacrylate, *iso*-octyl acrylate, lauryl acrylate, lauryl methacrylate, octadecyl acrylate, 2-ethyl-hexyl acrylate, 2-ethyl-hexyl methacrylate, styrene, 2,4,6-trimethyl-styrene, 2,4-dimethyl-styrene, 3-methyl-styrene, 4-methyl-styrene, 2-methyl-styrene, 4-*tert*-butyl-styrene, α ,2-dimethyl-styrene, α-methyl-styrene, methyl styrene, vinyl acetate, and cyanovinyl acetate.

The synthesis of polymers (random copolymers and terpolymers) of the present invention, which are effective in the lowering of the pour point and viscosity reduction of light, median and mainly heavy crudes oil, comprising seven stages:

1) *Preparation of the initiator.*

2) *Preparation of surfactant solutions ((Anionic(A) and / or nonionic (B))*

3) *Preparation of buffer solution*

4) *Preparation of the monomers (combination of two monomers for copolymers and three monomers for terpolymers)*

5) *Preparation of seed main reactor.*

6) *Preparation tank addition.*

7) *Polymerization of combinations of two or three monomers.*

For the synthesis of polymers using the semicontinuous method was used (Reyes-Mercado Y et al.) which is described below, this method is illustrative but not limitative:

1) *Initiator preparation*: In a balloon flask equipped with magnetic stirring, is placed a suitable amount of initiator, is dissolved in deionized water and kept stirring for 10 minutes. These amounts can vary between 0.5 and 15.0 g of initiator per 100.0 g of deionized water. As initiators can be used potassium, sodium or ammonium persulfates, as well as sodium or potassium methabisulfite and benzoyl hydroperoxide.

2) *Preparation of surfactant solutions*. In a flask equipped with magnetic stirring, are placed an appropriate amount of surfactant A (ionic) and surfactant B (nonionic), both are dissolved in deionized water and kept stirring for 40 minutes. These amounts can vary between 0.5 and 50.0g of surfactant per 100.0g of deionized water.

3) *Preparation of buffer solution*. The buffer ensures no abrupt changes in the pH of the system. In a balloon flask equipped with magnetic stirring ball, is placed an appropriate amount of buffer, (for example sodium or potassium bicarbonate) is dissolved in deionized water and kept stirring for 10 minutes. These amounts can vary between 0.5 and 15.0g of initiator per 100.0g of deionized water

4) *Preparation of the monomers*. In a volumetric flask, is placed the appropriate amount of monomer or monomers required (two monomers for copolymers and three monomers for terpolymers). The compositions of each monomer in the mixture can vary between 1% and 99%, preferably between 5% and 90% compared to total monomer. It requires a transfer agent (for example dodecyl or terdodecyl mercaptane) to control the molecular weights of polymers. The transfer agent is added to the mixture of monomers. The amount of transfer agent can vary between 0.0 and 12.0 g per 100.0g of monomer, according to the desired molecular weight. This mixture is stirred for about 5 minutes

5) *Preparation of seed in the main reactor*: The reactions were conducted in a glass reactor of one liter capacity with a heating jacket through which water is recirculated at constant temperature. Agitation is achieved by a propeller of two sheets of Teflon-coated, moved by a mechanical stirrer of varying acceleration. The reactor also has a condensation system, with connections for temperature monitoring, connection for inert gas injection and sampling connection. The reactor is filled with a solution of appropriate amounts of surfactant A and surfactant B, buffer solution, deionized water and a small amount of mixture of monomers. These amounts can vary between 1.0 and 25.0 g of solution per 100.0 g of monomers. Deionized water is added, wich can vary between 70 and 300g. Subsequently, the reactor is pressurized with nitrogen to ensure inert atmosphere. The temperature was set between 50 and 90 ° C to ensure the smooth progress of polymerization. After 10 to 40 minutes of stirring, is added the appropriate amount of initiator solution. This amount can vary between 1.0 and 20.0 g of initiator solution. Again, the reactor is pressurized with nitrogen to ensure polymerization.

6) *Preparation tank addition*. The addition tank was carried out in a glass flask of one liter capacity with connection to suction of dosing pump and with controlled magnetic stirring. Once the preparation of the seed proceed to slowly add the remaining monomer mixture, solutions of surfactant A, B and the remaining buffer in addition to

the tank. Finally, deionized water is added, which can vary between 70.0 and 300.0 g per 100.0 g of monomers.

7) *Copolymerization or terpolymerization of monomers.* It connects the addition tank to the main reactor (seed), through a metering pump. The ratio of feed addition tank ranges from 0.003 to 0.009 g / mL-min, more preferably 0.004 to 0.007 g /.mL-min. This rate of addition guarantees the existence of monomer deficiency in the main reactor and ensures that the pairs or trios of monomers react with each other and respectively forming random copolymers or terpolymers. Do not place the addition in the range of speeds of addition, will the formation of large sequences of a single monomer within the chains and even the formation of mixtures of homopolymers. According to the desired molecular weight, once the addition is necessary to complete the reaction by adding small amounts of initiator and increasing the temperature to 90 and 95 ° C for one hour. The copolymer or terpolymer was subsequently placed in sealed containers. Random copolymer or terpolymer reactions achieve conversions between 98 70 99.99% by weight (Castro LV et al, 2008).The products obtained have latex form, dispersion of latex in water easier to process because avoids the use of organic solvents, without health and the environment risks. Stressing further, that without this synthesis procedure, it is virtually impossible to obtain the random polymers (copolymers and terpolymers).

Once obtained copolymers and terpolymers were characterized using the instrumental methods:

1.-Infrared brand model Thermo Nicolet AVATAR 330, ®Spectrometer Fourier Transform using the method of film technique with software version 7.0 Omnic ®.

2.- Nuclear Magnetic Resonance Jeol Eclipse equipment, operating at 300 MHz and 75 MHz for ^{1}H and ^{13}C spectra respectively, using deuterated chloroform as solvent; the shifts are indicated in parts per million, about tetramethylsilane (TMS) signal, as internal standard.

3.- Size exclusion chromatograph Agilent® model 1100 (CET), with PLgel column and using tetrahydrofuran (THF) as eluent, to calculate the molecular distribution of copolymers and terpolymers and the polydispersity index (I).

Molecular masses, polydispersity indices and spectroscopic characteristics are now described in Tables 1 and 2, which does not mean limitation:

Table 1. Copolymers number molecular masses (Mn) and polydispersity index (I) measured by (CET).

Copolymers	Mn (g/mol)	I	Physical State
E-1	2938	1.4	Viscous semi solid
E-2	2213	1.2	Viscous semi solid
E-3	9279	2.1	Viscous semi solid
E-4	1691	1.5	Viscous semi solid
E-5	55278	2.8	Viscous semi solid

Table 2. Terpolymers number molecular masses (Mn) and polydispersity index (I) measured by (CET).

Terpolymers	Mn (g/mol)	I	Physical state
E-6	1448	1.9	Viscous semi solid
E-7	1109	3.3	Viscous semi solid
E-8	139900	2.3	Viscous semi solid
E-9	2057	1.8	Viscous semi solid
E-10	23488	1.7	Viscous semi solid
E-11	2223	3.3	Viscous semi solid
E-12	21547	2.1	Viscous semi solid
E-13	2954	1.7	Viscous semi solid

E-14	20701	1.9	Viscous semi solid
E-15	1184	2.0	Viscous semi solid
E-16	6816	2.7	Viscous semi solid

Examples

The following examples are presented to illustrate the best mode of random polymer synthesis, formulation and implementation as flow improvers in crudes oil with API gravities ranging from 9 to 30. These examples should not be regarded as limiting what is claimed.

E-1

Poly(styrene)$_p$-poly(acrylate)$_q$ (R_1=phenyl, R_2=Hydrogen, R_3=butyl acrylate), with the followign composition 30 g of monome A and 70 g of monomer B, with 8 % of transfer agent: viscous semisolid; I.R. ν cm $^{-1}$: 3082.7, 3060.3, 3026.5, 2926.3, 2854.5, 1943.5, 1870.6, 1801.7, 1729.9, 1601.6, 1493.4, 1452.6, 1355.4, 1252.3, 1160, 1068.2, 1029.08, 944.4, 841.3, 759.6, 699.6, 543.8; ^{13}C RMN ($CDCl_3$): 170.5, 145.4, 128.1, 127.8, 125.8, 70.6, 40.5, 32.0, 29.7, 28.9, 22.8, 21.0, 14.2.

E-2

Poly(acetate)$_u$-poly(acrylate)$_v$ (R_2=Hydrogen, R_3= butyl acrylate, R_4= Hydrogen), with the following composition 30 g of monomer A and 70 g of monomer B, with 8 % of transfer agent: viscous semisoli; I.R. ν cm $^{-1}$: 2959.4, 2931.7, 2873.6, 1736.6, 1459.9, 1371.7, 1237.7, 1167.6, 1119.1, 1023.5, 942.9; ^{13}C RMN ($CDCl_3$): 174.7, 170.3, 70.5, 69.9, 64.6, 62.2, 41.5, 40.4, 39.5, 31.9, 39.65, 29.7, 29.4, 28.9, 22.7, 20.9, 19.2, 14.1, 13.8.

E-3

Poly(styrene)$_m$-poly(acetate)$_n$ (R_1= phenyl, R_2= Hydrogen, R_4= Hydrogen), with the following composition 30 g of monomer A and 70 g of monomer B, with 2 % of transfer agent: viscous semisoli; I.R. ν cm $^{-1}$: 3445.7, 3081.8, 3059.5, 3025.5, 2923.6,

2851.5, 1943.8, 1870.5, 1803.3, 1736.2, 1601.1, 1492.8, 1452.0, 1372.2, 1244.8, 1118.5, 1028.2, 757.4, 698.6, 540.2; ^{13}C RMN ($CDCl_3$): 145.3, 128.0, 125.7, 70.6, 44.0, 40.6.

E-4

Poly(styrene)$_m$-poli(acetate)$_n$ (R_1= phenyl, R_2= Hydrogen, R_4= Hydrogen), with the following composition 30 g of monomer A and 70 g of monomer B, with 8 % of transfer agent: viscous semisolid; I.R. ν cm $^{-1}$: 3059.7, 3025.5, 2923.8, 2852.3, 1943.4, 1871.6, 1738.2, 1601.1, 1492.8, 1452.1, 1372.8, 1243.1, 1108.7, 1027.9, 757.2, 698.9, 540.3; ^{13}C RMN ($CDCl_3$): 170.5, 145.4, 128.1, 127.8, 125.6, 70.6, 40.6, 31.9, 29.6, 22.8, 21.0, 14.2.

E-5

Poly(styrene)$_m$-poli(acetate)$_n$ (R_1= phenyl, R_2= Hydrogen, R_4= Hydrogen), with the following composition 70 g of monomer A and 30 g of monomer B, with 0 % of transfer agent: Solid; I.R. ν cm $^{-1}$: 3453.6, 3025.4, 2922.8, 1943.9, 1870.8, 1732.2, 1601.4, 1493.3, 1452.7, 1373.4, 1242.9, 1119.8, 1025.9, 946.2, 757.6, 698.5, 539.4; ^{13}C RMN ($CDCl_3$): 170.4, 145.4, 128.0, 125.7, 70.6, 69.7, 67.1, 40.6, 39.3, 21.1.

E-6

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= phenyl, R_2=Hydrogen, R_3=C_4H_9, R_4= Hydrogen), with the following composition 30 g of monomer A, 20 g of monomer B and 50 g of monomer C, with 8 % of transfer agent: viscous semisolid; I.R. ν cm $^{-1}$: 2958.1, 2929.9, 2872.9, 1731.2, 1453.5, 1372.3, 1238.8, 1163.3, 1066.6, 1028.6, 700.8; ^{13}C RMN ($CDCl_3$): 175.3, 128.4, 127.8, 126.4, 70.5, 69.8, 64.3, 41.7, 41.2, 39.5, 31.9, 30.7, 29.7, 29.4, 28.9, 22.7, 21.0, 19.2, 13.8.

E-7

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= phenyl, R_2=Hydrogen, R_3=tert-butyl, R_4= hydrogen): with the following composition 30 g of monomer A, 50 g of monomer B and 20 g of monomer C, with 8 % of transfer agent: viscous semisolid; I.R. ν cm $^{-1}$: 3026.4, 2926.3, 1731.6, 1493.4, 1372.0, 1452.6, 1242.1, 1161.0, 1028.4, 759.7,

699.8; ^{13}C RMN ($CDCl_3$): 175.9, 170.5, 145.2, 143.8, 128.3, 113.9, 70.5, 63.8, 43.1, 1.2, 39.2, 33.8, 32.0, 29.7, 22.8, 21.1, 19.2, 14.2, 13.8.

E-8

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= $C_6H_4CH_3$, R_2=hydrogen, R_4= hydrogen, R_5=C_4H_9): with the following composition 30 g of monomer A, 50 g of monomer B and 20 g of monomer C, with 0 % of transfer; viscous semisolid; I.R. ν cm^{-1}: 3438.5, 3059.9, 3026.9, 2925.8, 1945.8, 1873.8, 1803.1, 1729.5, 1602.1, 1492.5, 1451.1, 1356.4,1249.7, 1156.9, 944.6, 840.9, 758.5, 700, 541.6; ^{13}C RMN ($CDCl_3$): 175.8, 170.5, 145.3, 128.1, 127.7, 125.9, 70.6, 63.8, 41.8, 30.6, 21.0, 19.1, 13.8.

E-9

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= $C_6H_4CH_3$, R_2= hydrogen, R_3= C_4H_9, R_4=hydrogen): with the following composition 20 g of monomer A, 50 g of monomer B and 30 g of monomer C, with 8 % of transfer agent; viscous semisolid; I.R. ν cm^{-1}: 3442.0, 3082.9, 3026.7, 2928.6, 1944.4, 1870.9, 1731.5 16017, 1493.7, 1453.0, 1373.0, 1242.0, 1160.7, 1028.0, 943.9, 841.3, 759.9, 841.3, 759.9, 699.0, 544.7; ^{13}C RMN ($CDCl_3$): 175.2, 128.4, 64.2, 41.3, 34.8, 31.9, 30.7, 29.7, 28.9, 22.7, 21.1, 19.2, 13.8.

E-10

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= C_6H_5, R_2=hydrogen, R_3= C_6H_{13}, R_4= hydrogen), with the following composition 20 g of monomer A, 50 g of monomer B and 30 g of monomer C, with 1 % of transfer agent; viscous semisolid; I.R. ν cm^{-1}: 3437.9, 3026.5, 2926.6, 1944.7, 1873.3, 1728.5, 1601.6, 1493.0, 1451.5, 1354.8, 1250.3, 1155.4, 1028.3, 759.3, 699.3; ^{13}C RMN ($CDCl_3$): 176.0, 170.6, 144.3, 128.3, 125.9, 70.5, 63.9, 41.2, 31.9, 29.7, 28.9, 22.8, 21.1.

E-11

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= $C_6H_4CH_3$, R_2= hydrogen, R_3= C_2H_5, R_4= hydrogen), with the following composition 20 g of monomer A, 70 g of monomer B and 10 g of monomer C, with 8 % of transfer agent; viscous semisolid; I.R. ν cm^{-1}: 3059.9, 3025.9, 2924.8, 2852.9, 1943.4, 1871.3, 1802.9, 1730.9, 1493.0, 1452.3,

1243.9, 1154.9, 1028.6, 758.0, 699.2, 541.1; ^{13}C RMN ($CDCl_3$): 175.9, 170.4, 145.3, 128.2, 125.8, 70.6, 63.8, 46.3, 40.6, 32.0, 30.5, 29.7, 29.4,, 22.8, 13.8.

E-12

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= C_6H_5, R_2= hydrogen, R_3= C_4H_9, R_4= hydrogen), with the following composition 20 g of monomer A, 70 g of monomer B and 10 g of monomer C, with 1 % of transfer agent; viscous semisolid; I.R. ν cm $^{-1}$: 3026.3, 2923.6, 1944.5, 1873.0, 1803.8, 1730.3, 1601.6, 1492.2, 1449.6, 1371.2, 1243.4, 1152.7, 1027.7,945.0, 908.5, 757.1, 700.3, 539.9; ^{13}C RMN ($CDCl_3$): 145.3, 128.0, 125.7, 70.6, 63.9, 44.3, 41.1, 40.5, 30.6, 19.1, 13.8.

E-13

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= C_6H_5, R_2= hydrogen, R_3= C_6H_{13}, R_4= hydrogen), with the following composition 20 g of monomer A, 10 g of monomer B and 70 g of monomer C, , with 8 % of transfer agent; viscous semisolid; I.R. ν cm $^{-1}$: 3447.2, 2959.4, 2870.5, 1730.9, 1604.2,1456.5, 1371.6, 1239, 1164.3, 1065.91026.3, 944.6, 840.4, 759.7, 702.0; ^{13}C RMN ($CDCl_3$): 175.2, 128.4, 64.2, 41.3, 34.8, 31.9, 30.7, 29.7, 28.9, 22.7, 21.1, 19.2, 13.8.

E-14

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= $C_6H_4CH_3$, R_2= hydrogen, R_3= C_4H_9, R_4= hydrogen), with the following composition 20 g of monomer A, 10 g of monomer B and 70 g of monomer C, with 1 % of transfer agent; viscous semisolid; I.R. ν cm $^{-1}$: 3446.2, 2959.0, 2873.5, 1732.2, 1453.0, 1372.9, 1239.5, 1163.8, 1117.9, 1066.3, 1024.2, 943.9, 701.6; ^{13}C RMN ($CDCl_3$): 175.0, 170.2, 0.5, 64.6, 41.4, 39.1, 35.3, 30.7, 20.9, 19.2, 13.8.

E-15

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= C_6H_5, R_2= hydrogen, R_3= C_6H_{13}, R_4= hydrogen), with the following composition 60 g of monomer A, 30 g of monomer B and 10 g of monomer C, with 8 % of transfer agent; viscous semisolid; I.R. ν cm $^{-1}$: 3026.6, 2925.9, 2854.3, 1732.9, 1601.6, 1492.8, 1451.4, 1372.2, 1241.3, 1156.9,

1026.6, 945.7, 758.2, 700.5; ^{13}C RMN ($CDCl_3$): 170.5, 128.3, 70.5, 41.2, 39.3, 31.9, 29.4, 22.8, 14.2, 13.8.

E-16

Poly(styrene)$_x$-poly(acetate)$_y$-poly(acrylate)$_z$ (R_1= C_6H_5, R_2= hydrogen, R_3= C_4H_9, R_4= hydrogen), with the following composition 60 g of monomer A, 30 g of monomer B and 10 g of monomer C, with 1 % of transfer agent; viscous semisolid; I.R. ν cm^{-1}: 3442.9, 3026.0, 2921.8, 1944.4.

The random polymers (copolymers and terpolymers), grounds of the present invention were formulated using various solvents and assessed as flow improvers, either reducing the viscosity and/or reducing the pour point in Mexican crude oils whose API gravity is between 9 to 30, the following results are illustrative way do not mean any limitation.

Formulations of copolymers and their assessment as pour point reducing agents for light and medium crude oils.

Prepared different concentrated solutions of alternating copolymers of 1 to 60 % by weight, preferably 5 to 40 % by weight, using solvents whose boiling point falls within the range of 35 to 200°C, preferably dichloromethane, chloroform, xylene, toluene, jet fuel, benzene, methyl ethyl ketone, kerosene, turbosine, naphtha, individually or in mixtures thereof, so added small volumes of dissolution and avoided the effect of the solvent influenced in the evaluation of the pour point. Alternating copolymers were evaluated in concentrations in the range of 100 to 4000 ppm.

Light crude oil used in the present invention was characterized as shown below in Table 3.

Table 3. Physicochemical and physical characterization of light, medium and heavy crude oils (Castro LV et al, 2009).

Parameter	Light	Medium	Heavy
API density	29.6	21.3	15.8
Salt content	23.0 kg/1000 bls	1090 kg/1000 bls	1.1 kg/1000 bls
Wax content (wt %)	3.02	3.83	4.27
Water by distillation (vol %)	0.8	1.8	0.10
Pour Point (°C)	-21	-24	-2
	SARA Analysis (wt %)		
Saturates	38.44	26.53	10.49
Aromatics	14.59	14.74	9.0
Resins	41.44	47.60	64.12
Asphaltenes	5.53	11.13	16.39

The copolymers were evaluated simultaneously with commercial copolymers type EVA (ethylene-vinyl acetate), as reducing agents of the pour point and like a reference.

The assessment procedure is described below: the sealed bottles with insert number and lid is indicated by the number of compounds to assess plus one that corresponds to the crude oil without additives; each of them was added with crude oil to the 80 mL mark. All the bottles were placed in a water bath at a controlled temperature in 60°C for 30 minutes, at the end of that time was added above the aliquot of the dissolution alternating copolymers and the commercial copolymers formulations; all the bottles shook for 4 minutes at a rate of 2 beats per second and later placed for 20 minutes in ultrasonic bath with controlled temperature of 60 °C. After agitation, the test pieces were placed according to method ASTM D-97 and left at least 22 hours at room temperature, the evaluation was the performed. All the copolymers, the reason of this invention, and commercial formulations were assessed at different concentrations in the range from 200 to 4,000 ppm. As reference was also prepared a sample of crude

oil only with the solvent (without polymer addition) and which is referred to as untreated.

As a demonstration, which does not involve limitation, results are displayed, in Figures 1 and 2, the evaluation of copolymers of examples 1-4, for a concentration range of 200 and 4000 ppm, crude light and medium respectively; commercial formulations are follows:

COM-01: {copolymer of ethylene and 75/25, vinyl acetate MN = 38678 Daltons (20 %) with solvent (80 %).}

COM-02: {ethylene and vinyl 60/40 (p. / p.), MN acetate copolymers = 52383 Daltons (20 %) with solvent (80 %).}

Figure 1 presents outcomes assessed in examples E1-E4 as pour point depressants in light crude. Example 4 is the only one that reduces in greater proportion the pour point, corresponding to the example that has lower molecular weight number. The pour point is significantly reduced in dosages for example 4 and COM-1 between 500 and 2000 ppm regarding oil without adding with copolymers (untreated).

E1 and E2 examples do not have an effect as pour point depressants. This can be explained by the lack of interaction between acrylates units of copolymers with components of crude oil, especially with waxes, while styrene-vinyl copolymers have better affinity with crude oil.

Figure 2 presents outcomes assessed in examples E1-E4 as pour point depressants in medium crude oil. The example E4 showed the best performance to be evaluated in medium crude oil, which contains more aromatic components and more content of asphaltenes compared to the light crude oil.

The effect of molecular mass in examples 3 and 4 is present to compare results in Figure 2, this last being the most satisfactory.

The copolymer COM-1 presents some reduction at the pour point in medium crude oil, but not in the same way did it with light crude oil. This difference in behavior can be attributed to the increase of asphaltenes in the medium crude oil (11.13 % weight), as well as the increase in molecular mass of these.

Random terpolymers formulation and their evaluation as viscosity reducing agents in heavy crude oil.

Tests consisted in the realization of temperature sweeps to determine the behavior of the viscosity of the heavy crude additived with random polymers, depending on temperature; all crude oil samples were subjected to a constant shear rate of γ= 50 sec^{-1}, in a temperature range of 20 to 80°C.

Prepared different concentrated solutions of each of the random terpolymers at 5 to 40 % by weight, using solvents whose boiling point falls within the range of 35-200°C, preferably xylene, toluene, benzene, methyl ethyl ketone, kerosene, turbosine, naphtha, individually or in mixtures, so added small volumes of dissolution and found that the effect of the solvent did not influence the assessment of viscosity. Random terpolymers were evaluated simultaneously with commercial type EVA copolymers (vinyl, with 25 % and 40 % ethylene-acetate copolymers weight of vinyl acetate), as reducing agents of viscosity in concentrations in the range of 250 to 4,000 ppm. The characterization of heavy crude oil used in this evaluation is indicated in Table 3.

The assessment procedure described below: the sealed bottles with insert number and lid is indicated by the number of compounds to assess plus one that corresponds to the crude without additives; each of them added crude oil to the 80 mL mark. All the bottles were placed in a water bath at a controlled temperature in 40 °C for 15 minutes, at the end of that time was added above the aliquot of the dissolution of the random terpolymers and the commercial copolymers formulations; all the bottles shook during 4 minutes, 2 beats per second and later 20 minutes in ultrasonic bath

with controlled temperature of 60 °C. After agitated remained at rest at room temperature, then perform the evaluation. All the terpolymers reason for this invention and commercial formulations were assessed at different concentrations in the ranger of 250 to 1000 ppm for a solution to 20 % of polymer in any solvents or mixtures of them mentioned above although preferably used xylene or toluene. Crude oil samples without polymer were used as untreated or reference.

An important parameter to reduce the viscosity of crude oil and improve fluidity is the manipulation of temperature. The temperature strongly influences the viscosity of high molecular mass of crude oil components. Increasing temperature increases the level of clutter the structures of the components of crude oil, resulting in reduce the viscosity drastically (Borthakur a. et al, 1996).

Heavy oil samples were performed rotational testing at different temperatures which provide information about the flow material properties and its behavior respect to temperature.

For this part of the evaluation it was used a rheometer to study the influence of the terpolymers on the behavior of heavy oil with temperature and rotational tests. The influence of polymers was evaluated at concentrations preferably from 250 to 10000 ppm (Nuñez SM *et al* 2001, Ronningsen HP *et al* 1991).

It was used a rheometer (Anton Parr) Physica MCR301 model. It was performed the measurement of viscosity at 20 ° C using a cutting speed range of 0.1 to 300 sec-1, with these measurements was made graphic representation of the coefficient of viscosity η depending on cutting speed γ, called viscosity curve $\eta = f(\gamma)$, similarly the measurement was made of shear τ depending on cutting speed γ (Nuñez SM *et al* 2001, Bharambe DP *et al* 2006).

By way of demonstration, which does not imply any limitation, are shown in Figures 3, 4, 5 and 6, the results of de evaluation described above, dosing at 500 and 1000 ppm

of a 20% solution of polymer at a temperature of 20°C (Torres E *et al* 2004, Ahlers W *et al* 2007):

Figure 3 in the top, shows the evolution of the viscosity of heavy oil without an additive (white) versus the cutting speed. It is also clear that all the tested terpolymers (E6-E10) reduced the oil viscosity along the selected shear rate range, from 0.1 to 300 s^{-1}, at a constant temperature of 20 °C.

The terpolymer which exhibits the best performance is the P(BuA-co-AV-co-S) 20/30/50 (E7), that has a low molecular weight ($\overline{M}_W$=3705 Daltons). Compositionally speaking is the one with greater styrene content, less composition of acetates and median acrylate groups.

In order to compare the terpolymers with the best viscosity reducing effect, is shown in Figure 4, where are reported the evaluations of heavy crude oil without an additive (white) and additived with terpolymers E12, E14 and E16, all of them of high molecular weight. The order of reduction of viscosity is E12> E16> E14. The above results clearly demonstrate the magnitude of the molecular mass number ($\overline{M}_W$) that must have the terpolymer. For a terpolymer is a good viscosity reducer it appears that must have a high composition of styrenic polymers, considerable composition of acrylate groups and low composition of acetate groups.

Figure 5 shows the viscosity curve of additived heavy crude with polymers E11, E12 and E16, at temperatures from 20 to 32°C and dosages of 1000 ppm, and is observed that the sample of heavy oil with additive E12 presents an initial reduction of 23.5%, and as the temperature increases to 30 ° C, reduced viscosity is about 25.1 %. In the same Figure a way of comparison were included the results of percentage reduction of E16 and E11.

Figure 6 shows the general behavior of heavy oil without an additive (untreated) and additived with different concentrations of polymer additives, and that is where it can

ratify the behavior of viscosity reduction with increasing temperature on additivated oil. It is necessary highlight the fact that at low temperatures (from 20 to 40 °C) the viscosity of heavy oil is reduced and at temperatures above 50°C is noted that oil is no longer sensitive to these polymers.

5

However, it is important to note that the main interest of this invention is focused on reducing the viscosity of heavy oil in the temperature range of 20 to 30°C, since this range represents the normal operating conditions at platforms and refineries.

10 The same Figure presents the results of the evaluation of two commercial copolymers (COM-01 and COM-02) as viscosity reducers. Neither reduces the viscosity of heavy crude. One of them has any influence even as viscosity reducer (COM-02). Even worse, the commercial copolymer (COM-01) increases the viscosity; in contrast, the random terpolymer E-12 significantly reduces the viscosity of heavy oil.

15

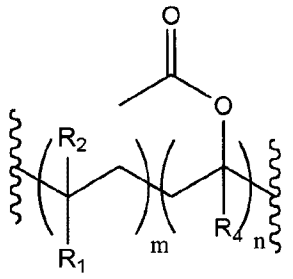
With the different sets of tests using synthesized terpolymer and copolymers and additivated to different types of Mexican crude, was possible to identify both the effect that caused each of the monomers and the effective polymer molecular mass range ($\overline{M}_W$). Also, it was possible to establish to the characterization tests should have
20 been submitted crude oil, if it wanted to evaluate the pour point or viscosity reduction.

For Mexican crudes, commercial copolymer COM-01 is a good pour point depressant but not so good viscosity reducer. When there are significant amounts of asphaltenes in crude oils, the rheological behavior of the structure of the copolymer COM-1 is
25 considerably reduced (Castro MF et al, 2008). In contrast E4 and E12 polymers proved to be good pour point depressants and viscosity reducers under conditions of processing various crudes oil used into platforms and refineries.

30

What is claimed is:

1. A method for producing random polymers, wherein said method comprises a semi-continuous emulsion polymerization performed in a main reactor, by feeding a pre-emulsion of monomers and a transfer agent, from one or several tanks by a respective metering pump, at a reaction temperature in the range between 50 and 95 °C, where a feed rate of the pre-emulsion is from 0.003 to 0.009 g/mL•min, where the amount of monomers used is between 5 and 95 wt%, and the amount of transfer agent varies between 0.001 and 12 grams per 100.0 grams of the mixture of monomers, wherein the random polymers are random copolymers having the formula:



where:

R_1, R_2 and R_4 are represented by independent radical groups listed below:

$R_1 = C_6H_5$, $CH_3C_6H_4$, $(CH_3)_2C_6H_3$, $(CH_3)_3C_6H_2$, $(CH_3)_3CC_6H_4$;

R_2 = H, CH_3;

R_4 = H, CN;

m = from 10 to 700;

n = from 1 to 220; and

wherein the random polymers are effective for reducing the viscosity and depressing the pour point of crude oils having an API gravity from 9 to 20°API.

2. The method of claim 1, wherein the rate of addition of the preemulsion is from 0.004 to 0.007 g/mL•min, and the amount of monomers used is between 10 and 90 %wt.

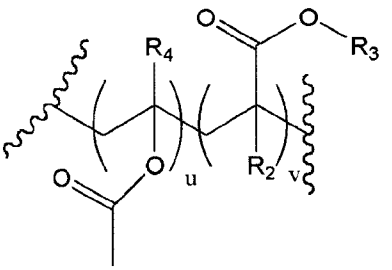
3. The method according to claim 1, wherein m is from 20 to 650 and n is from 10 to 200.

4. The method according to claim 1, wherein m is from 40 to 620 and n is from 20 to 170.

5. The method according to any one of claims 1 to 4, wherein said random polymers have number average molecular weights ranging between 2,000 to 90,000 Daltons.

6. The method according to claim 5, wherein said random polymers have number average molecular weights ranging between 5,000 and 80,000 Daltons.

7. A method for producing random polymers, wherein said method comprises a semi-continuous emulsion polymerization process performed in a main reactor, by feeding a pre-emulsion of monomers and a transfer agent to the main reactor at a rate of 0.003 to 0.009 g/mL•min, at a reaction temperature from 50 to 90°C, the amount of monomers is between 5 and 95 wt%, and the amount of transfer agent is between 0.001 and 12 grams per 100.0 grams of monomers, wherein said random polymers comprises random copolymers having the formula:



where:

R_2, R_3 and R_4 are represented by independent radical groups listed below:

R_2= H, CH_3;

R_3= CH_3, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{18}H_{37}$;

R_4= H, CN;

u = from 1 to 220;

v = from 1 to 50; and

wherein said random polymers are effective for reducing the viscosity and depressing the pour point of crude oil having an API gravity of 9 to 20° API.

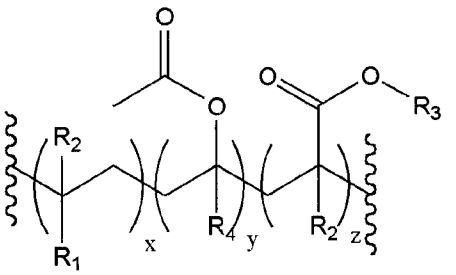
8. The method according to claim 7, wherein u is from 10 to 200 and v is from 10 to 40.

9. The method according to claim 7, wherein u is from 30 to 170 and v is from 15 to 30.

10. The method according to any one of claims 7 to 9, wherein said random polymers have number average molecular weights ranging between 2,000 and 90,000 Daltons.

11. The method according to claim 10, wherein said random polymers have number average molecular weights ranging between 5,000 and 80,000 Daltons.

12. A method for producing random terpolymers, wherein said method comprises a semi-continuous emulsion polymerization process performed in a main reactor, by feeding a pre-emulsion of monomers and a transfer agent to the main reactor at a rate from 0.003 to 0.009 g/mL•min, at a reaction temperature from 50 to 90°C, the amount of monomers is between 5 and 95 wt%, and the amount of transfer agent is between 0.001 and 12 grams per 100.0 grams of monomers, wherein said random terpolymers have the formula:



where:

R_1, R_2, R_3 and R_4 are represented by independent radical groups listed below:

R_1= C_6H_5, $CH_3C_6H_4$, $(CH_3)_2C_6H_3$, $(CH_3)_3C_6H_2$, $(CH_3)_3CC_6H_4$;

R_2= H, CH_3;

R_3= CH_3, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{18}H_{37}$;

R_4= H, CN;

x = from 2 to 900;

z= from 1 to 300;

y = from 1 to 226.

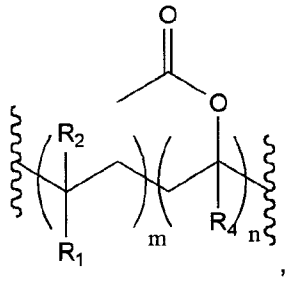
13. The method according to claim 12, wherein x is from 20 to 850, z is from 10 to 235 and y is from 10 to 210.

14. The method according to claim 12, wherein x is from 25 to 700, z is from 20 to 220 and y is from 20 to 200.

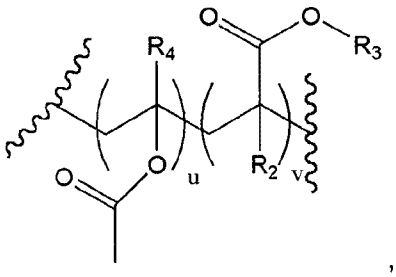
15. The method according to any one of claims 12 to 14, wherein said random terpolymers have number average molecular weights ranging from 1,000 to 140,000 Daltons.

16. The method according to claim 15, wherein said random terpolymers have number average molecular weights ranging from 2,000 to 100,000 Daltons.

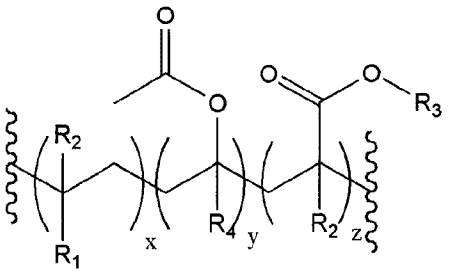
17. A method for producing a random copolymer selected from the group consisting of



,



, and



where:

R_1, R_2 and R_4 are represented by independent radical groups listed below:

R_1 = C_6H_5, $CH_3C_6H_4$, $(CH_3)_2C_6H_3$, $(CH_3)_3C_6H_2$, $(CH_3)_3CC_6H_4$;

R_2 = H, CH_3;

R_3= CH_3, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{18}H_{37}$;

R_4 = H, CN;

m = from 10 to 700;

n = from 1 to 220;

u = from 1 to 220;

v = from 1 to 50;

x = from 2 to 900;

y = from 1 to 226;

z = from 1 to 300;

said method comprising the steps of preparing a reaction mixture of monomers selected from the group consisting of acrylate, styrene and acetate monomers, at least one surfactant, a transfer agent and a buffer solution, and feeding said reaction mixture into a reactor at a temperature from 50 to 95 °C, at a rate of about 0.003 to about 0.009 g/ml·min to obtain said random polymer or copolymer,

the reaction mixture including said at least one monomer in an amount of 5 to 95 wt% and the amount of the transfer agent is between 0.001 and 12 grams per 100 grams of monomer, wherein said random polymer is effective in reducing the viscosity and depressing the pour point of crude oil having an API gravity of 9 to 20°API.

18. The method according to claim 17, wherein said random polymers have number average molecular weights ranging between 2,000 and 90,000 Daltons.

19. The method according to claim 18, wherein

m is 20 to 650;

n is10 to 200;

u is 10 to 200;

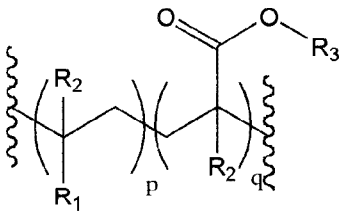
v is 10 to 40;

x is 20 to 850;

z is 10 to 235; and

y is 20 to 200.

20. A method for producing random polymers, wherein said method comprises a semi-continuous emulsion polymerization process performed in a main reactor, by feeding a pre-emulsion, including monomers and a transfer agent, to the main reactor at a rate of 0.003 to 0.009 g/mL-min, at a reaction temperature from 50 to 90°C, the amount of monomers is between 5 and 95 wt%, and the amount of transfer agent is between 0.0 and 12 grams per 100.0 grams of monomers, wherein said random polymer formulation comprises random copolymers having the formula:



R_1 = C_6H_5, $CH_3C_6H_4$, $(CH_3)_2C_6H_3$, $(CH_3)_3C_6H_2$, $(CH_3)_3CC_6H_4$;

R_2 = H, CH_3;

R_3= CH_3, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{18}H_{37}$;

p = from 1 to 700;

q = from 1 to 50; and

wherein the random polymers are effective for reducing the viscosity and depressing the pour point of crude oils having an API gravity of 9 to 20°API.

21. A random polymer formulation for improving the flow of crude oil having an API gravity between 9 and 20°, which depresses the pour point and reduces the viscosity, comprising a random polymer prepared in accordance with the method of any one of claims 1 to 20, at a concentration ranging from 1 to 60% by weight, and a solvent having a boiling point in the range of 35 to 200° C.

22. A random polymer formulation according to claim 21, wherein said solvent is selected from the group consisting of dichloromethane, chloroform, benzene, toluene, xylenes, jet fuel, naphtha, methyl ethyl ketone, kerosene, turbosine, individually and mixtures thereof.

23. A random polymer formulation according to claim 22, wherein the random polymer formulation comprises a mixture of random copolymers and/or terpolymers.

24. A random polymer formulation according to claim 23, wherein said mixture of random copolymers or terpolymers comprises mixture of random copolymers having number average molecular weights ranging between 2,000 to 90,000 Daltons.

25. A random polymer formulation according to claim 24, said mixture of random copolymers having number average molecular weights ranging between 5,000 to 80,000 Daltons.

26. A random polymer formulation according to claim 23, wherein said mixture of random copolymers or terpolymers comprises a mixture of random terpolymers having number average molecular weights ranging between 1,000 and 140,000 Daltons.

27. A random polymer formulation according to claim 26, said mixture of random terpolymers having number average molecular weights ranging between 2,000 to 100,000 Daltons.

28. A random polymer formulation according to claim 21 wherein the random polymer is a random terpolymer at a concentration of 5 to 40% by weight.

29. A random polymer produced by the method according to any one of claims 1 to 6, wherein said random polymer is a random polystyrene-polyacetate polymer and the pre-emulsion of monomers is a pre-emulsion of styrene and acetate monomers.

30. A random polymer produced by the method according to any one of claims 7 to 11, wherein said random polymer is a random polyacetate-polyacrylate polymer and the pre-emulsion of monomers is a pre-emulsion of acrylate and acetate monomers.

31. A random polymer produced by the method according to claim 20, wherein the random polymer is a random polystyrene-polyacrylate polymer and the pre-emulsion of monomers is a pre-emulsion of styrene and acrylate monomers.

32. A random polymer produced by the method according to any one of claims 12 to 16, wherein said random polymer is a random polystyrene-polyacetate-polyacrylate terpolymer.

33. The method of any one of claims 1 to 6, wherein said reaction mixture includes a monomer mixture consisting essentially of a styrene monomer

selected from the group consisting of styrene, 2,4,6-trimethyl-styrene, 2,4-dimethyl-styrene, 3-methyl-styrene, 4-methyl-styrene, 2-methyl-styrene, 4-*tert*-butyl-styrene, α,2-dimethyl-styrene, and α-methyl-styrene, and an acetate monomer selected from the group consisting of vinyl acetate, and cyanovinyl acetate.

34. The method of any one of claim 7 to 11, wherein said reaction mixture includes a monomer mixture consisting essentially of an acetate monomer selected from the group consisting of vinyl acetate and cyanovinyl acetate, and an acrylate monomer selected from the group consisting of methyl acrylate, *tert*-butyl methacrylate, butyl acrylate, butyl methacrylate, hexyl acrylate, hexyl methacrylate, *iso*-butyl acrylate, *iso*-butyl methacrylate, ethyl acrylate, ethyl methacrylate, *tert*-butyl acrylate, 3,5,5-trimethyl-hexyl acrylate, *iso*-decyl acrylate, *iso*-decyl methacrylate, *iso*-octyl acrylate, lauryl acrylate, lauryl methacrylate, octadecyl acrylate, 2-ethyl-hexyl acrylate, and 2-ethyl-hexyl rnethacrylate.

35. The method of any one of claims 12 to 16, wherein said reaction mixture includes a monomer mixture consisting essentially of a styrene monomer selected from the group consisting of styrene, 2,4,6-trimethyl-styrene, 2,4-dimethyl-styrene, 3-methyl-styrene, 4-methyl-styrene, 2 methyl-styrene, 4-*tert*-butyl-styrene, α,2-dimethyl-styrene, and α-methyl-styrene, an acrylate monomer selected from the group consisting of methyl acrylate, *tert*-butyl methacrylate, butyl acrylate, butyl methacrylate, hexyl acrylate, hexyl methacrylate, *iso*-butyl acrylate, *iso*-butyl methacrylate, ethyl acrylate, ethyl methacrylate, *tert*-butyl acrylate, 3,5,5 trimethyl-hexyl acrylate, *iso*-decyl acrylate, *iso*-decyl methacrylate, *iso*-octyi acrylate, lauryl acrylate, lauryl methacrylate, octadecyl acrylate, 2-ethyl-

hexyl acrylate, and 2-ethyl-hexyl methacrylate, and an acetate monomer selected from the group consisting of vinyl acetate, and cyanovinyl acetate.

36. The method of any one of claims 1 to 6, wherein said reaction mixture includes a monomer mixture consisting essentially of a styrene monomer which is methyl styrene, and an acetate monomer selected from the group consisting of vinyl acetate, and cyanovinyl acetate.

37. The method of any one of claims 12 to 16, wherein said reaction mixture includes a monomer mixture consisting essentially of a styrene monomer which is methyl styrene, an acrylate monomer selected from the group consisting of methyl acrylate, *tert*-butyl methacrylate, butyl acrylate, butyl methacrylate, hexyl acrylate, hexyl methacrylate, *iso*-butyl acrylate, *iso*-butyl methacrylate, ethyl acrylate, ethyl methacrylate, *tert*-butyl acrylate, 3,5,5 trimethyl-hexyl acrylate, *iso*-decyl acrylate, *iso*-decyl methacrylate, *iso*-octyi acrylate, lauryl acrylate, lauryl methacrylate, octadecyl acrylate, 2-ethyl-hexyl acrylate, and 2-ethyl-hexyl methacrylate, and an acetate monomer selected from the group consisting of vinyl acetate, and cyanovinyl acetate.

38. The method according to any one of claims 1 to 6, wherein said random polymers are random polystyrene-polyacetate polymers and the pre-emulsion of monomers is a pre-emulsion of styrene and acetate monomers.

39. The method according to any one of claims 7 to 11, wherein said random polymers are random vinyl acetate-acrylate copolymers and the pre-emulsion of monomers is a pre-emulsion of acrylate and acetate monomers.

40. The method according to claim 20, wherein said random polymers are random stvrene-acrylate copolymers and the pre-emulsion of monomers is a pre-emulsion of styrene and acrylate monomers.

41. The method according to any one of claims 12 to 16, wherein said random polymers are random stvrene-vinyl acetate-acrylate terpolymers.

FIGURE 1

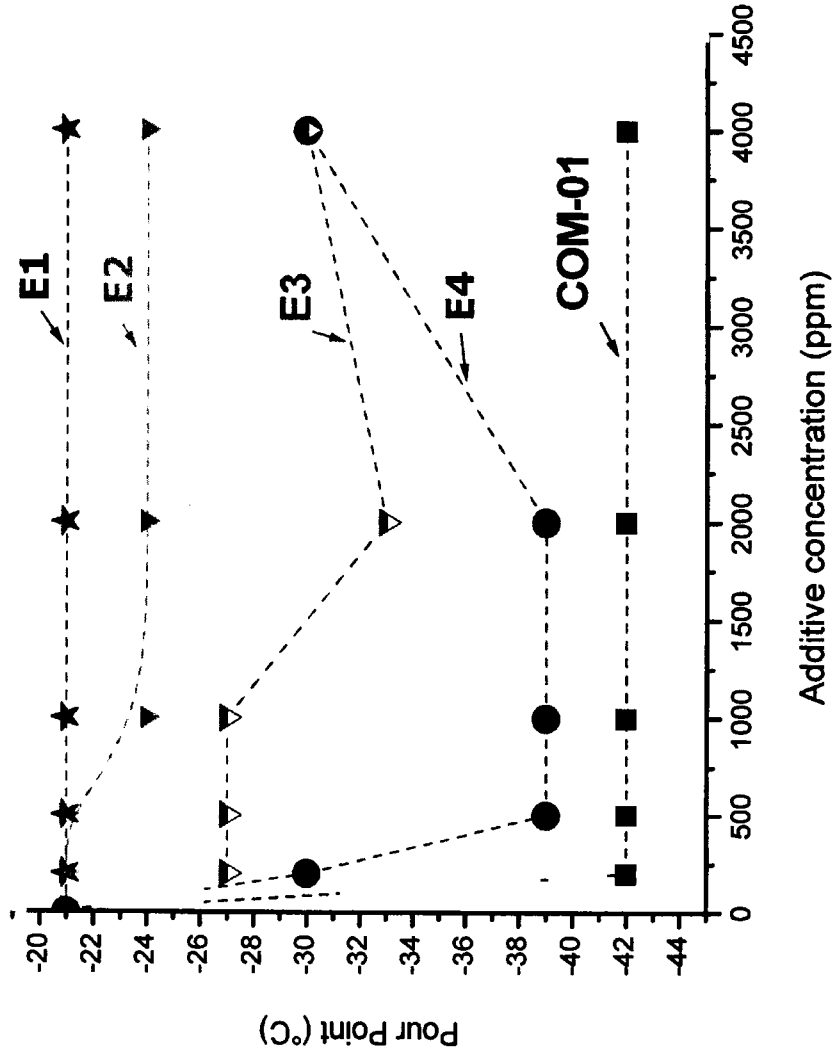

E1
E2
E3
E4
COM-01
Pour Point (°C)
-20
-22
-24
-26
-28
-30
-32
-34
-36
-38
-40
-42
-44
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Additive concentration (ppm)

FIGURE 2

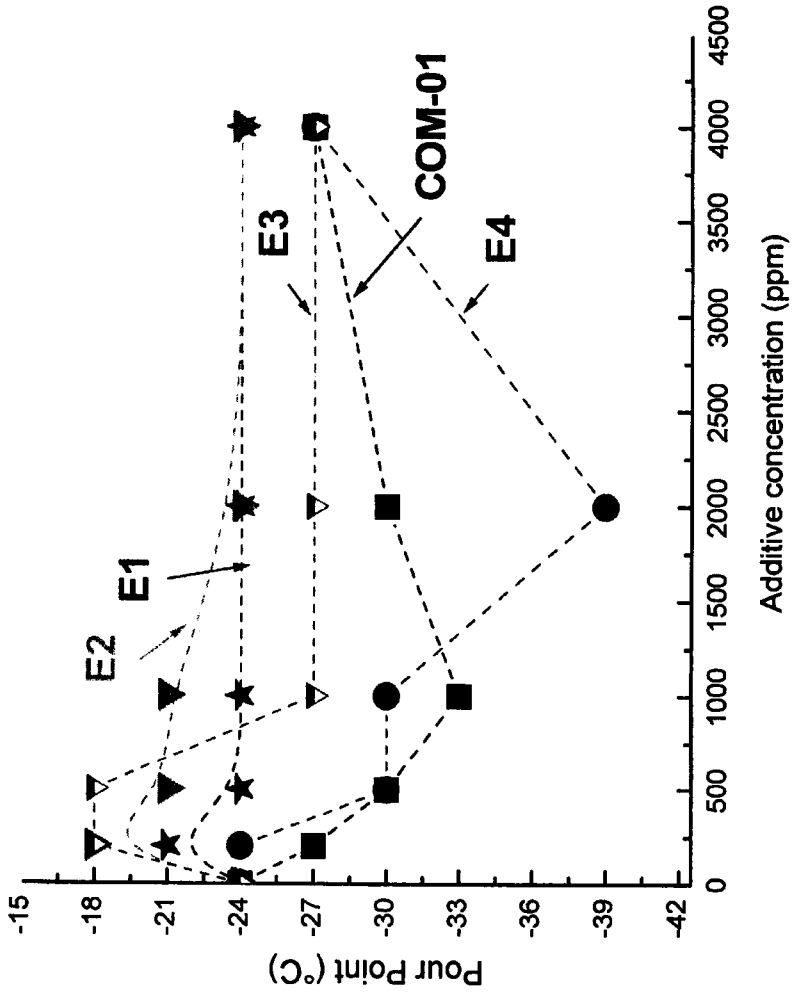

Pour Point (°C)
-15
-18
-21
-24
-27
-30
-33
-36
-39
-42
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Additive concentration (ppm)
E1
E2
E3
E4
COM-01

FIGURE 3

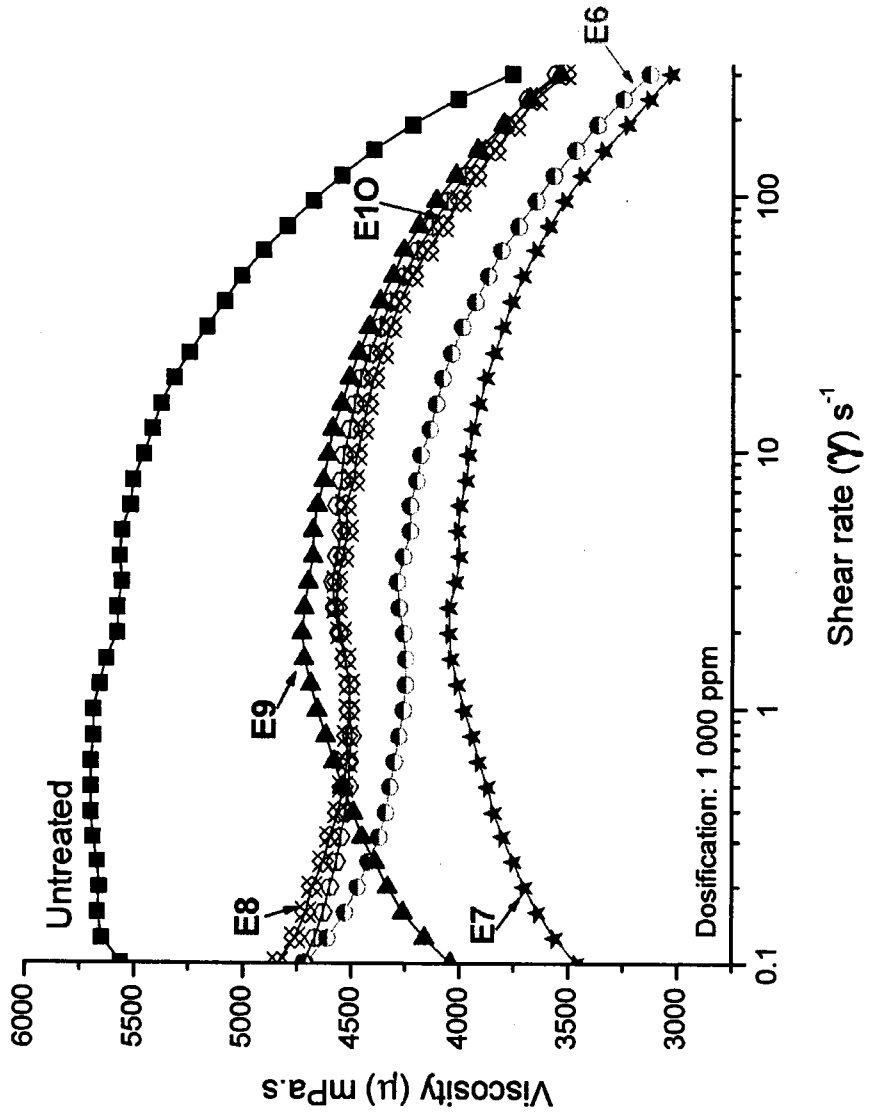

Viscosity (μ) mPa.s
6000
5500
5000
4500
4000
3500
3000
0.1
1
10
100
Shear rate (γ) s-1
Dosification: 1 000 ppm
Untreated
E9
E8
E10
E7
E6

FIGURE 4

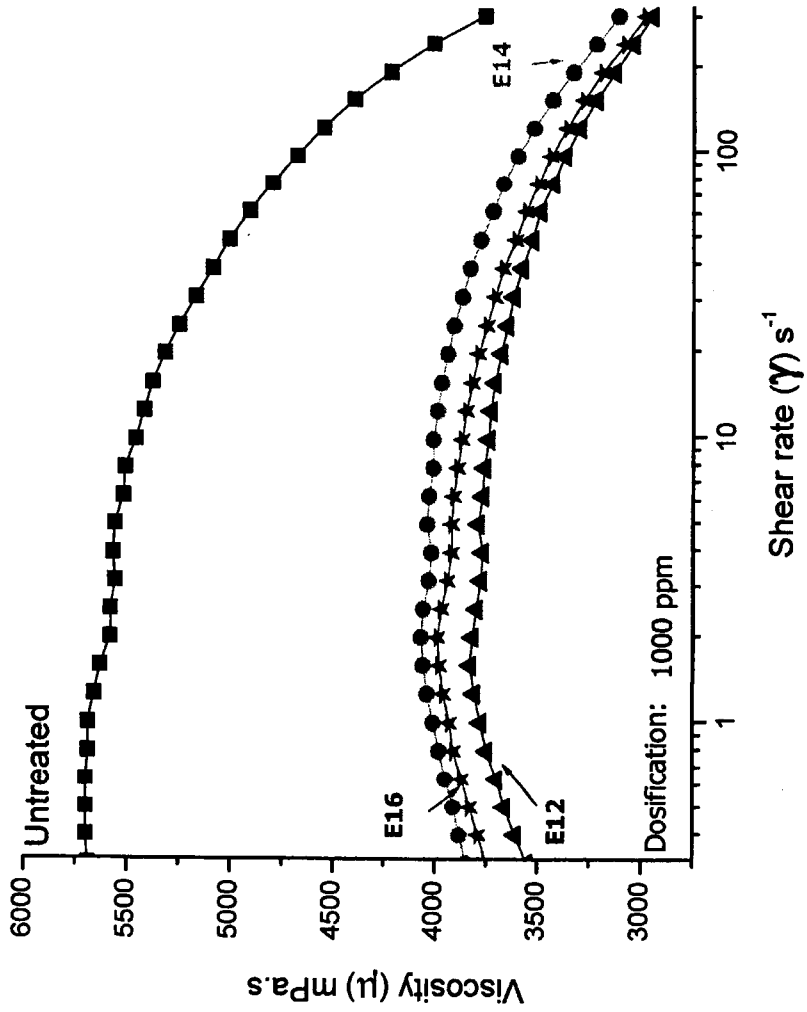

Viscosity (μ) mPa.s
6000
5500
5000
4500
4000
3500
3000
Untreated
E16
E12
E14
Dosification: 1000 ppm
1
10
100
Shear rate (γ) s-1

FIGURE 5

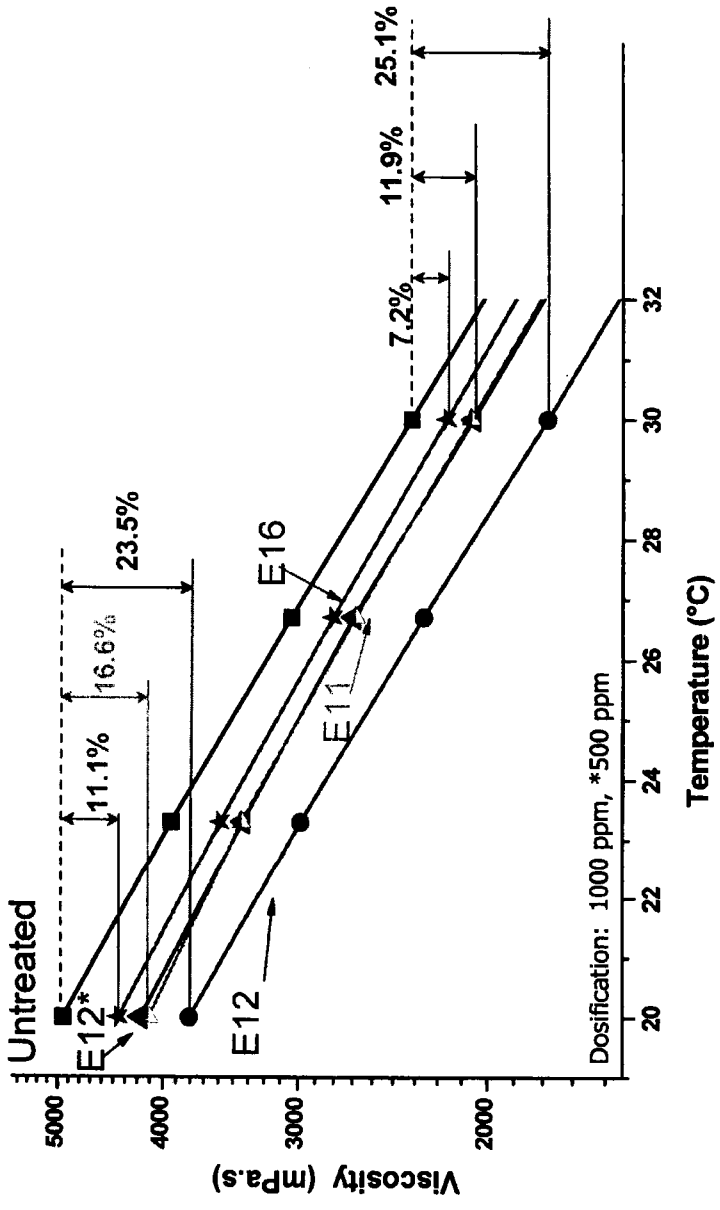
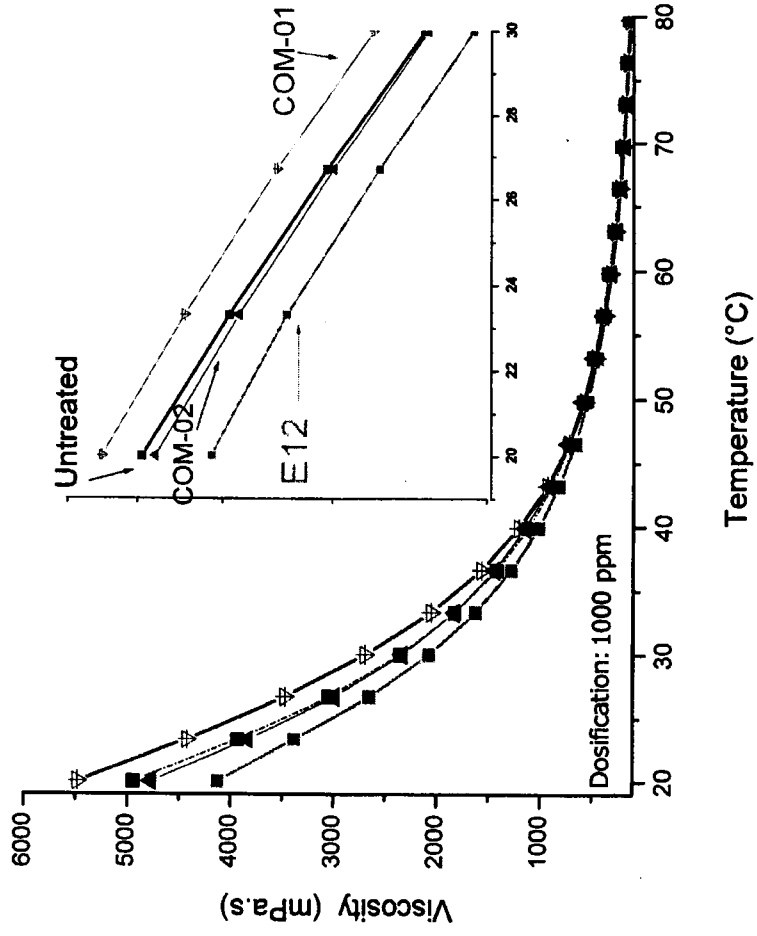
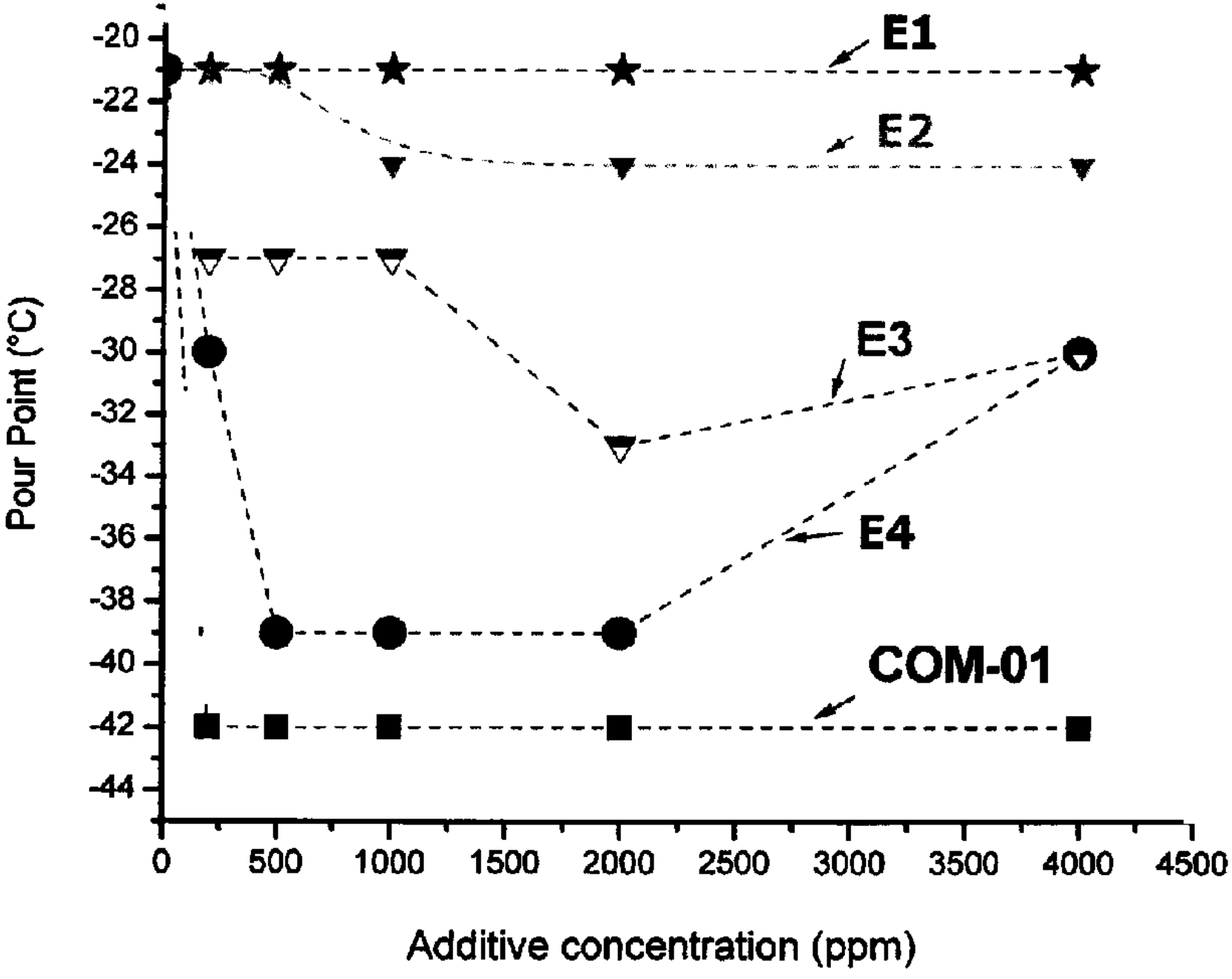

Untreated
E12*
E12
E11
E16
11.1%
16.6%
23.5%
7.2%
11.9%
25.1%
Viscosity (mPa.s)
5000
4000
3000
2000
Temperature (°C)
20
22
24
26
28
30
32
Dosification: 1000 ppm, *500 ppm

FIGURE 6


Viscosity (mPa.s)
6000
5000
4000
3000
2000
1000
20
30
40
50
60
70
80
Temperature (°C)
Dosification: 1000 ppm
Untreated
COM-01
COM-02
E12
20
22
24
26
28
30


E1
E2
E3
E4
COM-01
Pour Point (°C)
-20
-22
-24
-26
-28
-30
-32
-34
-36
-38
-40
-42
-44
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Additive concentration (ppm)